

## Geochemistry of syenite of the Phalaborwa Carbonatite Complex, South Africa

Masaki Yuhara<sup>1</sup>, Mika Kohno<sup>2</sup>, Hiroo Kagami<sup>3</sup>, Yoshikuni Hiroi<sup>4</sup>  
and Noriyoshi Tsuchiya<sup>5</sup>

<sup>1</sup> *Department of Earth System Science, Faculty of Science, Fukuoka University, 8-19-1, Nanakuma, Jonan-ku, Fukuoka 814-0180 (yuhara@fukuoka-u.ac.jp)*

<sup>2</sup> *National Institute of Polar Research, Kaga 1-chome, Itabashi-ku, Tokyo 173-8515*

<sup>3</sup> *Graduate School of Science and Technology, Niigata University, 2-8050, Ikarashi, Niigata 950-2181*

<sup>4</sup> *Department of Earth Sciences, Faculty of Science, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263-8522*

<sup>5</sup> *Department of Geoscience and Technology, Graduate School of Engineering, Tohoku University, Aramaki, Aoba-ku, Sendai 980-8579*

(Received February 3, 2003; Accepted May 12, 2003)

**Abstract:** We surveyed the Spitskop syenite pipe, one of the satellite bodies of the Phalaborwa Carbonatite Complex located in northeastern Transvaal, South Africa. This pipe is composed of the inner cumulus syenite and outer ring syenite. The brecciation zone between these syenites includes many blocks of syenite, pyroxenite, melanocratic rock, biotite gneiss and granitic rocks. Dolerite dykes intruded into the plug and brecciation zone. Fine- and coarse-grained syenites, melanocratic rock, alkali-feldspar granite and dolerite were collected from the brecciation zone of this pipe. The whole-rock and mineral chemistry suggests that syenites and melanocratic rocks of the brecciation zone were derived from the inner cumulus syenite magma. These rocks do not indicate any clear isochron. It may be a result of mixing of various rocks at the brecciation stage.

**key words:** mineral chemistry, whole-rock chemistry, syenites, Phalaborwa, South Africa

### 1. Introduction

In the Phalaborwa Carbonatite Complex located in northeastern Transvaal, South Africa, there is a world-famous Cu deposit. Copper sulphides, magnetite, baddeleyite, apatite and uranoan thorium have been mined from this deposit. Minor Ni, Au, Pt group metals, Ag, Se, Te, Th and U are also recovered from this complex.

The geology of the Phalaborwa Carbonatite Complex has been well studied because of its high economic interest. Numerous geological, petrological, mineralogical and chronological reports have been presented for the clinopyroxenites, phoscorites and carbonatites composing the main complex (e.g. Hall, 1912a, b; Shand, 1931; Hanekom *et al.*, 1965; Palabora Mining Company, 1976; Eriksson, 1984, 1989; Reischmann, 1995). In contrast, the syenites that surround the main complex and appear as pipes

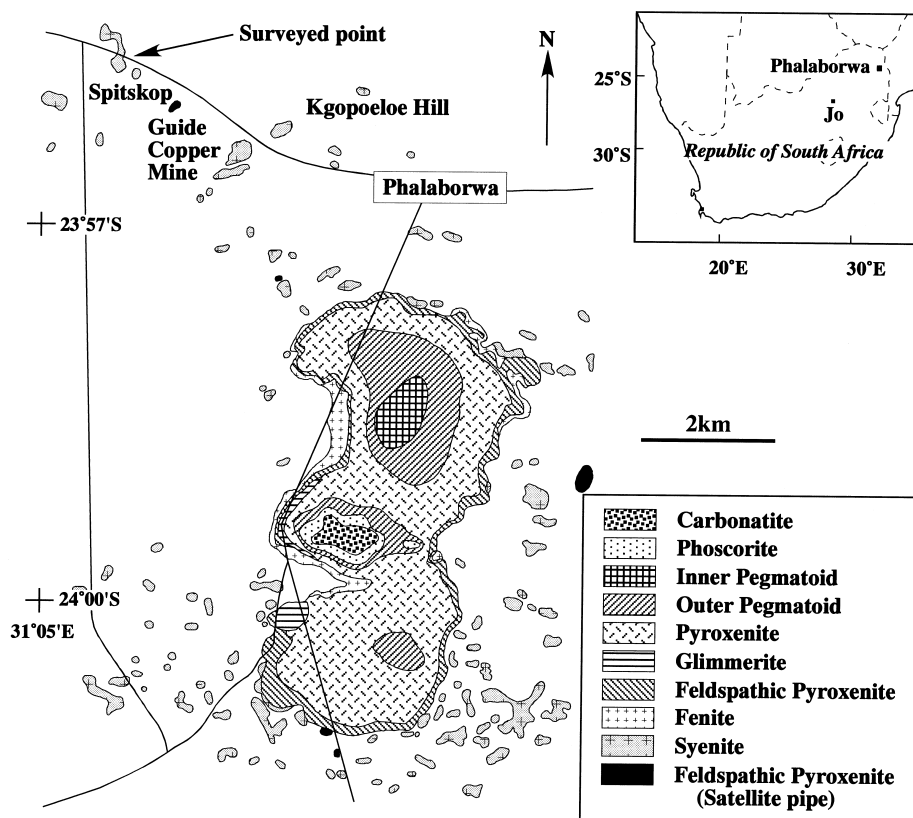


Fig. 1. Generalized geological map of the Phalaborwa Carbonatite Complex, South Africa (after Eriksson, 1984) with sample locality.  
Jo: Johannesburg.

have not been studied extensively, and therefore, there are few reports about the satellite bodies.

We had an opportunity to survey the Spitskop syenite pipe (Fig. 1), one of the satellite bodies, during a Japan–South Africa collaborative geological survey in August 1998. In this pipe, various rocks are included in syenite, and investigation of the field occurrences and petrological relationships of those rocks would give us a key to understand magmatic processes of the Phalaborwa Carbonatite Complex.

In this paper, we report the field occurrence, petrography, mineral and whole-rock chemistry, Sr and Nd isotopic compositions of syenites and related rocks from this syenite pipe.

## 2. Geological setting

The Phalaborwa Carbonatite Complex was formed by continuous intrusion of pyroxenite, syenite, ultramafic pegmatites and carbonatite into an Archaean terrain of

granites, gneiss, quartzites, granulites, amphibolites, and talc and serpentine schists (Hall, 1912a, b; Shand, 1931; Hanekom *et al.*, 1965; Palabora Mining Company, 1976; Eriksson, 1984). The main complex is an elongated pipe-like body with widths of about 6.5 km north to south, and about 2.5 km east to west (Fig. 1). Satellite bodies are concentrated on or near the periphery of the main complex, but some occur away from the main complex, several kilometers to the northeast and northwest. They form pipe-like bodies, and crop out as conspicuous bare rock studs and coniform hills (Fig. 2). These intrusions range from homogeneous rock bodies to highly brecciated bodies with multiple intrusions. The breccias are interpreted as forming at the upper part of the intrusion with passive infilling of magma lower in the pipe. The rock types of satellite bodies include feldspathic pyroxenite, peralkaline syenite, peralkaline quartz syenite, peralkaline granite and trachyte. The texture and grain size of the syenite vary considerably from fine-grained types through porphyritic to pegmatitic types.

According to Eriksson (1989), at the Spitskop pipe, brecciation is limited to a 1–2 m thick zone between an outer syenite forming a low rise above the general landscape and the vertical syenite pipe. A schematic diagram of this pipe is shown in Fig. 3. The outer syenite is peralkaline quartz syenite enclosing the pipe. Syenite, made up of acicular aegirine poikilitically enclosed in microcline, grades inward to a peralkaline quartz syenite. A distinctive flow structure is marked in the peralkaline quartz syenite by tabular crystals of orthoclase. Northeast-southwest trended dolerite dykes of various sizes have intruded into the main complex and satellite bodies.

It is thought that the timing of magmatism of the Phalaborwa Carbonatite Complex is about 2000 Ma, on the basis of an Rb-Sr isochron age of  $2012 \pm 19$  Ma on phlogopites (Eriksson, 1984), and an U-Pb age between 2047 and 2061 Ma (Eriksson, 1984; Heaman and LeCheminant, 1993; Reischmann, 1995; Horn *et al.*, 2000). Furthermore, based on the initial Sr isotopic ratios, it was shown that at least two sources produced magmas forming the carbonatites and pyroxenites of this complex (Eriksson, 1984). It is thought that the timing of activity of the dolerite dykes is about 1900 Ma (Briden, 1976)

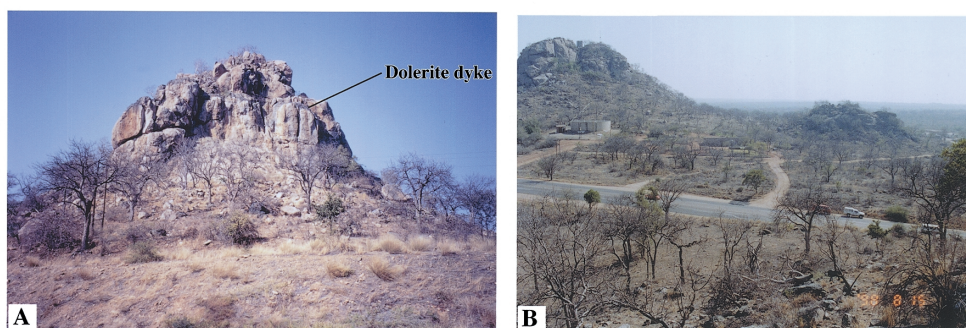


Fig. 2. Field occurrences of the syenite pipes.

A: The syenite pipe where samples were taken for this study. The stud part is inner syenite pipe, and the gently-sloping part is outer ring syenite. The bushes surrounding the plug are 4–5 m in height.

B: The syenite pipes located north of surveyed pipes.

based on palaeomagnetic data. More detailed work of Briden confirms that most cross-cutting dykes in the Phalaborwa Complex are Precambrian (Palabora Mining Company, 1976; Eriksson, 1989).

### 3. Field occurrence and petrography

We carried out a detailed survey at the brecciation zone between the outer ring syenite and inner cumulus syenite in a syenite plug of the Spitskop pipe (Figs. 2A, 3). Similar syenite pipes are located north of the surveyed pipe (Fig. 2B). At the brecciation zone, many blocks of syenites, melanocratic rock, pyroxenite, biotite gneiss and granitic rocks are observed (Fig. 4). Most of the inclusions have breccia-like shapes, and boundaries between matrices are clear (Fig. 4). A dolerite dyke has intruded into the syenite (Fig. 3); it looks like a dark gray band in the rock stud of Fig. 2. Syenite is divided into fine-grained and coarse-grained syenites, based on the grain size of phenocryst minerals (Fig. 4). Because they are locally brecciated, the relationship is not clear. The matrices of blocks are fine-grained syenite, medium-grained syenite and melanocratic rock. We collected fine-grained syenite, coarse-grained syenite, melanocratic rock, alkali-feldspar granite and dolerite from this plug (Fig. 2A). But we did not collect pyroxenite.

The fine-grained syenite is characterized by porphyritic texture (Fig. 5). It consists of alkali-feldspar, quartz, clinopyroxene, amphibole, and accessory titanite, opaque minerals, apatite, zircon and monazite. This syenite has a modal composition of alkali-feldspar syenite (Fig. 7). Phenocrystic alkali-feldspar is euhedral to subhedral, up to 4 mm in diameter. It contains inclusions of clinopyroxene and amphibole. Alkali-feldspar in the matrix is subhedral to anhedral, up to 0.5 mm in diameter. Quartz grains are anhedral and less than 0.8 mm in diameter. They contain inclusions of clinopyroxene and amphibole. Some quartz crystals show wavy extinction. Yellowish green to yellowish brown clinopyroxene is euhedral to anhedral, up to 2 mm in diameter, and occupies the intercrystalline space of alkali-feldspar with quartz and amphibole. Amphibole is bluish green to yellowish brown, euhedral to anhedral and up

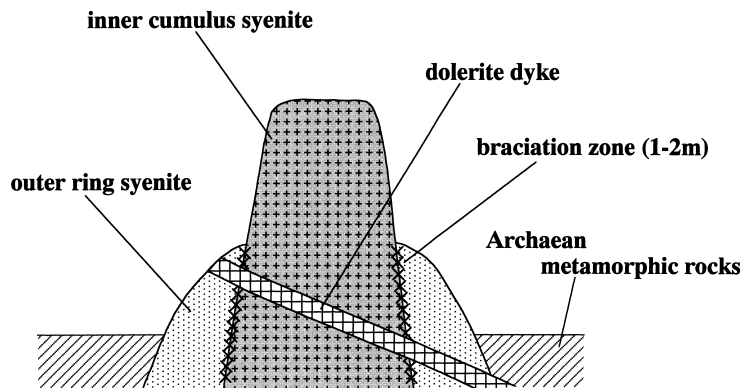


Fig. 3. Schematic diagram of the Spitskop syenite pipe.

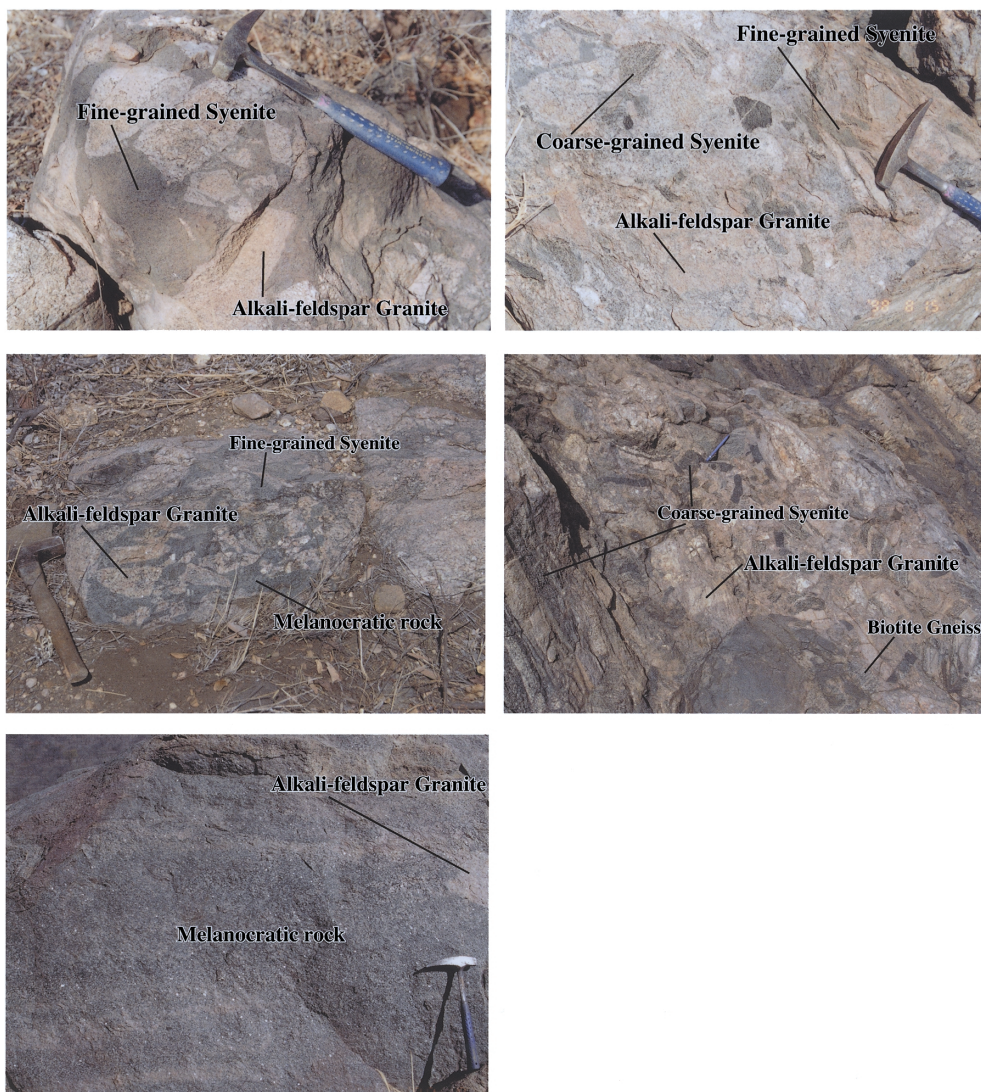


Fig. 4. Photographs showing the modes of occurrence of the syenites and related rocks.

to 1.5 mm in diameter. It contains clinopyroxene inclusions.

The coarse-grained syenite is alkali-feldspar syenite to alkali-feldspar quartz syenite (Fig. 7), with porphyritic texture (Fig. 5). It consists mainly of alkali-feldspar, quartz, clinopyroxene, amphibole, and accessory titanite, opaque minerals, apatite, rutile, zircon and monazite. Phenocrystic alkali-feldspar is euhedral to subhedral, up to 7 mm in diameter; and that in the matrix is subhedral to anhedral, up to 1.5 mm in diameter. It contains inclusions of clinopyroxene and amphibole. Quartz grains are anhedral and less than 1.2 mm in diameter. Some quartz crystals show wavy extinction. Yellowish green to yellowish brown clinopyroxene is euhedral to anhedral up to

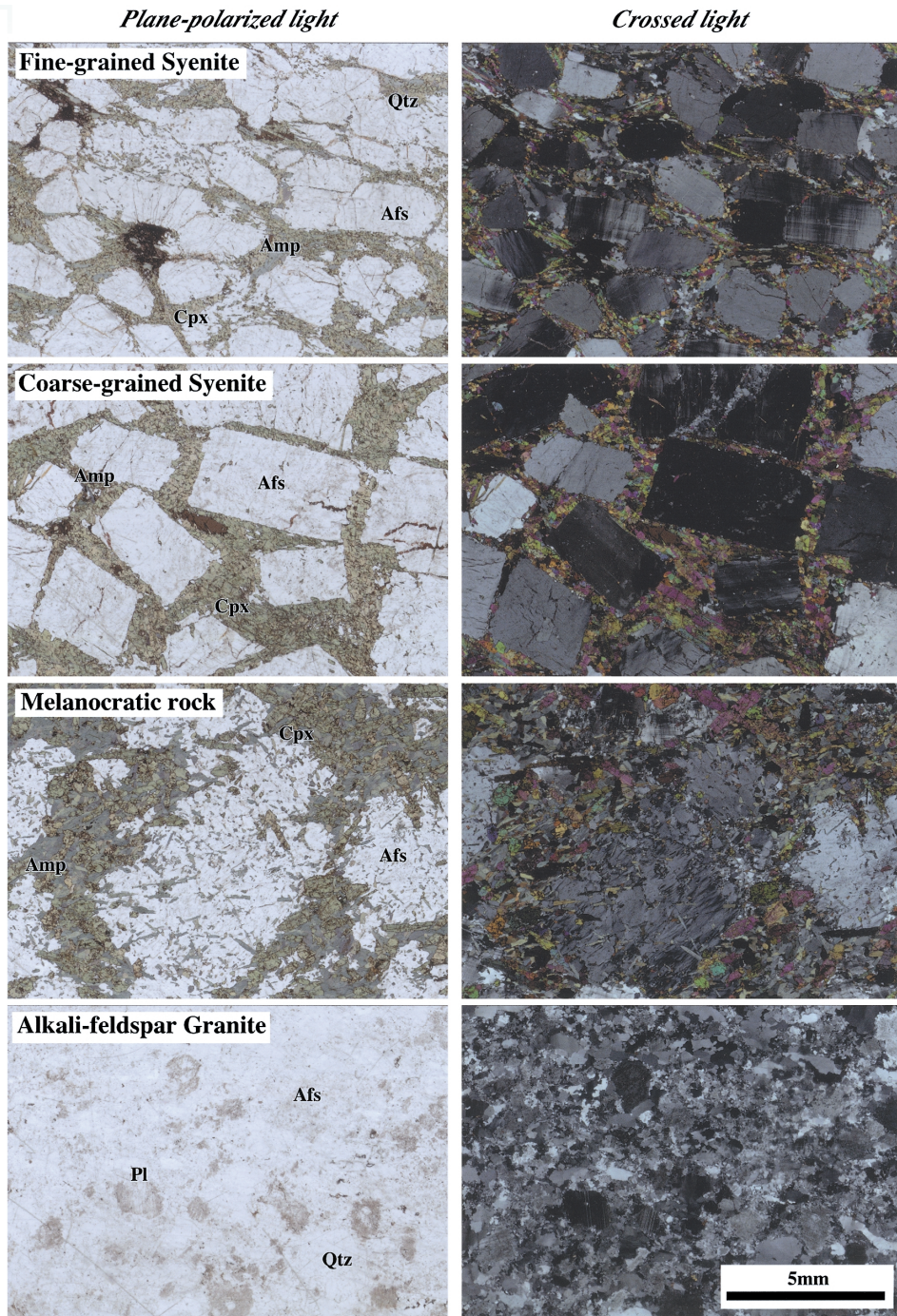


Fig. 5. Photomicrographs of syenite, melanocratic rock and alkali-feldspar granite.  
 Afs: alkali-feldspar, Pl: plagioclase, Qtz: quartz, Cpx: clinopyroxene, Amp: amphibole.

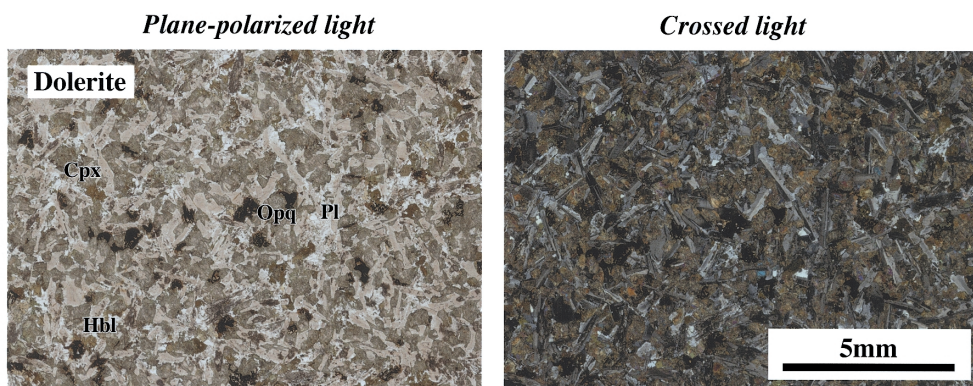


Fig. 6. Photomicrographs of dolerite.  
Pl: plagioclase, Cpx: clinopyroxene, Hbl: hornblende, Opq: opaque minerals.

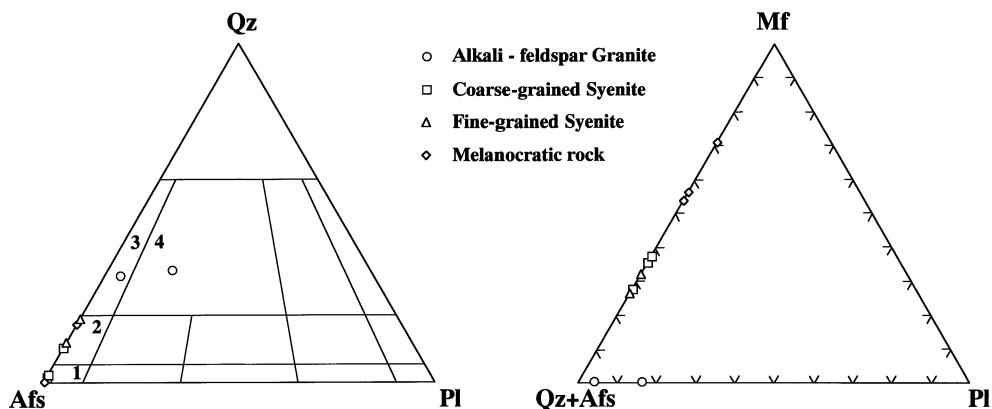


Fig. 7. Modal quartz (Qtz)-plagioclase (Pl)-alkali-feldspar (Afs) and mafic minerals (Mf)-plagioclase-quartz+alkali-feldspar diagrams of the syenite, melanocratic rock and alkali-feldspar granite.

1: alkali-feldspar syenite, 2: alkali-feldspar quartz syenite, 3: alkali-feldspar granite, 4: granite.

3.5 mm in diameter, and occupies the intercrystalline space of alkali-feldspar with quartz and amphibole. Amphibole is bluish green to yellowish brown, euhedral to anhedral and up to 2 mm in diameter.

The melanocratic rock consists of clinopyroxene, amphibole, alkali-feldspar, quartz and accessory titanite, opaque minerals, zircon and monazite, with a porphyritic texture (Fig. 5). The modal composition of this rock is alkali-feldspar syenite to alkali-feldspar quartz syenite (Fig. 7). Its mafic mineral content is higher than 50%. Yellowish green to yellowish brown clinopyroxene is euhedral to anhedral up to 6 mm in diameter. Amphibole is bluish green to yellowish brown, euhedral to anhedral and up to 2 mm in diameter. It occupies the intercrystalline space of clinopyroxene and alkali-feldspar with quartz. Phenocrystic alkali-feldspar is euhedral to subhedral, up

to 7 mm in diameter, and poikilitically contains inclusions of clinopyroxene and amphibole. Alkali-feldspar in the matrix is subhedral to anhedral, up to 0.8 mm in diameter. The former quartz grains are anhedral and less than 1 mm in diameter. Some quartz crystals show wavy extinction.

The alkali-feldspar granite is alkali-feldspar granite to granite (Fig. 7), with a porphyritic texture (Fig. 5). It consists mainly of alkali-feldspar, quartz and plagioclase with accessory amphibole, clinopyroxene, biotite, opaque minerals, zircon, apatite and titanite. Phenocrysts consist of alkali-feldspar, plagioclase and quartz. Alkali-feldspar is subhedral to anhedral, up to 2.5 mm in diameter. It contains inclusions of clinopyroxene and quartz. Quartz is anhedral up to 2 mm in diameter, most of it occupies intercrystalline space. Quartz shows wavy extinction. Plagioclase is subhedral to anhedral up to 2.5 mm in diameter. Myrmekite is formed between plagioclase and alkali-feldspar. Amphibole is bluish green (to pale yellowish brown), subhedral to anhedral and up to 0.5 mm in diameter. Clinopyroxene is yellowish green, subhedral to anhedral up to 0.5 mm in diameter. Dark reddish brown biotite flakes occur as euhedral to anhedral crystals 0.2–0.5 mm in diameter.

Major constituent minerals of the dolerite are plagioclase, clinopyroxene and hornblende with accessory opaque minerals (Fig. 6).

#### 4. Mineral chemistry

##### 4.1. Analytical procedures

Minerals were analyzed using an electron microprobe with a wavelength-dispersive X-ray analytical system (JEOL JXA-8800M) at the National Institute of Polar Research. Oxide ZAF correction was applied in the analysis. All analyses were performed under accelerating voltage of 15 kV and specimen current of 12 nA. Electron beam diameter was set at 10–15  $\mu\text{m}$  to minimize migration of alkaline components during the analyses. Natural minerals and synthetic oxides were used as standards. Mineral compositional data are presented in Appendixes 1, 2, 3 and 4.

##### 4.2. Clinopyroxene

Clinopyroxenes from syenites and melanocratic rock are aegirine, with very low contents of diopside and hedenbergite components. Chemical compositions of clinopyroxenes are almost constant irrespective of rock facies.

##### 4.3. Amphibole

Amphiboles from syenites and melanocratic rock are magnesioriebeckite. Fe/Mg ratios of magnesioriebeckites from the coarse-grained syenite are higher than those from the fine-grained syenite, and vary widely (Fig. 8). Magnesioriebeckites from the melanocratic rock indicate Fe/Mg ratios lower than those in the fine-grained syenites, with partial overlap.

##### 4.4. Alkali-feldspar

Alkali-feldspars are chemically homogeneous. In addition, they are nearly uniform irrespective of rock facies. Most alkali-feldspars do not show compositional



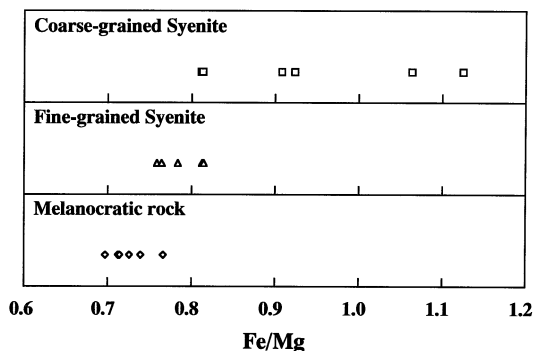


Fig. 8. Fe/Mg ratios of amphiboles in the syenites and melanocratic rock.

zonation.

#### 4.5. Plagioclase

Plagioclases from the alkali-feldspar are albite, having very low anorthite (An) contents. They do not show compositional zonation.

## 5. Whole-rock chemistry

### 5.1. Analytical procedures

The major and trace element concentrations of samples were analyzed using the XRF (RIGAKU ZSX100e) at Fukuoka University by the method of Yuhara and Taguchi (2003). Their chemical compositions are given in Table 1.

Isotopic separation was performed at Saga University using the experimental procedure of Kawano *et al.* (1999). Isotopic analyses were performed on the thermal ionization mass spectrometer (MAT262) equipped with nine dynamic faraday cups at Niigata University.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios were normalized to  $^{86}\text{Sr}/^{88}\text{Sr}=0.1194$  and  $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$ , respectively. The normalized  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were corrected using the NBS-987 standard of  $^{87}\text{Sr}/^{86}\text{Sr}=0.710241$ . The  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios were corrected with the Japanese standard JNdi-1 (Nd isotopic reference of the Geological Survey of Japan) of  $^{143}\text{Nd}/^{144}\text{Nd}=0.512106$ , which was well-documented using the international standard La Jolla of  $^{143}\text{Nd}/^{144}\text{Nd}=0.511849$  (Tanaka *et al.*, 2000). Sm, Nd, Rb and Sr concentrations were determined by an isotope dilution method using  $^{87}\text{Rb}$ - $^{84}\text{Sr}$  and  $^{149}\text{Sm}$ - $^{145}\text{Nd}$  mixed spikes. Rb-Sr and Sm-Nd isochron ages and initial Sr and Nd isotope ratios were calculated by the computer program of Kawano (1994) which used the equation of York (1966) and the decay constants of  $\lambda^{87}\text{Rb}=1.42 \times 10^{-11}/\text{y}$  (Steiger and Jäger, 1977) and  $\lambda^{147}\text{Sm}=6.54 \times 10^{-12}/\text{y}$  (Lugmair and Marti, 1978). Analytical errors for  $^{87}\text{Rb}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were 0.5% ( $1\sigma$ ) and 0.01% ( $1\sigma$ ) and that for  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios were 0.1% ( $1\sigma$ ) and 0.01% ( $1\sigma$ ), respectively. Detailed isotopic analytical procedures were reported by Miyazaki and Shuto (1998). The Rb-Sr and Sm-Nd isotopic data are given in Table 2.

Table 1. Whole-rock chemical compositions of the syenites and related rocks.

Sample No.	98081501	98081502	98081503	98081504	98081505	98081501A	98081501B	98081501C	98081501D	98081501E	98081501F
Rock facies	C.Sy.	A.G.	C.Sy.	F.Sy.	M.R.	C.Sy.	F.Sy.	M.R.	M.R.	A.G.	Do.
SiO <sub>2</sub> (wt%)	60.54	74.23	62.93	63.95	60.39	59.63	62.09	58.05	57.52	74.01	49.61
TiO <sub>2</sub>	0.49	0.02	0.92	0.83	1.39	1.09	1.23	0.55	1.09	0.03	1.19
Al <sub>2</sub> O <sub>3</sub>	13.27	14.18	12.03	10.74	6.61	10.30	10.47	8.76	6.54	14.28	13.09
FeO*	7.53	0.23	7.81	8.45	11.64	11.43	9.28	10.66	12.67	0.14	14.36
MnO	0.13	0.02	0.07	0.09	0.42	0.10	0.15	0.40	0.44	0.01	0.21
MgO	0.88	0.07	0.35	0.39	3.55	0.52	0.93	3.98	4.16	0.06	4.86
CaO	0.45	0.21	0.47	0.51	0.92	0.75	0.52	0.75	0.97	0.24	9.17
Na <sub>2</sub> O	3.87	4.27	3.76	3.98	5.46	5.29	4.28	5.13	6.06	4.51	2.76
K <sub>2</sub> O	11.01	6.04	10.09	9.15	6.13	8.63	8.89	8.10	6.15	5.82	1.14
P <sub>2</sub> O <sub>5</sub>	0.01	0.08	0.03	0.03	0.14	0.04	0.06	0.19	0.27	0.07	0.25
Total	98.18	99.35	98.46	98.12	96.65	97.78	97.90	96.57	95.87	99.17	96.64
Ba(ppm)	824	376	797	572	433	682	462	615	453	360	672
Cr	n.d.	6	4	7	145	n.d.	n.d.	111	128	7	147
Cu	5	14	n.d.	n.d.	2	n.d.	n.d.	n.d.	n.d.	16	191
Nb	12	n.d.	28	31	52	29	51	3	29	n.d.	13
Ni	n.d.	8	n.d.	n.d.	61	n.d.	n.d.	56	59	7	49
Rb	415	190	390	346	211	339	340	287	209	178	47.0
Sr	76.7	97.5	63.1	68.5	542	75.5	83.9	548	400	110	196
V	36	6	30	33	85	44	31	84	102	6	300
Y	29	10	18	19	67	17	23	28	56	8	44
Zn	102	6	50	56	471	69	127	495	534	6	135
Zr	859	57	557	976	1293	401	1339	385	312	88	248

A.G.: alkali-feldspar granite, F.Sy.: fine-grained syenite, C.Sy.: coarse-grained syenite, M.R.: melanocratic rock, Do.: dolerite.

FeO\*: total iron as FeO, n.d.: not detected.

## 5.2. Major and trace elements

The SiO<sub>2</sub> content of the fine-grained syenite ranges from 62.1 wt% to 64.0 wt%, and that of the coarse-grained syenite ranges from 59.6 wt% to 62.9 wt% (Table 1). The melanocratic rock has SiO<sub>2</sub> content ranging from 57.5 wt% to 60.4 wt%. The SiO<sub>2</sub> content of the alkali-feldspar granite is about 74.1 wt%. The dolerite has SiO<sub>2</sub> content of 49.6 wt%. Major and trace element variations are illustrated in Harker diagrams (Figs. 9, 10). The melanocratic rock has higher FeO\*, MgO, Na<sub>2</sub>O, Cr, Ni, Sr, V, Y, Zn contents, and lower Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Rb contents than those of the fine- and coarse-grained syenites, which have nearly the same SiO<sub>2</sub> contents (Figs. 9, 10). The chemical compositions of the fine- and coarse-grained syenites are nearly the same.

The chemical data of feldspathic pyroxenite, breccia matrixes, syenites and granites

Table 2. Rb-Sr and Sm-Nd isotopic data of the syenites and related rocks.

Sample No.	Rb(ppm)	Sr(ppm)	<sup>87</sup> Rb/ <sup>86</sup> Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr(2σ)	Sm(ppm)	Nd(ppm)	<sup>147</sup> Sm/ <sup>144</sup> Nd	<sup>143</sup> Nd/ <sup>144</sup> Nd(2σ)
98081501	415	76.7	16.33	1.15610(1)	3.74	16.9	0.1340	0.511172(13)
98081502	190	97.5	5.726	0.88958(1)	0.485	2.44	0.1203	0.511264(25)
98081503	390	63.1	18.91	1.30647(1)	1.91	8.74	0.1318	0.511210(14)
98081504	346	68.5	15.20	1.13471(1)	1.69	7.64	0.1336	0.511344(14)
98081505	211	542	1.133	0.75232(1)	19.7	72.4	0.1647	0.511652(14)
98081501A	339	75.5	13.47	1.08497(1)	2.37	9.94	0.1439	0.511385(24)
98081501B	340	83.9	12.08	1.02214(1)	2.95	15.1	0.1178	0.511198(18)
98081501C	287	548	1.527	0.78472(1)	4.33	25.8	0.1014	0.510912(14)
98081501D	209	400	1.518	0.76927(1)	17.0	77.3	0.1330	0.511403(14)
98081501E	178	110	4.764	0.87181(1)	0.580	3.77	0.09297	0.511172(14)
98081501F	47.0	196	0.6957	0.72667(1)	5.66	23.4	0.1464	0.511671(13)

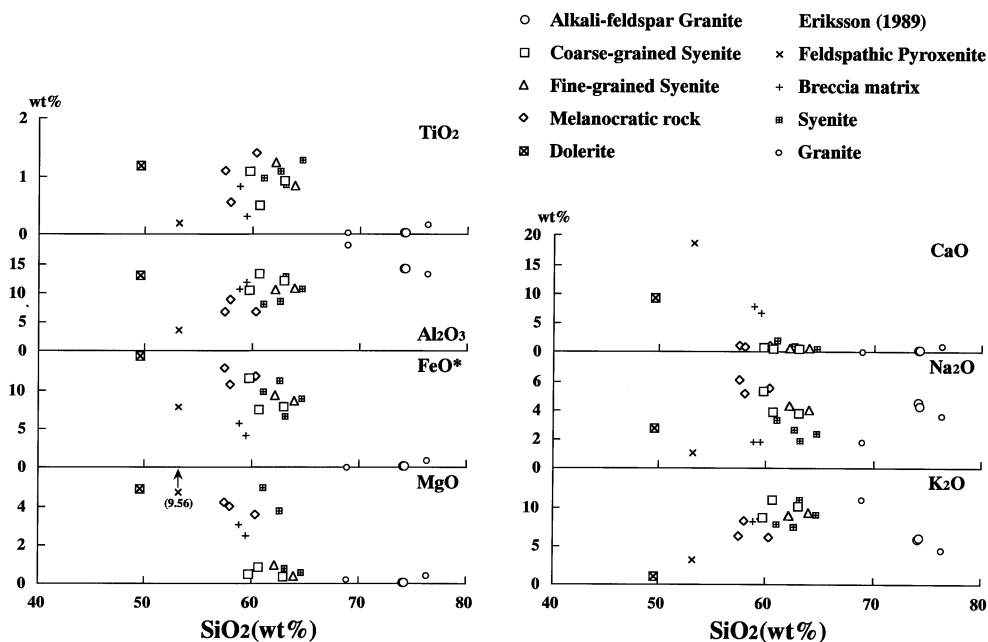


Fig. 9. Major element variations of the syenites and related rocks.

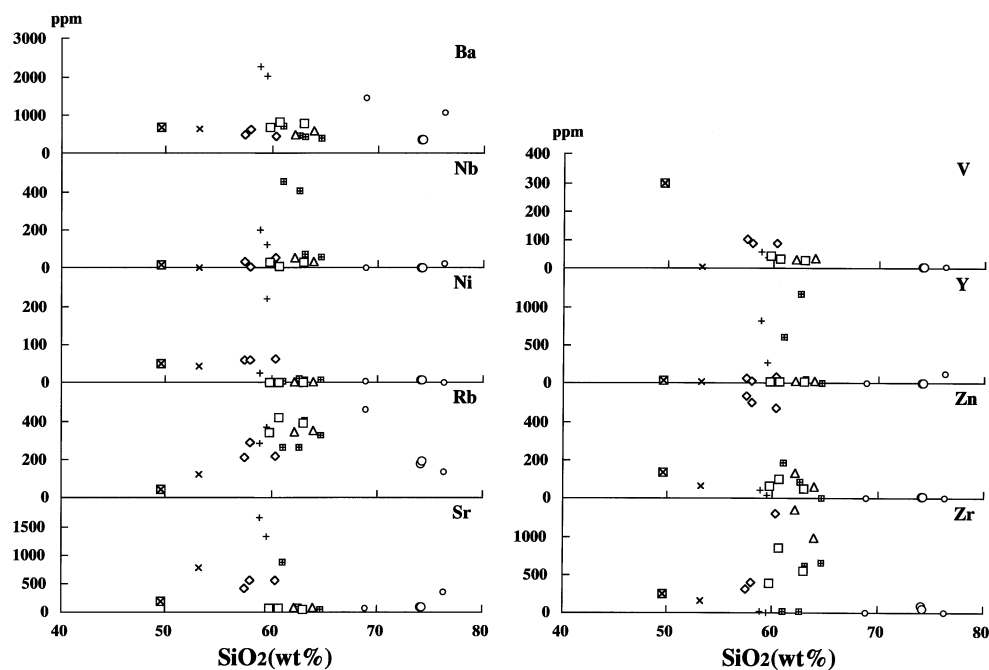


Fig. 10. Trace element variations of the syenites and related rocks. Symbols are the same as those in Fig. 9.

from satellite bodies reported by Eriksson (1989) are also plotted on the same diagrams for comparison. The feldspathic pyroxenite and breccia matrices were collected from the Guide Copper Mine and Kgopoele pipe, respectively (Fig. 1). The granites are the country rock of the Kgopoele pipe. Syenites were collected from the Spitskop pipe. The two syenite samples having lower  $\text{SiO}_2$  contents are from the outer ring syenite, and the others are from the inner cumulus syenite.

$\text{MgO}$ ,  $\text{Na}_2\text{O}$ , Nb, Rb, Sr, Y, Zr contents of the outer ring syenite differ from those of the fine- and coarse-grained syenites, while the chemical compositions excluding  $\text{Na}_2\text{O}$  of the inner cumulus syenite overlap the ranges of the fine- and coarse-grained syenites. The contents of many elements in the breccia matrices differ from those of the melanocratic rocks, having nearly the same  $\text{SiO}_2$  contents. The  $\text{SiO}_2$  content of the feldspathic pyroxenite is lower than those of the syenite and related rocks in the Spitskop pipe. The chemical compositions excluding Ba, Rb, Sr, Y of the alkali-feldspar granite are similar to those of granite.

In a total-alkalis vs. silica diagram (Fig. 11; Wilson, 1989), the fine-grained syenite and coarse-grained syenite are plotted within syenite, nepheline syenite and syenite fields, respectively. The melanocratic rock is plotted within syenite and nepheline syenite fields. The alkali-feldspar granite is plotted within the alkali granite field.

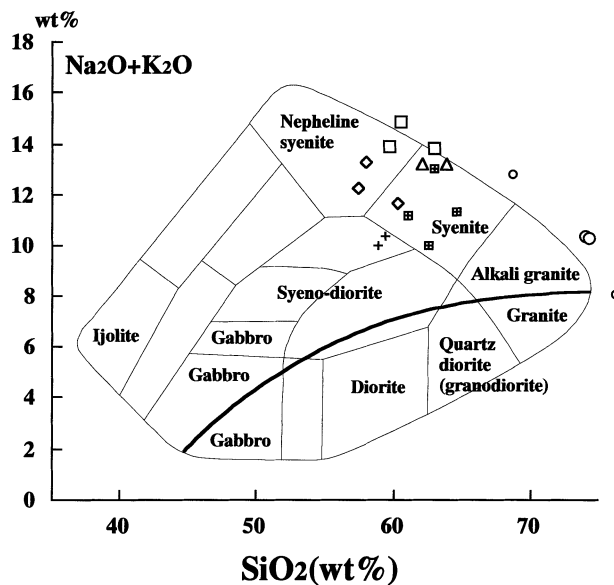


Fig. 11. Total-alkalis vs silica diagram of the syenites and melanocratic rocks with classification and nomenclature of plutonic rocks of Wilson (1989). The curved bold line subdivides the alkalic from subalkalic rocks. Symbols are the same as those in Fig. 9.

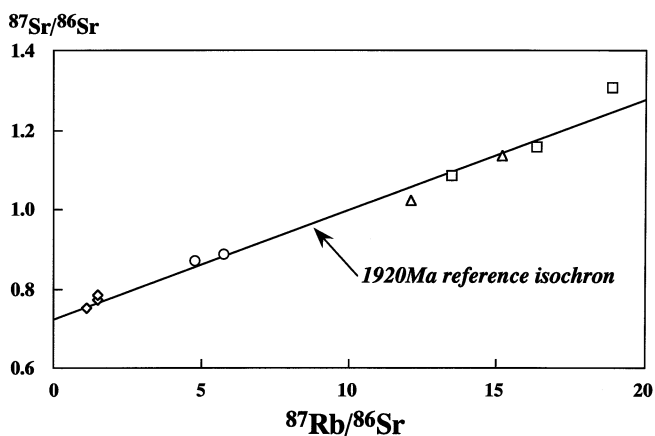


Fig. 12. Rb-Sr whole-rock isochron diagram of the syenites and melanocratic rocks. Symbols are the same as those in Fig. 9.

### 5.3. Nd-Sr isotopes

The Rb-Sr whole-rock isochron diagram is shown in Fig. 12. The fine-grained syenite, coarse-grained syenite, melanocratic rock and alkali-feldspar granite give Rb-Sr whole-rock isochron ages of 2496 Ma, 2824 Ma, 4945 Ma and 1288 Ma with initial Sr isotope ratios (SrI) of 0.5863, 0.5193, 0.6679 and 0.7838, respectively. Because the age

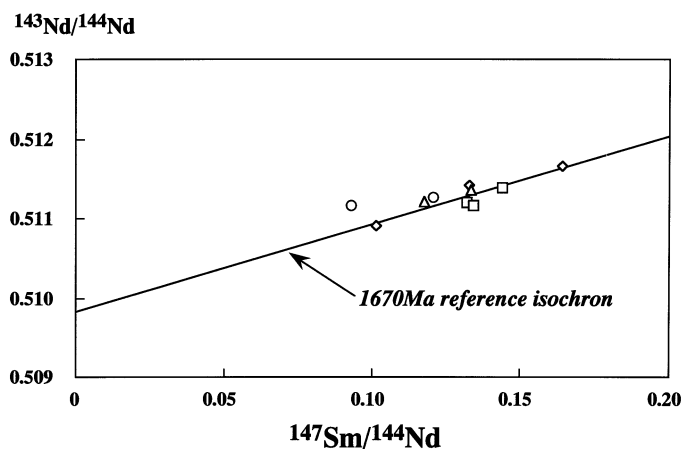


Fig. 13. Sm-Nd whole-rock isochron diagram of the syenites and melanocratic rocks. Symbols are the same as those in Fig. 9.

of the alkali-feldspar granite is much younger than the age of dolerite dyke activity and SrI has very low values for terrestrial rocks and meteorites, they are pseudo-isochrons. Thus, syenites and related rocks disperse and do not give clear isochrons. However, syenites (excluding 98081503) and melanocratic rocks are plotted alongside of a reference isochron of 1920 Ma.

An Sm-Nd whole-rock isochron diagram is shown in Fig. 13. Syenites and melanocratic rocks give a Sm-Nd whole-rock isochron age of 1670 Ma with a large error of 515 Ma. This age is younger than the time of dolerite dyke activity, and might be also a pseudo-isochron.

## 6. Discussion

Clinopyroxenes in the syenites and related rocks from the Spitskop pipe are aegirine. This has been already pointed out by Eriksson (1989), but their chemical compositions were not reported. The Na contents of clinopyroxenes analyzed in this pipe are much higher than those in the main complex reported by Eriksson (1989). The syenite and melanocratic rock contain amphibole, which is magnesioriebeckite. The Ca content of the amphibole in the Spitskop pipe is lower than that (richterite to winchite) in the main complex reported by Eriksson (1989). It is thought that this is caused by the difference in the formation process, *i.e.* the former crystallized from Ca-poor magma, while the latter were products of metasomatism between the country rock and pyroxenite and carbonatite magmas.

Whole-rock chemical compositions of the fine- and coarse-grained syenites are nearly the same (Figs. 9, 10). The chemical compositions of the inner cumulus syenite overlap the range of the fine- and coarse-grained syenites. Chemical compositions of alkali-feldspars and clinopyroxenes in the fine- and coarse-grained syenites are also nearly the same. In addition, Fe/Mg ratios of amphiboles increase from the fine-grained syenite to coarse-grained syenite (Fig. 8). They suggest that the fine- and

coarse-grained syenites are members of the inner cumulus syenite. The high FeO\*, MgO, Na<sub>2</sub>O and low Al<sub>2</sub>O<sub>3</sub> contents of the melanocratic rocks are the results of the high clinopyroxene and amphibole contents (Fig. 7). The low K<sub>2</sub>O contents of those rocks are due to the low alkali-feldspar contents. The chemical compositions of the clinopyroxenes and alkali-feldspars in the melanocratic rock are similar to those in the fine- and coarse-grained syenites. The Fe/Mg ratios of amphiboles in the melanocratic rock are lower than those in the fine-grained syenite, and those in the coarse-grained syenite are the highest (Fig. 8). Whole-rock chemical compositions of the melanocratic rocks are different from those of pyroxenites in the main complex and satellites bodies reported by Eriksson (1989). They suggest that the melanocratic rocks are early mafic mineral accumulation facies of the inner cumulus syenite. The wide variation of Fe/Mg ratio of the coarse-grained syenite (Fig. 8) suggests chemical differentiation of magma. The alkali-feldspar granite might be a country rock, because chemical compositions of them are similar to granites, which are the country rock of the Kgopoele pipe. According to Eriksson (1989), chemical compositions of the outer ring syenite and the inner cumulus syenite in the Spitskop pipe can be modeled by crystallizing aegirine, feldspar and apatite. However, it is necessary to incorporate an amphibole component into the calculations.

Syenites and related rocks do not indicate any clear isochron (Figs. 11, 12). The lack of a clear isochron might be caused by mixing of various rocks made up of syenite, melanocratic rock, pyroxenite and host rocks consisting of biotite gneiss and granitic rocks at the brecciation stage. The arrangements of the melanocratic rocks and syenites are steeper than the reference isochron of 1920 Ma. They suggest a possibility that the syenites and melanocratic rocks were influenced by materials having high <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>87</sup>Rb/<sup>86</sup>Sr ratios. Most of the syenites and melanocratic rocks, which were produced from the same magma, are plotted alongside the reference isochron of 1920 Ma. Because this age is sandwiched between the U-Pb ages of ca. 2050 Ma from the main complex and 1900 Ma of the dolerite dykes, there is a possibility that the Spitskop pipe was formed at this age. The age of the syenites, both in the main complex and as satellites, is less certain. Palaeomagnetic data indicate a duration of magmatism up to 200 Ma (Briden, 1976; Morgan and Briden, 1981). One syenite pipe has a pole position identical to the 2047 Ma clinopyroxenite of the main complex, whereas a syenite adjacent to the northern periphery of the main complex has a pole position similar to that of some large dolerite dykes which cut the complex, considered to be the Mashonaland dolerites dated at 1950 Ma (Eriksson, 1989). For detailed discussion of the crystallization age of this syenite pipe, it is necessary to determine mineral ages.

#### Acknowledgments

We thank Mr. Nick Baglow (Council for Geoscience, South Africa) for support during the field survey. Thanks are also due to Dr. Y. Kawano (Saga University) for convenience on isotopic separation. This study was supported mainly by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science, Sports and Culture to Dr. K. Shiraishi (No. 0904116) for the field survey and to Dr. M. Arima (No. 13373005) for part of the analytical work.

## References

- Briden, J.C. (1976): Application of palaeomagnetism to proterozoic tectonics. *Philos. Trans. R. Soc. London*, **280**, 405–416.
- Eriksson, S.C. (1984): Age of carbonatite and phoscorite magmatism of the Phalaborwa Complex (South Africa). *Isotope Geosci.*, **2**, 291–299.
- Eriksson, S.C. (1989): Phalaborwa: a saga of magmatism, metasomatism & miscibility. *Carbonatites*, ed by K. Bell. New York, Unwin Hyman, 221–254.
- Hall, A.L. (1912a): The Palabora plutonic complex of the low country and its relationship to the pegmatites of the Leydsdorp mics-fields. *Trans. Geol. Soc. S. Afr.*, **15**, 4–17.
- Hall, A.L. (1912b): The crystalline metamorphic limestone of Lulukop and its relationship to the Palabora Plutonic Complex. *Trans. Geol. Soc. S. Afr.*, **15**, 18–25.
- Hanekom, H.J., van Staden, C.M., Smit, P.J. and Pike, D.R. (1965): The geology of the Palabora Igneous Complex. *S. Afr. Geol. Surv., Mem.*, **54**, 179 p.
- Heaman, L.M. and LeCheminant, A.N. (1993): Paragenesis and U-Pb systematics of Baddeleyite (ZrO<sub>2</sub>). *Chem. Geol.*, **110**, 95–126.
- Horn, I., Rudnick, R.L. and McDonough, W.F. (2000): Precise elemental and isotope ratio determination by simultaneous solution nebulization and laser ablation-ICP-MS: application to U-Pb geochronology. *Chem. Geol.*, **164**, 281–301.
- Kawano, Y. (1994): Calculation program for isochron ages of Rb-Sr and Sm-Nd systems using personal computer. *Geoinformatics*, **5**, 13–19 (in Japanese with English abstract).
- Kawano, Y., Nishi, N. and Ishisaka, T. (1999): Preparation of samples for Sr and Nd isotopic analysis at petrochemical laboratory. *J. Fac. Cul. Edu. Saga Univ.*, **4**, 139–146 (in Japanese with English abstract).
- Lugmair, G.W. and Marti, K. (1978): Lunar initial <sup>143</sup>Nd/<sup>144</sup>Nd: differential evolution of the Lunar crust and mantle. *Earth Planet. Sci. Lett.*, **39**, 349–357.
- Miyazaki, T. and Shuto, K. (1998): Sr and Nd isotope ratios of twelve GSJ rock reference samples. *Geochem. J.*, **32**, 345–350.
- Morgan, G.E. and Briden, J.C. (1981): Aspects of Precambrian palaeomagnetism, with new data from the limpopo mobile belt and Kaapvaal craton in southern Africa. *Phys. Earth Planet. Inter.*, **24**, 1442–1468.
- Palabora Mining Company Limited Mine, Mine Geological and Mineralogical Staff (1976): The geology and the economic deposits of copper, iron, and vermiculite in the Palabora Igneous Complex: A brief review. *Econ. Geol.*, **71**, 177–192.
- Reischmann, T. (1995): Precise U/Pb age determination with baddeleyite (ZrO<sub>2</sub>), a case study from the Phalaborwa Igneous Complex, South Africa. *S. Afr. J. Geol.*, **98**, 1–4.
- Shand, S.J. (1931): The granite-syenite-limestone complex of Palabora, eastern Transvaal, and the associated apatite deposits. *Trans. Geol. Soc. S. Afr.*, **34**, 81–105.
- Steiger, R.H. and Jäger, E. (1977): Subcommittee on geochronology: convention on the use of decay constants in geo- and cosmochronology. *Earth Planet. Sci. Lett.*, **36**, 359–362.
- Tanaka, T., Togashi, S., Kamioka, H., Amakawa, H., Kagami, H., Hamamoto, T., Yuhara, M., Orihashi, Y., Yoneda, S., Shimizu, H., Kunimaru, T., Takahashi, K., Yanagi, T., Nakano, T., Fujimaki, H., Shinjo, R., Asahara, Y., Tanimizu, M. and Dragusanu, C. (2000): JNdi-1: a neodymium isotopic reference in consistency with LaJolla neodymium. *Chem. Geol.*, **168**, 279–281.
- Wilson, M. (1989): *Igneous Petrogenesis*. London, Unwin Hyman, 466 p.
- York, D. (1966): Least-squares fitting of a straight line. *Can. J. Phys.*, **44**, 1079–1086.
- Yuhara, M. and Taguchi, S. (2003): Major and trace element analyses of silicate rocks using X-ray fluorescence spectrometer ZSX100e. *Fukuoka Univ. Sci. Rep.*, **33**, 25–34 (in Japanese with English abstract).



## Appendix 1. Chemical compositions of constituent minerals of fine-grained syenite (98081501B).

Mineral	Pyroxene						Amphibole						
	Anal. Pt. No.	238	239	240	241	246	247	229	231	232	234	235	237
								core	rim	core	rim	core	rim
SiO <sub>2</sub> (wt%)	53.29	53.36	53.38	52.60	53.21	53.16	55.34	54.92	55.19	55.75	55.15	55.36	
TiO <sub>2</sub>	0.51	0.72	1.03	0.72	0.94	1.30	0.39	0.44	0.28	0.44	0.43	0.33	
Al <sub>2</sub> O <sub>3</sub>	0.59	0.85	0.75	0.79	0.57	0.45	0.28	0.32	0.36	0.28	0.31	0.32	
FeO*	25.01	24.96	25.78	25.02	24.41	25.42	14.83	15.21	15.43	15.20	15.08	15.42	
MnO	0.32	0.28	0.24	0.35	0.34	0.33	1.19	1.35	0.94	0.91	1.14	1.15	
MgO	1.49	1.07	1.16	1.25	1.36	1.29	12.51	12.08	11.84	12.46	12.27	11.78	
CaO	3.12	1.85	1.72	2.53	2.34	1.88	0.75	0.88	0.82	0.81	0.84	0.86	
Na <sub>2</sub> O	10.79	11.01	10.30	10.28	10.48	10.91	6.58	6.78	6.72	6.77	6.65	6.91	
K <sub>2</sub> O	0.00	0.00	0.01	0.00	0.00	0.00	2.81	3.07	2.63	3.04	2.96	2.49	
P <sub>2</sub> O <sub>5</sub>	0.03	0.00	0.00	0.03	0.01	0.00	0.02	0.03	0.00	0.00	0.01	0.00	
F	0.03	0.00	0.18	0.03	0.05	0.00	1.98	2.40	1.71	1.77	2.06	2.15	
Total	95.18	94.10	94.55	93.60	93.71	94.74	96.68	97.48	95.92	97.43	96.90	96.77	
Cations	(O=6)						(O=23)						
Si	2.089	2.115	2.128	2.108	2.125	2.099	7.932	7.823	7.999	7.959	7.903	7.926	
Ti	0.015	0.021	0.031	0.022	0.028	0.039	0.042	0.047	0.030	0.048	0.046	0.036	
Al	0.027	0.040	0.035	0.037	0.027	0.021	0.048	0.054	0.062	0.047	0.053	0.053	
Fe <sup>3+</sup>	0.585	0.534	0.444	0.502	0.478	0.539							
Fe <sup>2+</sup>	0.235	0.293	0.415	0.337	0.338	0.301							
Fe*							1.975	2.013	2.078	2.016	2.008	2.052	
Mn	0.011	0.009	0.008	0.012	0.012	0.011	0.145	0.163	0.115	0.110	0.138	0.139	
Mg	0.089	0.063	0.069	0.075	0.081	0.076	2.673	2.565	2.557	2.652	2.621	2.514	
Ca	0.131	0.079	0.073	0.109	0.100	0.080	0.116	0.135	0.127	0.124	0.129	0.131	
Na	0.820	0.846	0.796	0.799	0.812	0.835	1.828	1.872	1.889	1.874	1.847	1.917	
K	0.000	0.000	0.001	0.000	0.000	0.000	0.513	0.557	0.486	0.554	0.541	0.454	
P	0.001	0.000	0.000	0.001	0.000	0.000	0.002	0.004	0.000	0.000	0.001	0.000	
F	0.003	0.000	0.023	0.003	0.007	0.000	0.897	1.080	0.782	0.798	0.932	0.975	
Total	4.003	4.000	4.000	4.002	4.001	4.001	15.274	15.233	15.343	15.384	15.287	15.222	

\*Total Fe

\*\*Fe<sup>2+</sup> and Fe<sup>3+</sup> were calculated assuming ideal stoichiometry.

Mineral	Alkali - feldspar									
	Anal. Pt. No.	220	221	222	223	224	225	226	227	228
		core	-	rim	core	-	rim	core	-	rim
SiO <sub>2</sub> (wt%)	65.07	64.85	65.26	65.34	64.92	65.25	65.20	65.39	65.34	
TiO <sub>2</sub>	0.02	0.01	0.00	0.00	0.02	0.01	0.01	0.00	0.01	
Al <sub>2</sub> O <sub>3</sub>	17.73	17.93	17.73	17.30	17.14	18.26	17.88	17.58	17.90	
FeO*	0.65	0.59	0.45	0.67	0.56	0.40	0.52	0.63	0.58	
MnO	0.02	0.00	0.01	0.05	0.07	0.07	0.00	0.00	0.00	
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
CaO	0.02	0.03	0.01	0.01	0.02	0.00	0.00	0.00	0.00	
Na <sub>2</sub> O	0.32	0.26	0.30	0.27	0.33	0.20	0.21	0.29	0.27	
K <sub>2</sub> O	16.14	16.25	16.33	16.11	16.00	16.38	16.36	16.29	16.46	
P <sub>2</sub> O <sub>5</sub>	0.01	0.00	0.00	0.00	0.00	0.01	0.03	0.00	0.00	
F	0.00	0.00	0.00	0.00	0.00	0.00	0.16	0.00	0.00	
Total	99.98	99.92	100.09	99.75	99.06	100.58	100.37	100.18	100.56	
Cations	(O=8)									
Si	3.013	3.005	3.018	3.030	3.032	3.002	3.002	3.022	3.011	
Ti	0.001	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	
Al	0.967	0.980	0.966	0.946	0.944	0.990	0.971	0.958	0.972	
Fe*	0.028	0.025	0.019	0.029	0.024	0.017	0.023	0.027	0.025	
Mn	0.001	0.000	0.000	0.002	0.003	0.003	0.000	0.000	0.000	
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Ca	0.001	0.002	0.001	0.000	0.001	0.000	0.000	0.000	0.000	
Na	0.029	0.024	0.026	0.025	0.030	0.018	0.019	0.026	0.024	
K	0.953	0.961	0.964	0.954	0.953	0.961	0.961	0.960	0.967	
P	0.001	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.000	
F	0.000	0.000	0.000	0.000	0.000	0.000	0.023	0.000	0.000	
Total	4.994	4.997	4.994	4.986	4.988	4.992	4.977	4.993	4.999	
an	0.001	0.002	0.001	0.000	0.001	0.000	0.000	0.000	0.000	
ab	0.030	0.024	0.026	0.026	0.030	0.018	0.019	0.026	0.024	
or	0.969	0.974	0.973	0.974	0.968	0.982	0.981	0.974	0.976	

\*Total Fe

Appendix 2. Chemical compositions of constituent minerals of coarse-grained syenite (98081501A).

Mineral Anal. Pt. No.	Clinopyroxene					Amphibole						
	36	38	39	41	43	44	55	58	59	61	63	64
SiO <sub>2</sub> (wt%)	52.00	52.68	52.29	52.89	52.95	52.56	53.86	54.23	53.24	54.15	54.16	54.10
TiO <sub>2</sub>	0.58	0.58	0.94	1.56	0.87	0.93	0.48	0.41	0.43	0.48	0.46	0.55
Al <sub>2</sub> O <sub>3</sub>	0.64	0.58	0.52	0.67	0.51	0.67	0.45	0.39	0.51	0.39	0.38	0.37
FeO*	25.61	24.57	24.35	23.68	24.91	24.95	17.99	17.02	18.64	16.15	16.06	15.58
MnO	0.22	0.27	0.38	0.13	0.21	0.22	0.48	0.24	0.49	0.50	0.49	0.60
MgO	1.12	1.47	1.41	1.48	0.93	1.35	10.55	11.51	10.35	11.11	12.31	11.96
CaO	1.82	2.71	2.60	2.34	1.43	2.27	0.60	0.67	0.58	0.87	0.73	0.87
Na <sub>2</sub> O	13.33	12.35	12.51	12.06	13.43	13.12	8.24	7.90	8.04	7.57	7.82	7.64
K <sub>2</sub> O	0.01	0.00	0.00	0.00	0.00	0.00	1.48	1.88	1.33	2.33	2.14	2.32
P <sub>2</sub> O <sub>5</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
F	0.00	0.00	0.00	0.00	0.00	0.00	0.81	0.41	0.63	0.86	0.80	0.89
Total	95.33	95.21	95.00	94.81	95.24	96.07	94.94	94.66	94.24	94.41	95.35	94.88
Cations	(O=6)						(O=23)					
Si	1.995	2.034	2.022	2.057	2.033	2.003	8.032	8.109	8.032	8.078	8.003	8.022
Ti	0.018	0.017	0.027	0.046	0.025	0.027	0.053	0.046	0.049	0.054	0.051	0.061
Al	0.029	0.026	0.024	0.031	0.023	0.030	0.080	0.069	0.090	0.068	0.066	0.064
Fe <sup>3+</sup>	0.822	0.793	0.787	0.674	0.800	0.795						
Fe <sup>2+</sup>	0.000	0.000	0.000	0.096	0.000	0.000						
Fe*							2.494	2.365	2.614	2.240	2.206	2.146
Mn	0.007	0.009	0.012	0.004	0.007	0.007	0.061	0.031	0.063	0.064	0.062	0.076
Mg	0.064	0.085	0.081	0.086	0.053	0.077	2.345	2.566	2.326	2.471	2.712	2.644
Ca	0.075	0.112	0.108	0.098	0.059	0.093	0.096	0.108	0.093	0.139	0.116	0.138
Na	0.991	0.924	0.938	0.909	1.000	0.969	2.382	2.289	2.351	2.190	2.241	2.198
K	0.000	0.000	0.000	0.000	0.000	0.000	0.281	0.359	0.257	0.443	0.403	0.440
P	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
F	0.000	0.000	0.000	0.000	0.000	0.000	0.382	0.194	0.302	0.404	0.375	0.416
Total	4.001	4.000	3.999	4.001	4.000	4.001	15.824	15.942	15.875	15.747	15.860	15.789

\*Total Fe

\*\*Fe<sup>2+</sup> and Fe<sup>3+</sup> were calculated assuming ideal stoichiometry.

Mineral Anal. Pt. No.	Alkali-feldspar								
	45	46	47	48	49	50	51	52	53
	core	-	rim	core	-	rim	core	-	rim
SiO <sub>2</sub> (wt%)	63.88	64.46	63.17	64.00	63.98	63.66	63.89	63.54	63.70
TiO <sub>2</sub>	0.05	0.00	0.01	0.04	0.00	0.00	0.00	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	17.01	17.78	17.72	17.94	17.96	17.85	17.72	17.63	18.15
FeO*	0.75	0.63	0.49	0.45	0.40	0.54	0.59	0.39	0.52
MnO	0.00	0.02	0.00	0.00	0.05	0.00	0.07	0.00	0.00
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.00	0.00	0.04	0.00	0.00	0.00	0.02	0.03	0.01
Na <sub>2</sub> O	0.37	0.31	0.33	0.23	0.23	0.42	0.26	0.23	0.26
K <sub>2</sub> O	16.34	16.17	16.26	16.53	16.39	15.88	16.23	16.46	16.39
P <sub>2</sub> O <sub>5</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
F	0.09	0.00	0.00	0.06	0.16	0.00	0.00	0.00	0.13
Total	98.49	99.37	98.02	99.25	99.17	98.35	98.78	98.28	99.16
Cations	(O=8)								
Si	3.012	3.006	2.993	2.991	2.988	2.997	3.000	3.001	2.979
Ti	0.002	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000
Al	0.945	0.977	0.990	0.988	0.989	0.990	0.981	0.981	1.000
Fe*	0.033	0.027	0.021	0.020	0.018	0.023	0.026	0.017	0.023
Mn	0.000	0.001	0.000	0.000	0.002	0.000	0.003	0.000	0.000
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ca	0.000	0.000	0.002	0.000	0.000	0.000	0.001	0.002	0.001
Na	0.034	0.028	0.030	0.021	0.021	0.038	0.024	0.021	0.024
K	0.983	0.962	0.983	0.986	0.977	0.954	0.973	0.992	0.978
P	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
F	0.014	0.000	0.000	0.009	0.023	0.000	0.000	0.000	0.018
Total	5.009	5.001	5.019	5.008	4.995	5.002	5.008	5.014	5.005
an	0.000	0.000	0.002	0.000	0.000	0.000	0.001	0.002	0.001
ab	0.033	0.028	0.029	0.021	0.021	0.038	0.024	0.021	0.024
or	0.967	0.972	0.968	0.979	0.979	0.962	0.975	0.977	0.975

\*Total Fe

## Appendix 3. Chemical compositions of constituent minerals of melanocratic rock (98081501C).

Mineral	Clinopyroxene						Amphibole								
	Anal. Pt. No.	75	78	79	80	81	83	84	87	88	89	90	92	93	
SiO <sub>2</sub> (wt%)	52.38	52.73	52.91	52.67	52.47	52.55	52.58	54.77	54.42	54.12	54.06	53.68	53.76		
TiO <sub>2</sub>	0.78	0.69	2.05	1.17	0.68	0.67	0.77	0.29	0.35	0.44	0.36	0.34	0.24		
Al <sub>2</sub> O <sub>3</sub>	0.64	0.79	0.37	0.40	0.62	0.67	0.71	0.33	0.31	0.31	0.31	0.34	0.29	0.28	
FeO*	24.48	24.43	23.56	24.52	24.61	24.46	24.19	14.02	14.37	14.88	14.33	14.53	13.87		
MnO	0.33	0.26	0.46	0.39	0.22	0.34	0.34	0.95	1.08	1.00	1.00	1.16	0.99		
MgO	1.33	1.26	1.42	1.45	1.46	1.38	1.38	12.77	12.32	12.54	12.50	12.69	12.36		
CaO	2.74	2.51	1.89	2.09	2.71	2.71	2.62	1.06	1.07	1.10	1.17	1.06	1.06		
Na <sub>2</sub> O	12.59	12.55	13.55	13.00	12.66	12.97	12.64	7.85	7.74	7.76	7.98	7.87	7.93		
K <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.47	2.69	2.79	2.60	2.88	2.70		
P <sub>2</sub> O <sub>5</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
F	0.00	0.00	0.00	0.00	0.00	0.17	0.00	1.47	1.94	1.49	1.98	1.81	1.99		
Total	95.27	95.22	96.21	95.69	95.43	95.92	95.23	95.98	96.29	96.43	96.32	96.31	95.18		
Cations	(O=6)							(O=23)							
Si	2.018	2.033	2.008	2.017	2.016	2.008	2.025	7.952	7.870	7.876	7.821	7.811	7.857		
Ti	0.023	0.020	0.059	0.034	0.020	0.019	0.022	0.031	0.038	0.049	0.039	0.037	0.026		
Al	0.029	0.036	0.017	0.018	0.028	0.030	0.032	0.056	0.052	0.053	0.058	0.049	0.048		
Fe <sup>3+</sup>	0.789	0.788	0.748	0.785	0.791	0.782	0.779								
Fe <sup>2+</sup>	0.000	0.000	0.000	0.000	0.000	0.000	0.000								
Fe*								1.892	1.931	2.013	1.927	1.965	1.884		
Mn	0.011	0.008	0.015	0.013	0.007	0.011	0.011	0.117	0.132	0.123	0.123	0.142	0.122		
Mg	0.076	0.072	0.080	0.083	0.084	0.079	0.079	2.765	2.657	2.721	2.696	2.752	2.694		
Ca	0.113	0.104	0.077	0.086	0.112	0.111	0.108	0.165	0.166	0.172	0.181	0.165	0.166		
Na	0.941	0.938	0.997	0.965	0.943	0.961	0.944	2.211	2.170	2.190	2.238	2.220	2.248		
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.458	0.497	0.518	0.479	0.534	0.503		
P	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
F	0.000	0.000	0.000	0.000	0.000	0.022	0.000	0.676	0.885	0.687	0.908	0.831	0.918		
Total	4.000	3.999	4.001	4.001	4.001	4.001	4.000	15.647	15.513	15.715	15.562	15.675	15.548		

\*Total Fe

\*\*Fe<sup>2+</sup> and Fe<sup>3+</sup> were calculated assuming ideal stoichiometry.

Mineral	Alkali-feldspars										
	Anal. Pt. No.	65	66	67	68	69	70	71	72	73	
		core	-	rim	core	-	rim	core	-	rim	
SiO <sub>2</sub> (wt%)	64.26	63.41	63.12	64.06	63.54	63.71	63.82	64.24	64.75		
TiO <sub>2</sub>	0.00	0.00	0.00	0.00	0.07	0.00	0.02	0.00	0.04		
Al <sub>2</sub> O <sub>3</sub>	18.01	17.98	17.52	17.73	17.93	18.04	17.82	17.94	18.04		
FeO*	0.47	0.52	0.47	0.61	0.47	0.38	0.47	0.50	0.38		
MnO	0.02	0.03	0.00	0.04	0.00	0.01	0.03	0.00	0.00		
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
CaO	0.00	0.01	0.02	0.00	0.01	0.00	0.04	0.00	0.00		
Na <sub>2</sub> O	0.35	0.28	1.16	0.31	0.27	0.30	1.43	0.23	0.28		
K <sub>2</sub> O	16.21	16.45	15.25	16.29	16.55	16.33	14.90	16.32	16.33		
P <sub>2</sub> O <sub>5</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
F	0.00	0.22	0.00	0.19	0.06	0.19	0.06	0.00	0.06		
Total	99.32	98.90	97.54	99.23	98.90	98.96	98.59	99.23	99.88		
Cations	(O=8)										
Si	2.998	2.974	2.996	2.991	2.984	2.981	2.990	3.000	2.999		
Ti	0.000	0.000	0.000	0.000	0.002	0.000	0.001	0.000	0.001		
Al	0.990	0.994	0.980	0.975	0.993	0.995	0.984	0.987	0.985		
Fe*	0.020	0.023	0.021	0.026	0.020	0.016	0.020	0.022	0.016		
Mn	0.001	0.001	0.000	0.001	0.000	0.000	0.001	0.000	0.000		
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
Ca	0.000	0.001	0.001	0.000	0.000	0.000	0.002	0.000	0.000		
Na	0.032	0.026	0.107	0.028	0.024	0.027	0.130	0.021	0.025		
K	0.965	0.984	0.923	0.970	0.992	0.975	0.891	0.972	0.965		
P	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
F	0.000	0.033	0.000	0.028	0.009	0.028	0.009	0.000	0.009		
Total	5.006	5.003	5.028	4.991	5.015	4.994	5.019	5.002	4.991		
an	0.000	0.001	0.001	0.000	0.000	0.000	0.002	0.000	0.000		
ab	0.032	0.026	0.103	0.028	0.024	0.027	0.127	0.021	0.025		
or	0.968	0.973	0.895	0.972	0.976	0.973	0.871	0.979	0.975		

\*Total Fe

## Appendix 4. Chemical compositions of constituent minerals of alkali-feldspar granite (98081501E).

Mineral	Alkali-feldspar												
	Anal. Pt. No.	169	170	171	172	173	174	175	176	177	178	186	189
SiO <sub>2</sub> (wt%)	64.66	64.42	64.37	64.69	64.56	63.61	64.36	64.19	63.74	63.94	64.91	64.17	
TiO <sub>2</sub>	0.02	0.03	0.00	0.04	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.03	
Al <sub>2</sub> O <sub>3</sub>	18.32	18.35	18.43	17.85	18.39	18.10	18.44	18.36	18.01	18.44	18.27	18.55	
FeO*	0.04	0.06	0.00	0.08	0.04	0.05	0.03	0.06	0.04	0.03	0.00	0.00	
MnO	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.00	
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
CaO	0.03	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.05	0.05	0.00	0.00	
Na <sub>2</sub> O	0.31	0.75	0.40	0.27	0.19	0.36	0.27	0.32	0.36	0.26	0.32	0.28	
K <sub>2</sub> O	15.88	15.40	16.16	16.50	16.38	16.25	16.22	16.27	16.47	16.38	16.32	16.22	
P <sub>2</sub> O <sub>5</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Total	99.26	99.01	99.37	99.46	99.56	98.37	99.32	99.21	98.69	99.10	99.84	99.25	
Cations	(O=8)												
Si	3.003	2.998	2.993	3.011	2.998	2.994	2.994	2.992	2.995	2.987	3.004	2.988	
Ti	0.001	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	
Al	1.003	1.006	1.010	0.979	1.006	1.004	1.011	1.009	0.997	1.015	0.997	1.018	
Fe*	0.002	0.003	0.000	0.004	0.002	0.003	0.001	0.003	0.002	0.001	0.000	0.000	
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Ca	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.003	0.002	0.000	0.000	
Na	0.028	0.067	0.036	0.024	0.017	0.033	0.024	0.029	0.033	0.024	0.029	0.025	
K	0.941	0.914	0.959	0.980	0.970	0.976	0.963	0.968	0.987	0.976	0.964	0.963	
P	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
F	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Total	4.979	4.989	4.998	5.000	4.993	5.010	4.993	5.001	5.018	5.005	4.994	4.995	
an	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.003	0.002	0.000	0.000	
ab	0.029	0.069	0.036	0.024	0.017	0.033	0.024	0.029	0.032	0.024	0.029	0.025	
or	0.970	0.931	0.963	0.975	0.983	0.967	0.976	0.971	0.965	0.974	0.971	0.975	

\*Total Fe

Mineral	Plagioclase									
	Anal. Pt. No.	153	154	155	156	157	158	159	160	161
		core	-	rim	core	-	rim	core	-	rim
SiO <sub>2</sub> (wt%)	67.59	67.65	67.74	68.32	68.13	67.85	67.88	68.50	67.96	
TiO <sub>2</sub>	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.01	
Al <sub>2</sub> O <sub>3</sub>	19.73	19.75	19.32	19.79	19.64	19.69	19.37	19.49	19.36	
FeO*	0.04	0.08	0.02	0.13	0.04	0.03	0.12	0.13	0.13	
MnO	0.02	0.06	0.00	0.02	0.00	0.00	0.00	0.00	0.00	
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	
CaO	0.21	0.48	0.25	0.11	0.09	0.08	0.19	0.08	0.15	
Na <sub>2</sub> O	11.48	11.60	11.96	12.00	12.06	12.11	12.15	11.91	11.88	
K <sub>2</sub> O	0.14	0.19	0.05	0.09	0.07	0.09	0.09	0.13	0.14	
P <sub>2</sub> O <sub>5</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Total	99.21	99.81	99.34	100.48	100.03	99.85	99.80	100.25	99.63	
Cations	(O=8)									
Si	2.978	2.970	2.985	2.977	2.981	2.975	2.981	2.989	2.986	
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Al	1.025	1.022	1.003	1.016	1.013	1.018	1.003	1.003	1.003	
Fe*	0.002	0.003	0.001	0.005	0.002	0.001	0.005	0.005	0.005	
Mn	0.001	0.002	0.000	0.001	0.000	0.000	0.000	0.000	0.000	
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	
Ca	0.010	0.023	0.012	0.005	0.004	0.004	0.009	0.004	0.007	
Na	0.981	0.980	1.022	1.014	1.023	1.030	1.035	1.008	1.012	
K	0.008	0.011	0.003	0.005	0.004	0.005	0.005	0.007	0.008	
P	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
F	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Total	5.005	5.011	5.026	5.023	5.027	5.033	5.038	5.017	5.021	
an	0.010	0.022	0.011	0.005	0.004	0.004	0.009	0.004	0.007	
ab	0.982	0.967	0.986	0.990	0.992	0.991	0.986	0.989	0.985	
or	0.008	0.011	0.003	0.005	0.004	0.005	0.005	0.007	0.008	

\*Total Fe