ATTI

DELLA

SOCIETÀ TOSCANA

DI

SCIENZE NATURALI

RESIDENTE IN PISA

MEMORIE - SERIE A

VOL. LXXVII - ANNO 1970

PROCESSI VERBALI 1970

ARTI GRAFICHE PACINI MARIOTTI - PISA - 1970

INDICE

MEMORIE

BOTTARI F., MACCHIA B. - Stereochimica delle reazioni con acido tricloroacetico e acido cloridrico di alcuni ossidi di stilbene sostituiti . . Pag. 1

LARDICCI L., MENICAGLI R. - Sulla correlazione tra il (—)(S)-2-metil-1-butanolo e composti otticamente attivi contenenti gruppi fenilici: determinazione della relazione potere rotatorio-purezza ottica . . . . » 25

CECCANTI G. M., GIACOMELLI G. P., LARDICCI L. - Su alcuni composti organometallici otticamente attivi contenenti gruppi fenilici . . . . . » 40

DI FRAIA T. - Resti di un villaggio della cultura tipo Serra d'Alto a Saldone presso Metaponto (Lucania) . . . . » 54

GRIFONI CREMONESI R. - I materiali preistorici della Toscana esistenti al Museo Civico di Grosseto . . . . » 78

RAU A., TONGIORGI M. - Tane ad U fossili del «genere» *Corophioides* negli «Scisti verdi» (Carnico inferiore) dei Monti Pisani . . . . . . » 92

RAMA S., PAGGI A. - Sulla utilità dell'impiego di lasers nello studio di fumi da combustione . . . . » 102

MENCHETTI S. - Sulla arsenpolibasite del Canale dell'Angina (Alpi Apuane) » 111

BONATTI S., FRANZINI M., SCHIAFFINO L. - The Bagnone meteorite . . . » 123

CAPEDRI S. - Le geminazioni dei plagioclasi in relazione all'origine delle ofioliti appenniniche ad albite . . . . » 134

BRONDI A., GHEZZO C., GUASPARRI G., RICCI C. A., SABATINI G. - Le vulcaniti paleozoiche nell'area settentrionale del Complesso effusivo atesino. Nota I - Successione stratigrafica, assetto strutturale e vulcanologico nella Val Sarentina . . . . » 155

GRAZZINI M. - Idrogranati nelle brecce ofiolitiche di Vincigliata (Firenze) » 201

MORI G., TOZZI C. - Resti di un insediamento piceno al Colle del Telegrafo a Pescara . . . . » 217

FERRARI G. A., MAGALDI D., RASPI A. - Osservazioni micromorfologiche e sedimentologiche su alcuni paleosuoli dei dintorni di Grosseto . . » 231

FONDI R. - *Prolagus sardus* WAGNER (*ochotonidae, lagomorpha, mammalia*) da una breccia ossifera della Montagnola senese . . . . . . » 260

DI FRAIA T. - Tracce di uno stanziamento neolitico all'aperto presso Paterno (L'Aquila) . . . . » 289

BRANDI G. P., CERRINA FERONI A., DECANDIA F. A., GIANNELLI L., MONTEFORTI B., SALVATORINI G. - Il Pliocene del bacino del Tevere fra Celleno (Terni) e Civita Castellana (Viterbo). Stratigrafia ed evoluzione tettonica . . . . Pag. 308

SIGHINOLFI G. P. - Investigations into the deep levels of the continental crust: petrology and chemistry of the granulite facies terrains of Bahia (Brazil) . . . . » 327

RIVALENTI G. - Genetical problems of banded amphibolites in the Frederikshåb district, South West Greenland . . . . » 342

RIVALENTI G., SIGHINOLFI G. P. - Geochemistry and differentiation phenomena in basic dikes of the Frederikshåb district, South West Greenland » 358

PROCESSI VERBALI

Adunanza del 15 gennaio 1970 . . . . Pag. 381

Adunanza del 12 marzo 1970 . . . . » 383

Adunanza del 14 maggio 1970 . . . . » 385

Adunanza del 9 luglio 1970 . . . . » 385

Adunanza del 12 novembre 1970 . . . . » 386

Adunanza straordinaria del 10 dicembre 1970 . . . . » 387

Statuto . . . . » 389

Regolamento . . . . » 395

Elenco dei soci per l'anno 1970 . . . . » 399

Atti Soc. Tosc. Sci Nat., Mem., Serie A, **77** (1970).
pagg. 358-380, ff. 6.

G. RIVALENTI, G. P. SIGHINOLFI (*)

GEOCHEMISTRY AND DIFFERENTIATION PHENOMENA IN BASIC DIKES OF THE FREDERIKSHÅB DISTRICT, SOUTH WEST GREENLAND

Abstract — The basement rocks in the Frederikshåb district are intersected by several generations of basic post-orogenic dikes whose age varies from pre-Cambrian to Mesozoic. In this work samples belonging to the following generations have been geochemically examined: MD 1, MD 2, MD 3 (pre-Ketilidian dolerites), TD (Mesozoic dikes), Lamprophyres (younger dikes but of unknown age). Major and trace elements (V, Cu, Zr, Ni, Co, Cr, Sr, Ba, Y, Rb, Sc and Zn) have been determined. MDs have a general composition similar to the one of continental tholeiites, while TDs and Lamprophyres clearly show alkalic affinities.

Several geochemical trends have been statistically tested for MDs and the trends conform with those expected in a classical igneous differentiation.

Variations which can be observed among the dikes of the same generation have been related to local differentiations of the magma chamber. Small variations among the various generations have been attributed to a slight evolution of the magma. Differentiations are also present in the same dike from margin to center and, in one examined case, in a vertical sense too. The center is slightly more differentiated in respect to the chilled margins and the upper part in respect to the lower. Some hypotheses are investigated to account for the mechanism of differentiation within the dike. These hypotheses also explain the irregular behaviour of some elements and ratios such as Rb, K/Rb, etc..

INTRODUCTION

The basement area between Qagssip kangerdluarssuạ and the inland ice (Fig. 1), Frederikshåb district, South West Greenland, the petrology and geology of which has already been described by RIVALENTI and ROSSI [1970], is intersected by several generations of post-orogenic basic dikes. Basic dikes from different regions of Greenland have already been described by several authors (see for

(*) Istituto di Mineralogia, Università di Modena (Italy).

RIVALENTI G. (1966) - Problema della genesi degli gneiss anfibolici della serie «dioritico-kinzigitica» delle Alpi Pennine. *Periodico Mineral.*, **35**, 933-957.

RIVALENTI G., ROSSI A. - The geology and petrology of the precambrian rocks between Qagssip kangerdluarssua and the inland ice, Frederikshåb district, South-West Greenland. Accepted for publication on *Rapp. Grønlands geol. Unders.* in 1970.

RIVALENTI G., SIGHINOLFI G. P. (1969) - Geochemical study of Graywackes as a possible starting material of para-amphibolites. *Contr. Mineral. and Petrol.*, **23**, 173-188.

SCOSSIROLI R. E. - Manuale di statistica per ricercatori. *Spa*: *Ing. C. Olivetti & C.* 1962.

SIGHINOLFI G. P. (1966) - Determinazione di alcuni elementi minori in campioni di rocce standards. *Periodico Mineral.*, **35**, 769-780.

SIGHINOLFI G. P. (1968) - The zirconium content in some standard rock samples. *Atti Soc. Tosc. Sci. Nat., Mem.* Ser. A, **47**, 626-629.

TURNER F. J., VERHOOGEN J. (1960) - Igneous and metamorphic petrology. New York and London: Mc Graw-Hill Book Company, Inc.

WAARD D. DE (1965) - The occurrence of garnet in the granulite-facies terrane of the Adirondack Highlands. *J. Petrol.*, **6**, 165-191.

WAARD D. DE (1967) - The occurrence of Garnet in the granulite-facies terrane of the Adirondack Highlands and elsewhere, an amplification and a reply. *J. Petrol.*, **8**, 210-232.

WAGER L. R. (1960) - The major element variation of the layered series of the Skaergaard intrusion and a re-estimation of the average compositon of the hidden layered series and of the successive residual magma. *J. Petrol.*, **1**, 364-398.

WAGER L. R., DEER W. A. (1939) - Geological investigations in East Greenland. Part III. The petrology of the Skaergaard intrusion, Kangerdlugssuak. *Medd. Grønland*, **105**, 1-352.

(*ms. pres. il 9 novembre 1970; ultime bozze il 12 gennaio 1971*)

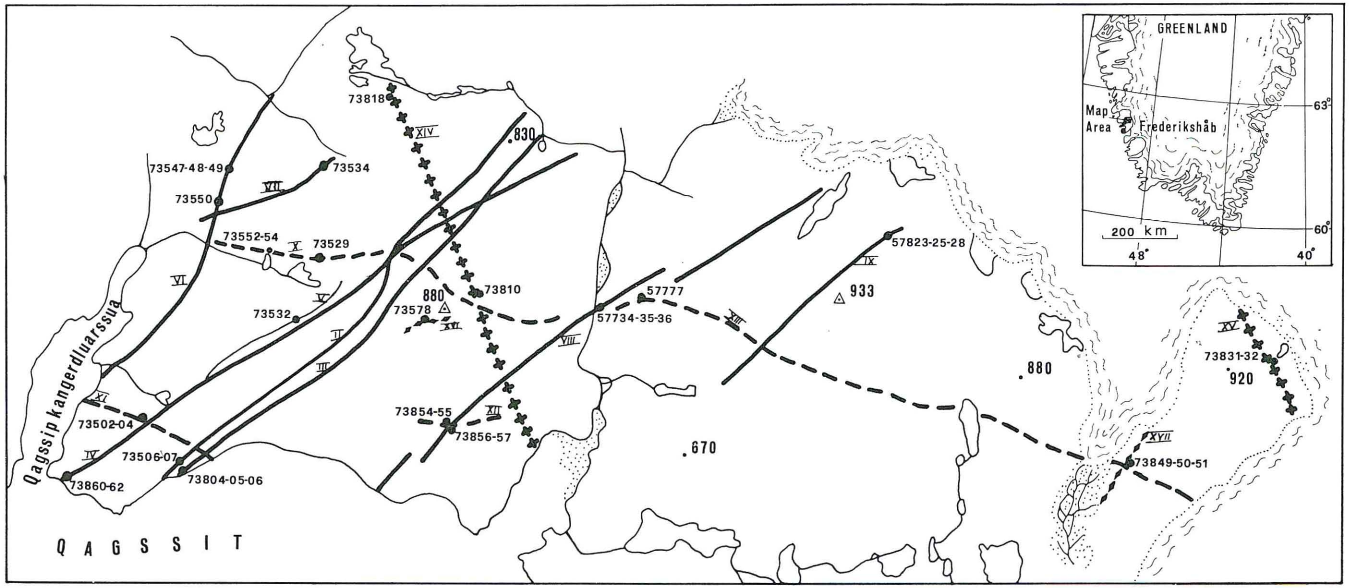

Fig. 1 - Sketch map showing the location of the studied area and the dikes. Only the dikes from which a sample has been collected are reported. The real thickness is not respected. Solid line = MD 2; dashed line = MD 3; line formed by crosses = TD; line formed by rhombs = Lamprophyres.

istance JENSEN [1962]; HENRIKSEN [1969a]; WATT [1969]). The present work represents a contribution to a better knowledge of the phenomena which affect the dikes. The various generations of the basic dikes have been labelled by the GGU (Geological Survey of Greenland) geologist in the following way: MD 1, MD 2, MD 3, BD, TD, Lamprophyres (JENSEN [1966]). The first three generations are thought to be pre-Ketilidian. In effect they cut basament gneisses at least 2600 m.y. old, but appear to be older than the ketilidian supracrustal succession which is reckoned to be about 2000 m.y. old (HENRIKSEN [1969b]). BDs most probably are Gardar dikes. The TD generation is most likely to be Mesozoic, as a Mesozoic age has been discovered on a TD dike cropping out S of the Frederikshåb town (LARSEN [1966]). The age of Lamprophyres is doubtful, though most probably they are relatively younger dikes. In the area investigated in this study no MD 1 and BD have been found. Even if the non-occurrence of MD 1 is possibly due to imperfect field observations, the BD generation probably fade out towards N as they have not been found in neighbouring areas too (CHADWICK [1969]). The field description of the dikes has already been made in a preceding work (RIVALENTI, ROSSI [1970]). It is nevertheless worth summarizing briefly the main features. The dike thickness varies from a maximum of 300 m to a minimum of a few cm. The thickest dikes are found in the MD 2 generation, in which two sub-generations can be locally distinguished in the field on the basis of their mutual intersections. Their general strike is towards NE but varies from NNE to ENE. The MD 3 dikes have a general strike towards SE and have a maximum thickness of 80 m. TDs are represented only by three dikes one of which is unimportant. Lamprophyres are constituted only by two thin dikes. All the dikes show chilled contacts. A common feature in MD dikes is that they can have a « én échelon » structure. Sometimes, at least in the case of the biggest dikes, they stop suddenly with a swarming of a lot of minor dikes and veins. All these features should indicate that the actual exposed part of the dikes represents a shallow depth, as is also reported by CHADWICK [1969] who studied the pattern of dike intrusion and fractures in this region.

The locality of the samples considered in this work is shown on the sketch map of Fig. 1, where only the dikes from which a sample has been collected are represented. In the map a sample of MD 1 is not reported because it was collected in another nearby area.

The aim of this work it to study the geochemistry of these dikes. Particular care has been devoted to the investigation of eventual chemical variations in time among the various generations and in space within single dikes.

In order to characterise the dikes better a short petrographic description is given below.

PETROLOGY

The description of the main petrological features can be found in RIVALENTI and ROSSI [1970]. The characters of the samples examined in this work are reported in Table 1. The following observations can be made.

MD dikes. - They are all characterized by an ophitic intergrowth of plagioclase and clino-pyroxene. From the rims to the center the grain size increases, the texture passing from the porphyritic to the doleritic. Plagioclase, often zoned, varies slightly in composition from the contacts (more calcic) to the center of the dikes. Plagioclase determinations of Table 1 are referred mainly to the center of the crystals. Pyroxene is usually of augitic type, but pigeonite and enstatite may also appear near the contacts. Olivine (from Fo 80% to Fo 50%) is usually limited only to the contacts. Olivine, pigeonite and enstatite, when they occur, are partially re-absorbed and show augitic rims. Biotite, which is normally a reddish-brown type, increases towards the center and is often strictly associated to opaque (magnetite). Brown and green hornblende may be also present. Alteration (deuteric?) of the preceding minerals gives chlorite, epidote, uralite etc.. No metamorphic feature can be seen to have affected these dikes. MD 2 dikes are rarely intersected by thin hydrothermal veins.

TD dikes. - They have a sub-doleritic (intergranular) texture and are characterized by a fairly acid plagioclase (up to 35% anorthite) and by larger amounts of biotite and sometimes apatite in respect to MDs. Olivine can also be present in appreciable amounts. Primary brown hornblende is a common minor constituent. Zeolites may occur as fillings of small vesicles. Opaque are always present.

Lamprophyres. - Of the two examined dikes, one (XVI) presents a spessartite-like mineralogical assemblage and the other is a strongly zoned dike, the composition of which varies from an ultramafic assemblage at the contacts to a camptonitic type at the center. The amphibole of the first dike is strongly zoned (pleochroism at the center X = pinkish yellow, Y = reddish brown, Z = deep brown; at the periphery the colours become darker and greener). A partial chemical analysis carried out on the amphibole of this rock has given these results:

$$TiO_2 = 5.30,\ Fe_2O_3 = 2.99,\ FeO = 15.60,\ CaO = 10.85,\ MgO = 8.65,\ Na_2O = 2.81,\ K_2O = 1.12$$

The high alkali content reveals that the crystals are largely composed of a barkevikitic term, while the high Ti indicates that the composition is displaced towards a kaersutitic member. Kaersutitic hornblende is common in camptonitic rocks and in some alkaline plutons (DEER, HOWIE, ZUSSMAN [1963], Vol. 2, p. 321); recently it has also been described in mafic inclusions of alkali basalts by AOKI [1970].

The second dike at the contact is largely formed by partially serpentinized olivine, the composition of which varies from Fo 86% to Fo 75%. Pyroxene, abundant, is strongly pinkish and rich in ilmenite inclusions. Towards the center, biotite, amphibole (again of a kaersutitic type) and apatite increase.

CHEMICAL DATA

We have considered one dike of the MD 1 generation (one sample), 8 dikes of the MD 2 generation (21 samples), 4 dikes of the MD 3 generation (8 samples), 2 dikes of the TD generation (4 samples), 2 Lamprophyres (4 samples). The analytical results for major and trace elements as well as Niggli numbers and some element ratios are reported in Table 2. The CIPW norms for 19 complete analyses are given in Table 3.

The examination of the norms reveals the MD dikes to be tholeiites (or olivine tholeiites when normative olivine and hyperstene appear) following YODER and TILLEY [1962]. The same characters have also been noted by HENRIKSEN [1969 a] in the MD dikes of the Ivigtut region.

Only one sample (73860) is slightly differentiated in an ande-

TABLE 3 - *CIPW norms for the complete analyses*

		84541	73506	73804	73860	73549	73534	73856	73857	57734	57735
Q		6.00	2.07	—	8.28	0.12	—	—	0.62	—	0.43
or		1.48	4.37	4.19	6.44	2.84	1.59	1.54	2.95	1.42	1.59
ab		14.80	17.17	19.54	18.01	22.07	15.90	14.38	19.96	17.59	20.13
an		33.81	26.63	26.09	21.19	25.62	34.29	30.84	37.89	30.91	36.27
ne		—	—	—	—	—	—	—	—	—	—
wo	di	7.43	6.85	7.55	6.56	10.90	8.45	7.83	5.43	9.38	7.16
en	di	4.87	3.01	3.19	2.47	5.45	5.21	4.00	2.42	4.92	4.10
fs	di	2.04	3.83	4.39	4.21	5.22	2.75	3.64	2.98	4.18	2.75
en	hy	15.55	11.68	10.89	8.04	10.88	15.82	14.79	8.96	10.04	11.34
fs	hy	6.51	14.87	14.99	13.72	10.40	8.34	13.43	11.03	8.53	7.59
fo		—	—	0.50	—	—	0.89	0.44	—	3.12	—
fa		—	—	0.76	—	—	0.52	0.44	—	2.92	—
mt		4.23	2.96	2.46	3.61	2.90	2.39	2.96	2.44	2.57	5.31
il		1.21	4.35	4.18	4.75	2.53	1.12	2.49	2.70	2.11	1.61
ap		0.36	0.76	0.78	0.90	0.45	0.19	0.45	0.52	0.28	0.14

		57823	57828	73552	73502	57777	73818	73832	73578	73849
Q		—	—	6.42	2.87	—	—	—	—	—
or		4.08	3.43	2.42	2.30	2.07	15.24	12.05	4.19	1.36
ab		18.27	20.47	17.42	19.62	19.11	32.14	31.46	19.82	1.69
an		25.79	30.27	26.65	25.22	28.80	11.92	13.76	9.62	9.56
ne		—	—	—	—	—	—	—	3.51	—
wo	di	7.71	5.59	9.97	10.48	9.13	1.76	1.14	16.04	8.24
en	di	3.66	2.80	5.03	4.86	4.68	0.88	0.59	9.16	6.66
fs	di	3.94	2.67	4.70	5.51	4.21	0.84	0.52	6.17	0.61
en	hy	11.58	12.41	10.03	9.48	9.55	3.81	8.74	—	28.02
fs	hy	12.46	11.82	9.37	10.74	8.60	3.67	7.79	—	2.57
fo		1.18	0.12	—	—	3.35	4.39	1.40	3.49	12.33
fa		1.40	0.12	—	—	3.32	4.66	1.38	2.59	1.24
mt		3.54	4.67	4.54	3.62	2.30	4.99	7.38	10.11	18.70
il		3.49	3.13	2.53	3.49	2.35	7.73	6.08	9.95	7.69
ap		0.50	0.43	0.47	0.50	0.33	6.14	5.90	4.17	0.71

sitic sense. TD samples have an evident alkaline tendency. It is worth noting how, on the one hand, the TDs are sensibly differentiated, as can be seen from their normative *ab* content, and on the other, they are still highly mafic because of the high iron content. The CIPW norms of the two samples of Lamprophyres show that one is an ultramafic rock with an anomalous high titanium content and the other, previously classified as spessartite on a mineralogical basis, is an alkali basalt.

If the samples are plotted on an alkali-alumina diagram (KUNO [1960, 1968]), it can be seen that MDs plot in the tholeiitic field, except two which plot in the alumina-basalt field. The TDs and Lamprophyres constantly plot in the alkali-basalt field. Similar indications are given by an AFM diagram (see for instance NOCKOLDS and ALLEN [1953]; GREEN and POLDERVAART [1958]; MACDONALD and KATSURA [1964]). In such a plot the MD samples follow a tholeiitic trend, though slightly shifted towards an iron-rich trend, while TDs and Lamprophyres approximate an alkalic trend. The general chemistry (mainly the high Ti content) makes TDs and Lamprophyres similar to the «high-titania alkali-olivine basalts» described by ROBINSON [1969].

CONDIE et al. [1969] report the averages of major and trace elements for several basaltic groups. By comparing our results (Table 2) with those averages, we see that the MD dikes are similar to the continental tholeiites and that TDs present marked affinities with alkalic suites.

By plotting the samples on K/Rb vs. K and Sr/Ba vs. K diagrams (Figs. 2 and 3) it can be seen that MDs generally plot in the continental tholeiite field, while in one diagram (K/Rb vs. K) TDs fall in the alkali basalt field and in the other one sample falls in the alkali basalt field and the other three plot outside of all fields. It may be noted that the average MD values of Sr is considerably lower than the value reported by ENGEL et al. [1965] for the continental tholeiites, and that similarity exists with the Sr-depletion trend of the Tasmanian and Antarctic tholeiites and with the Wyoming diabases (CONDIE et al. [1969]).

DISCUSSION OF SOME GEOCHEMICAL TRENDS

Some geochemical trends of major and trace elements have been examined by statistical analysis for MD samples only. TDs and lamprophyres have not been statistically tested, the number

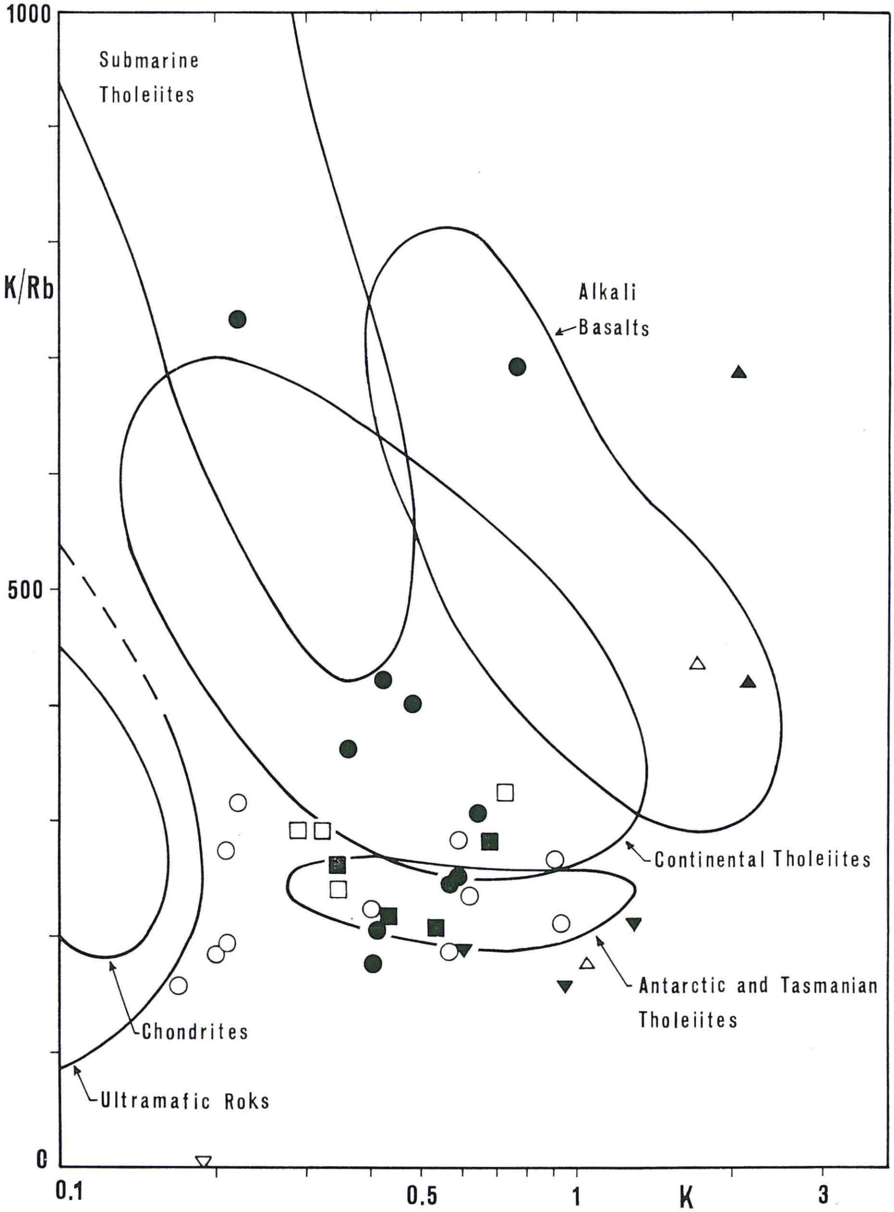

Fig. 2 - K vs. K/Rb diagram. The areas outlined for the major rock types are redrawn from CONDIE et al. [1969]. Solid symbols = samples from center or from the inner part of the dikes; open symbols = samples from contacts. (O) = MD 2; (□) = MD 3; (Δ) = TD; (∇) = Lamprophyres.

of samples being too small. The results of the statistical calculations (mean values, correlation coefficient *r*, *t* test) are summarized in Table 4. From Table 4 it can be seen that some of the most obvious igneous variation trends are present in the dikes, suck as those presented by the couples *mg-k*, *mg*-Cr, *mg*-Ni, *mg*-Zr, MnO-FeO, MnO-total Fe, Ca-Sr, Rb-K and P_2O_5-TiO_2. Most of them are easily un-

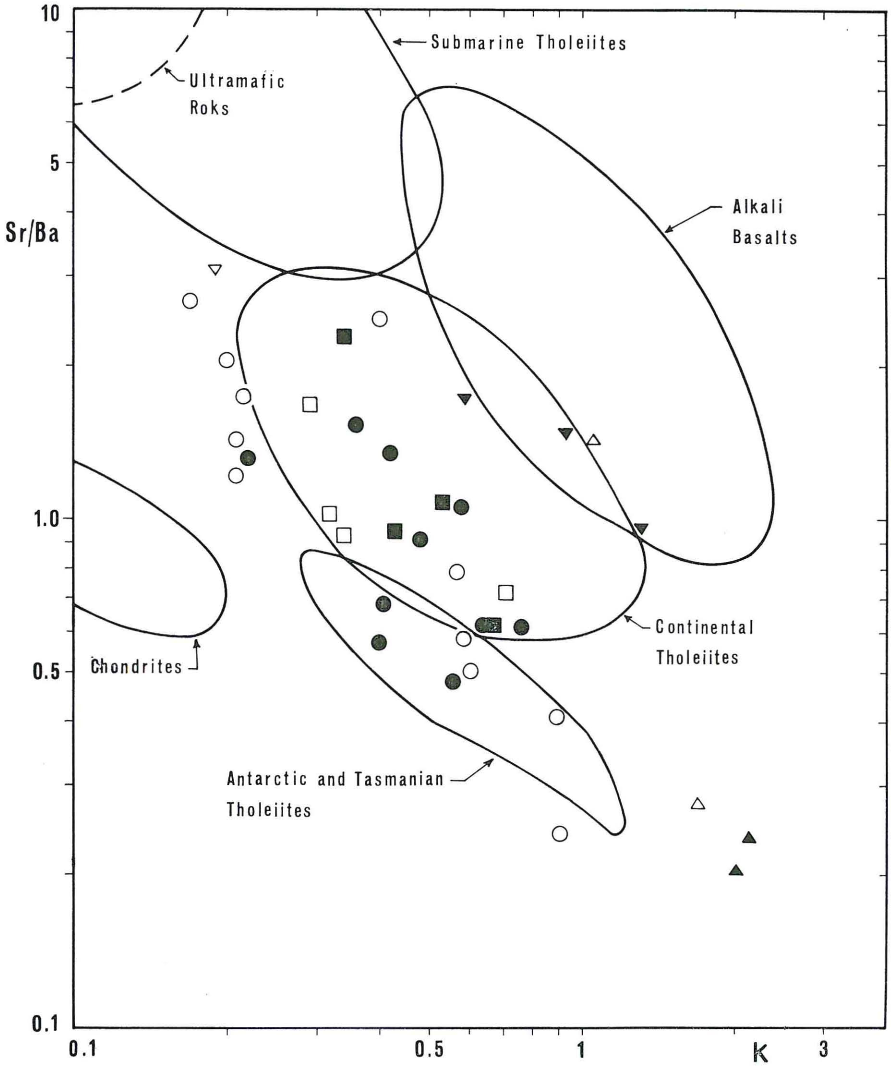

Fig. 3 - K vs. Sr/Ba diagram. Symbols and references as in Fig. 2.

derstandable and will not be discussed. Some other relationships deserve some remarks.

mg-TiO_2 and Cr-TiO_2. There is in both cases a good negative correlation (Fig. 4). From the summary data of RONOV and MIGDISOV [1965], Ti strongly increases from ultramafic to mafic rocks and decreases from mafic to felsic rocks. Cr and *mg* regularly decrease

TABLE 4 - *Statistical calculations for MD samples*

x	y	$\bar{x}$	$\bar{y}$	n	r_{xy}	t	t'
mg	*k*	0.47	0.13	30	—0.57	3.71	2.05
mg	TiO_2	0.47	1.54	30	—0.90	10.68	2.05
mg	Zr	0.47	91	30	—0.83	7.76	2.05
mg	Cr	0.47	150	30	0.59	3.83	2.05
mg	Ni	0.47	116	30	0.79	6.87	2.05
MnO	TiO_2	0.203	1.54	30	0.80	7.08	2.05
MnO	FeO	0.203	10.50	30	0.85	8.58	2.05
MnO	tot. Fe	0.203	14.52	30	0.79	6.88	2.05
MnO	V	0.203	303	30	0.48	2.91	2.05
MnO	Zn	0.206	132	26	0.52	2.96	2.07
MnO	Y	0.203	33	30	0.63	4.28	2.05
TiO_2	P_2O_5	1.54	0.21	29	0.64	4.45	2.05
TiO_2	V	1.54	303	30	0.51	3.10	2.05
TiO_2	Zr	1.54	91	30	0.90	10.66	2.05
TiO_2	Cr	1.54	150	30	—0.65	4.48	2.05
TiO_2	Y	1.54	33	30	0.66	4.63	2.05
CaO	Sr	9.77	150	30	—0.16	0.86	2.05
CaO	Ba	9.77	180	30	—0.84	8.05	2.05
Sr	Na_2O	150	2.30	30	0.72	5.44	2.05
Sr	Ba	150	180	30	0.49	2.94	2.05
K	Ba	0.45	180	30	0.84	8.30	2.05
Zn	FeO	132	10.77	26	0.50	2.83	2.07
Zn	tot. Fe	132	14.82	26	0.56	3.32	2.07
Y	tot. Fe	33	14.52	30	0.51	3.12	2.05
Y	Zr	33	91	30	0.57	3.70	2.05
K	Rb	0.45	17	30	0.78	6.66	2.05

$\bar{x}$ and $\bar{y}$ = mean values of the variables.
n = number of samples.
r_{xv} = correlation coefficient.
t = Student's test values; t' = tabular (5% probability).

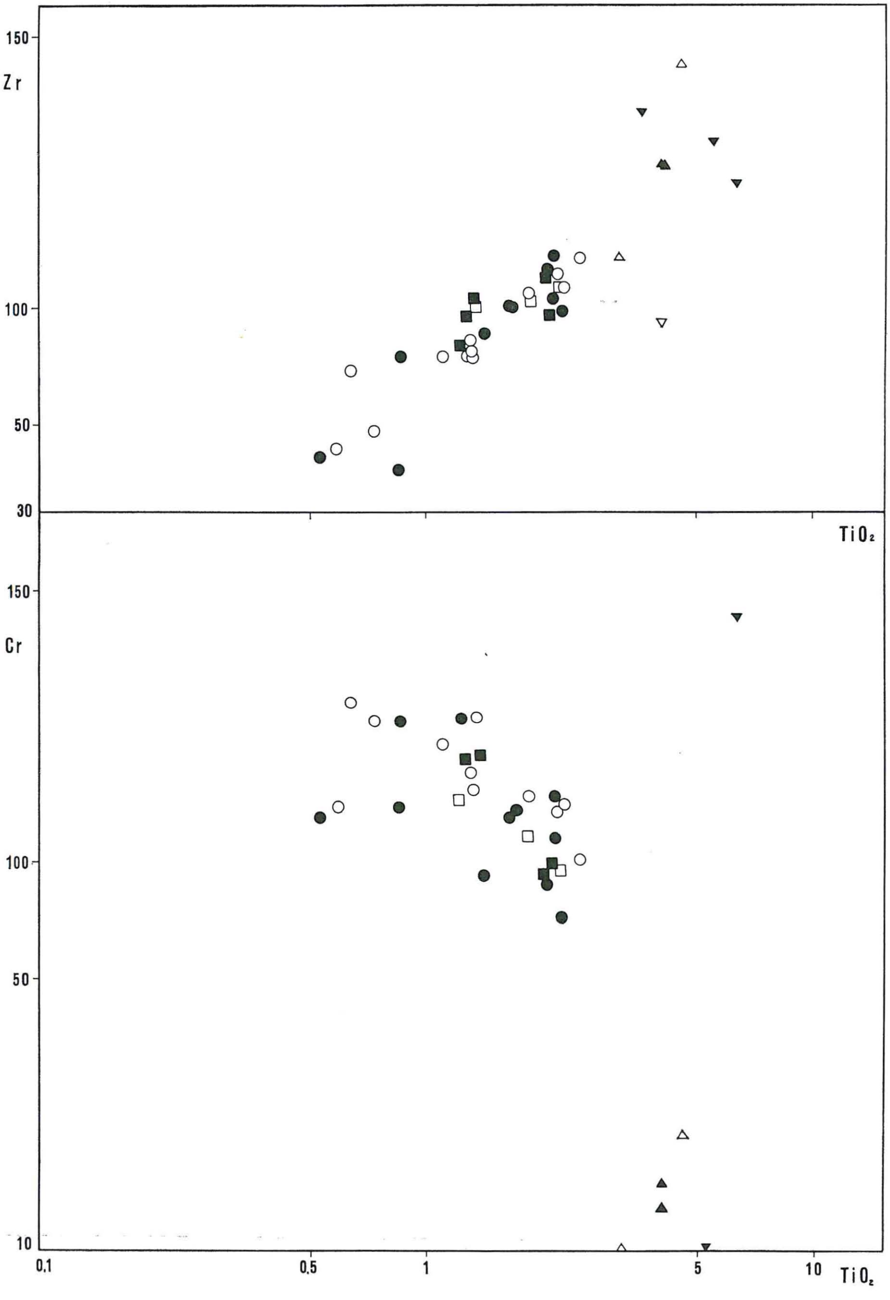

Fig. 4 - TiO_2 vs. Cr and Zr diagram. Symbols as in Fig. 2.

from ultramafics to felsics. Therefore a negative correlation has to be expected in the range from ultramafic to mafic rocks.

TiO_2-Zr. The positive correlation between these elements is very interesting because, as is well known, Ti and Zr have different behaviour during a fractional differentiation. Most probably the Ti-Zr correlation depends on the peculiar stage of differentiation of MD dikes, as in this stage both tend to become enriched in the residual liquids.

MnO-TiO_2, MnO-V, MnO-Zn, TiO_2-V and TiO_2-Zn. The positive correlations between these couples are explainable because all these elements have a tendency to enter the ferromagnesian minerals, following the geochemical behaviour of iron (see for example WAGER and MITCHELL [1951]). The degree of correlation, high for some couples and low for others, may depend on the fact that elements can enter various phases in different ways. For instance, NAUMOV and GURIN [1967] have pointed out that Ti is concentrated in titanomagnetite (and ilmenite), and V in magnetite and possibly in pyroxene.

Ba-CaO, Ba-K (Fig. 5) and Na_2O-Sr. There is a fairly high correlation in all the cases, negative in the first, positive in the other

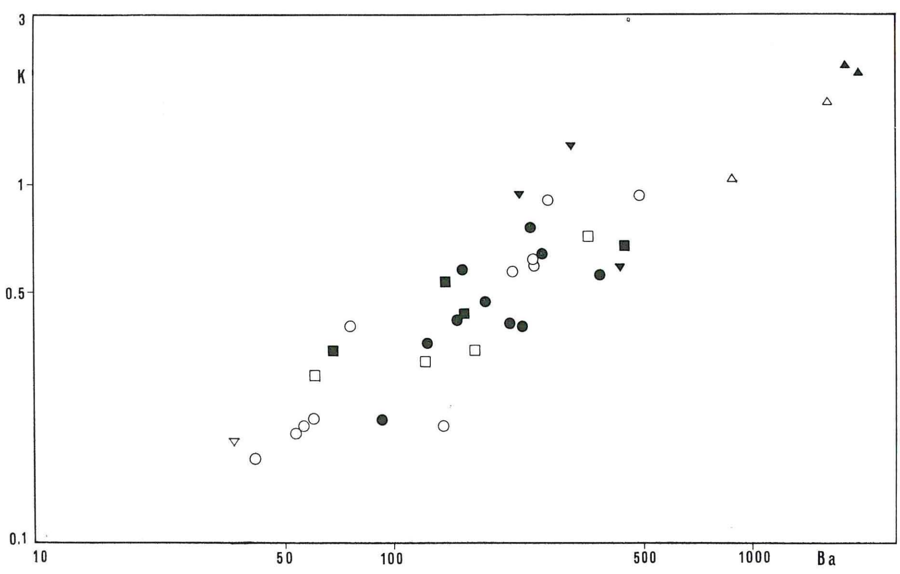

Fig. 5 - Ba-K diagram. Symbols as in Fig. 2.

two. These trends could be explained in the following way: among the various phases, Ba and K can be concentrated only in feldspar and biotite, but the amount of biotite in these dikes is always very low. Therefore, the bulk of K and Ba must be supplied by plagioclase, as there is no K-feldspar. As is well known K and Ba contents increase from the calcic to the sodic terms of plagioclase (HEIER [1962]; EWART, TAYLOR [1969]). Thus the negative correlation between Ca and Ba could indicate that the variations in the Ca content of the rock are essentially a consequence of variations in the An content of plagioclase, while the amount of Ca given by the pyroxene has to remain roughly constant. The Na-Sr relationship can be explained in a similar way: Sr can only enter plagioclase in this case and, as HEIER [1962] points out, its amount increases from labradorite to oligoclase. This also accounts for the (weak) correlation between Sr and K.

K-Rb. There is an obvious positive correlation (Fig. 6), highly significant ($r = 0.78$) in spite of the anomalous K/Rb ratio of some samples. These anomalies will be discussed later on.

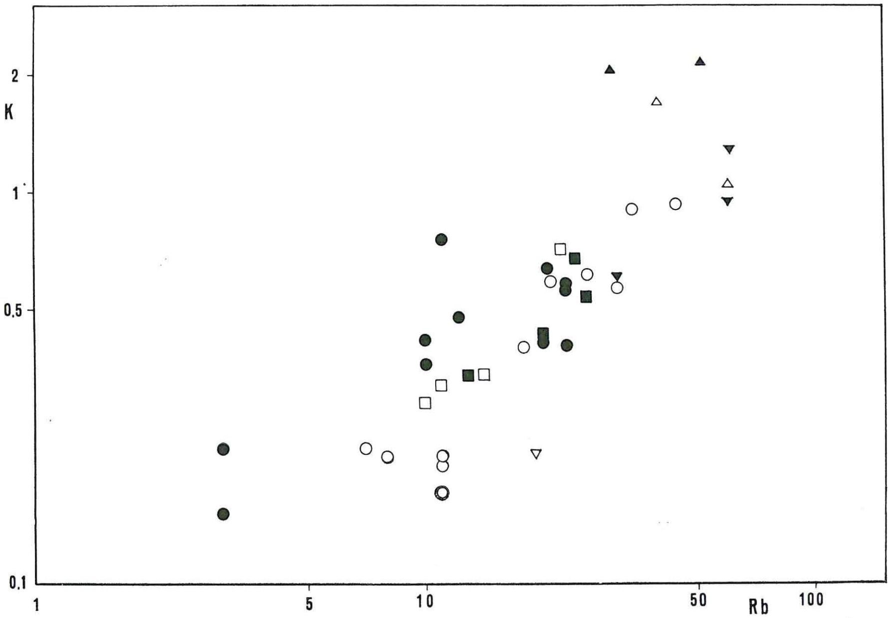

Fig. 6 - Rb-K diagram. Symbols as in Fig. 2.

DIFFERENTIATION TRENDS

Differentiation in MD dikes. - From the examination of the analyses it can be seen that differences exist within single generations of dikes, even if only the contacts, which presumably better represent the original composition (CONDIE et al. [1969]), are considered. These differences, which are reflected in the geochemical trends of Table 4, discussed above, indicate that the magma had suffered local differentiations in the various parts of the magma chamber before the emplacement of the dikes. Furthermore, slight differences also exist among the average composition of the various MD generations and much bigger differences among MDs and the following. Unfortunately, only one sample was available for MD 1, therefore no reliable observations can be made about the variations among this and the successive generations. It can be observed (Table 2) how most elements in the various MD generations vary, although slightly, in the sense that the younger one results faintly more differentiated than MD 2 (and MD 1). These observation are also supported if the solidification index (KUNO [1960]) is plotted vs. the various oxides: the average S.I. for the MD 2 contacts (and for MD 1 sample) is slightly higher than that of MD 3 contacts. Also, the behaviour of the trace elements conform to this pattern, as Cr and Ni, for instance, decrease from the older to the younger dikes, while Ba, Sr, Zr, Mn increase. Rb remains roughly constant in MD 2 and MD 3 contact samples, as does the K/Rb ratio.

Besides these differentiation trends, which are essentially consequent local differentiation phenomena in the magma chamber and evolutions of it in time, other differences can be observed within single dikes. In particular the dikes are seen to have different composition from contacts to center and, in the sole case examined, in the vertical sense as well. The most significant differences observed between the centers and the margins have been set out in Table 5. In this table the results relative to nine outcrops of MD dikes, one TD and one Lamprophyre are reported. The samples of the dike IV have not been considered in the following discussion because the rock is weathered.

From consideration of major and trace elements it can be seen that Mg, Ni, Cr and Co decrease generally from the contacts to the center, though the variations are small, while elements such as K, Na and Sr generally increase. These variations suggest that the center of the dikes is slightly differentiated in respect to the contacts, as found for istance by RAGLAND et al. [1968].

Nevertheless, some variation trends do not fit with the pattern just observed. It has been shown, for istance, that when all the MD samples are considered Ti is strongly negatively correlated to *mg* (r = —0.90, Table 4). But, if we consider the variations in the single dikes, while MD 3 conform to the normal trend, MD 2 do not in four cases out of six, because Ti decreases with *mg* at the center. Other anomalies are seen in the behaviour of the K/Rb ratio, which increases towards the center in all the MD 2 dikes, while in MD 3 it decreases slightly. As the center of the dikes seems to have suffered a slight differentiation, K/Rb should be expected to decrease from the contact to the center in relation to increasing K (SHAW [1968]). The increase at the center is dependent on an abnormal decrease of Rb. This obviously affects the Rb/Sr ratio as well, which therefore decreases at the center, while, as can be observed from the data of GUNN and WATKINS [1969], it should be expected to increase with differentiation. It is worth noting that the K/Rb ratio values are fairly constant at the contacts, while at the center they vary considerably, sometimes attaining values of the order of those of the oceanic tholeiites.

Samples of the same dike (dike VIII), but collected at different heights, have enabled us to check for any vertical compositional variations. The summary data of Table 5 show that, while the lower and upper contacts have a very similar composition, the centers present much stronger differences. In particular, Mg, Cr, Ni and Cu are concentrated in the lower center, while Al, K, Ti, Zr, Ba, Rb and Sr (see also Table 2) increase strongly in the upper center, the latter thus being more differentiated. The vertical differentiation of the central part is evidenced also by the K/Rb and Rb/Sr ratios, the first of which decreases strongly (from 733 to 205) towards the higher levels, while the second increases.

Differentiation in TDs and Lamprophyres. - Only one dike of the TD generation has been examined to verify the presence of eventual differentiations between the margin and center. No significant conclusions can be drawn for this dike owing to the contrasting trends of the various elements.

TABLE 5 - *Some of the more significant variations in the dikes*

	MgO		TiO_2		K_2O		Cr		Ni	
Dike	contact	center	contact	center	contact	center	contact	center	contact	center
MD 2										
II	5.90	6.15	2.29	2.14	0.74	0.91	140	147	117	105
III	5.94	5.42	2.20	2.15	0.71	0.78	135	116	113	89
VI	6.56	6.45	1.33	0.86	0.48	0.51	235	230	84	76
VIII (120m)	7.80 8.10	6.20	1.11 0.74	0.85	0.24 0.20	0.27	200 230	138	140 163	94
VIII (820 m)	7.80	4.57	1.31	1.42	0.26	0.50	171	92	148	70
IX	6.80	6.18	1.84	1.65	0.69	0.58	149	131	113	107
MD 3										
X	6.05	6.10	1.33	1.34	0.41	0.64	173	175	96	145
XI	5.76	5.54	1.84	2.14	0.39	0.41	116	95	94	90
XII	6.77	5.80	2.25	2.04	0.86	0.81	94	92	113	92
TD										
XV	4.55	5.11	3.20	4.04	2.04	2.48	10	15	19	18
Lamprophyre										
XVII	21.00	9.90	4.05	6.35	0.23	1.54	5100	430	213	400

TABLE 5 (*continued*)

	Rb		Sr		Rb/Sr		K/Rb		Zr	
Dike	contact	center	contact	center	contact	center	contact	center	contact	center
MD 2										
II	26	11	124	147	0.210	0.075	235	691	113	106
III	21	21	144	161	0.146	0.130	281	305	123	138
VI	18	10	188	202	0.096	0.049	222	420	75	75
VIII (120m)	11 11	3	109 110	124	0.101 0.100	0.024	182 155	733	75 48	38
VIII (820 m)	11	20	80	143	0.137	0.140	191	205	77	86
IX	31	12	168	165	0.184	0.073	184	400	107	101
MD 3										
X	14	26	154	151	0.091	0.172	243	204	100	102
XI	11	13	147	156	0.075	0.083	291	262	104	96
XII	22	24	252	272	0.087	0.088	323	279	114	122
TD										
XV	39	30	450	406	0.087	0.074	436	687	335	232
Lamprophyre										
XVII	21	60	110	295	0.191	0.203	90	212	93	207

The Lamprophyre is very strongly chemically zoned, as the mineralogical observations might lead one to expect. In particular, the contact is characterized by a strong enrichment of Mg, iron and Cr, while Ti, Ca, K, Na and Zr concentrate at the center.

Interpretation. - While the variations among the dikes of the same generation and among the various generations can be easily interpreted in terms of an obvious slight magma chamber differentiation, the interpretation of the phenomena occurring in the same dike is puzzling. Several mechanisms can be investigated to explain a transversal differentiation in a dike. GIBB [1968], investigating ultramafic zoned dikes, invokes mainly a mechanism of flow to explain the different distribution of olivine. The variations observed in the present work do not conform to Gibb's distribution types, which are characterized by an olivine enrichment at the center. This indicates that flow mechanisms, such as those prospected by Gibb, did not act in our case.

Convective currents are also unlikely to be responsible for the within-dike differentiations, as it is generally held that convective currents do not occur in such small bodies (CARR [1954]; WALKER [1956]; WAGER [1963]). In the present case, therefore, other hypotheses must be investigated. Two tentative explanations might be the following.

i) The margin represents the undifferentiated original magma, as is considered by several authors (see for instance CONDIE et al. [1969]). The chilled contacts can thus be considered as a « frozen » system, while the coarse-grained, matrix-free center had to remain in a molten state for a longer period. Given these conditions, one is lead to think that no interactions occurred between contact and center after the rapid solidification of the former. In this case the center could have changed its composition in respect to the contact through a vertical differentiation mechanism. This mechanism may have been provided by a combined downwards gravitative precipitation of first-formed crystals and an upwards migration of salic material. Such a migration implies that the viscosity of the magma has to be low, which may be caused by a high volatile content, and that a thermal upwards gradient exists. This mechanism leads to a progressive upwards increase in acidity of the center in respect to the chilled contacts avay from the magma chamber. The high volatile content, besides influencing the viscosity of the magma, could at the limit have caused gaseous transfer-like phenomena. In this connection, as Rb follows a gaseous phase easier than K (AHRENS et al. [1952]; TAYLOR *et* al. [1956]; BOWDEN [1966]), the downwards increase of the K/Rb ration is explained. Thus this ratio can also reach values which are abnormally high in respect to the contacts.

ii) After the formation of the thin « frozen » crust at the contacts with the composition of the original magma, the remaining part of the magma undergoes cooling, which slows down progressively towards the center. This causes a fractional crystallization with progressive enrichment of salic elements and volatiles in the residue melt at the center. The more felsic composition of the upper center, in the dike vertically examined, can be caused by a more advanced fractional crystallization, probably under the influence of a high volatile content. This implies that the volatiles were concentrated in the upper levels, probably already during the magma emplacement. The behaviour of Rb and of the ratios where it enters, can be explained as in the preceding hypothesis.

The above prospected hypotheses require that the within-dike differentiation occurs when the magma is no more affected by rapid upwards moviments. The lack of evident flow features conforms to this point of view.

The differentiation schemes just prospected do not fit at all with the trasversal differentiation in the Lamprophyre. To explain the ultramafic chemistry of the margin an accumulation process must be admitted, as it is unlikely that its ultramafic composition should be regarded as representative of one of the original magma. Segregation of olivine, pyroxene, kaersutite, titanomagnetite etc. from an alkali basalt magma under hydrous conditions at a deep of about 25-30 km can lead to the formation of an ultramafic cumulate (AOKI [1970]).

The anomalous behaviour of Rb and related ratios in MD 2 dikes has already been explained by the above prospected hypotheses. Nevertheless, another interpretation could be given by a wall-rock Rb contamination affecting the margins of the dikes. Since the Rb content of the dikes is always very low, it can easily be influenced even by a slight contamination from the Rb-rich migmatitic country gneisses. The presence of rare hydrothermal veins in MD 2 dikes makes it possible. The strongest objection to the hypothesis of contamination is that the K/Rb ratio in the contacts remains fairly constant, while spreading at the center, and moreover, that the MD 2 contact values are similar to those of MD 3 contact, which have never been found to be affected by any hydrothermal vein.

CONCLUSIONS

The preceding description and discussion have shown that:

i) the MD dikes generally have a composition which falls in the field of the continental tholeiites, while TDs and Lamprophyres have a more alkalic tendency;

ii) the variation trends for major and trace elements conform to those of a normal fractional differentiation;

iii) younger dike generations are slightly differentiated in respect to the older one;

iv) within single generations the various dikes present different compositions, even when considering only the contacts, thus indicating that the magma chamber has undergone local differentiation phenomena;

v) a small differentiation exists between chilled margins and centers of the MD dikes. Nevertheless the variations between one dike and another, even within the same generation, are greater than those within the same dike. A marked vertical differentiation, with increasing acidity upwards, has also been found in one of the MD 2 dikes examined. This mainly affects the central part.

Two hypotheses have been proposed to explain the variations: *a*) « freezing » of the margin and mechanism of differentiation at the center by combined downwards precipitation of first formed crystals and upwards migration of felsic elements and volatiles; *b*) fractional crystallization advancing towards the center but not affecting the chilled margins and leading to an enrichment of felsic elements and volatiles at the center. A strongly-zoned lamprophyric dike with ultramafic margins does not fit in the above-considered schemes of differentiation;

vi) variations across the MD 2 dikes of some elements and ratios (Ti, Rb, K/Rb and Rb/Sr) do not conform with the normal differentiation pattern. The anomalous increase of the K/Rb ratio at the more differentiated center has been interpreted by a Rb migration together with volatiles. This migration is connected with either of the mechanisms of differentiation above prospected. A wall-rock Rb contamination of the MD 2 contacts has been proposed as another possible explanation of the anomalous behaviour of Rb and related ratios.

ANALYTICAL METHODS

Si and Al have been determined by X-ray fluorescence following the procedure described by DE VECCHI et al. [1968].

Mn, total Fe, Mg, Ca, Na, K, Zn have been determined by atomic absorption spectroscopy following SIGHINOLFI [1969].

Ti, Zr, Cr, Ba, Y, Rb have been determined (analyst Sighinolfi) by non-destructive X-ray fluoresecnce, following the methods described by HAHN-WEINHEIMER and ACKERMANN [1963]. Calibration curves were constructed from standard rock samples W-1, T-1, AGV-1, BCR-1, GSP-1, and BR. The analytical error for most elements is estimated to be 3% while for Rb about 10%.

Ferrous iron has been determined by the semimicro procedure of MEYROWITZ [1963].

V, Ga, Cu, Ni, Co, Sc have been analyzed by optical spectroscopy (analyst Bollingberg). The error for all elements is 10%, excluding Sc, which was semiquantitatively determined (error 50%).

P_2O_5 and controls on major element determinations have been carried out by Sørensen, following BORGEN [1967].

ACKOWLEDGEMENTS

The Authors wish to express their gratitude to Dr. K. Ellitsgaard-Rasmussen, Director of the geological Survey of Greenland, for the permission to publish this paper and to Dr. B. Chadwick for having borrowed us one sample of MD 1 dike. We appreciate the cooperation of Dr. H. Ackermann, Dr. I. Sørensen, Dr. H. Bollingberg, Dr. E. Piccirillo and Dr. A. Gregnanin in carring out the chemical analyses. Special thanks are due to Prof. G. Marinelli, Prof. F. Barberi and Prof. G. Gottardi for critical and constructive reviews of the manuscript and helpful discussion.

REFERENCES

AHRENS L. H., PINSON W. H., KEARNS M. M. (1952) - Association of Rb and K and their abundance in common igneous rocks and meteorites. *Geochim. et Cosmochim. Acta*, **2**, 229-242.

AOKI K. (1970) - Petrology of kaersutite-bearing ultramafic and mafic inclusions in Iki island, Japan. *Contr. Mineral. and Petrol.*, **25**, 270-283.

BORGEN I. I. (1967) - Analytical procedures used in the geochemical laboratory of the Survey. *Grønlands Geol. Unders. Rapp.*, **10**, 1-44.

BOWDEN P. (1966) - Li in the younger granites of northern Nigeria. *Geochim. et Cosmochim. Acta*, **30**, 555-564.

CARR J. M. (1954) - Zoned plagioclases in layered gabbros of the Skaergaard intrusion, East Greenland. *Mineralog. Mag.*, **30**, 367-375.

CHADWICK B. (1969) - Patterns of fracture and dyke intrusion near Frederikshåb, Southwest Greenland. *Tectonophysic*, **8**, 247-264.

CONDIE K. C., BARSKY C. K., MUELLER P. A. (1969) - Geochemistry of Precambrian diabase dikes from Wyoming. *Geochim. et Cosmochim. Acta*, **33**, 1371-1388.

DEER W. A., HOWIE R. A., ZUSSMAN J. (1963) - Rock-forming minerals. Vol. 2 Chain silicates. Longmans.

DE VECCHI G., PICCIRILLO E., QUARENI S. (1968) - Contributo all'analisi rapida di rocce mediante fluorescenza ai raggi X. *Rend. Soc. Ital. Miner. Petrog.*, **24**, 1-14.

ENGEL A. E. J., ENGEL C. G., HAVENS R. G. (1965) - Chemical characteristics of oceanic basalts and the upper mantle. *Bull. Geol. Soc. Amer.*, *76*, 719-734.

EVART A., TAYLOR S. R. (1969) - Trace element geochemistry of the rhyolitic volcanic rocks, Central North Island, New Zealand. Phenocryst data. *Contr. Mineral. and Petrol.*, **22**, 127-146.

GIBB F. G. (1968) - Flow differentiation in the xenolithic ultrabasic dykes of the Cuillins and the Strathaird Peninsula, Isle of Skye, Scotland. *J. Petrology*, **9**, 411-443.

GREEN J., POLDERVAART A. (1958) - Petrochemical fields and trends. *Geochim. et Cosmochim. Acta*, **13**, 87-122.

GUNN B. M., WATKINS N. D. (1969) - The petrochemical effect of the simultaneous cooling of adjoining basaltic and rhyolitic magmas. *Geochim. et Cosmochim. Acta*, **33**, 341-356.

HAHN-WEINHEIMER P., ACKERMANN H. (1963) - Quantitative roentgenspektralanalytische Bestimmungen von K, Rb, Sr, Ba, Ti, Zr und P. *Z. Anal. Chem.*, **194**, 81-101.

HEIER K. S. (1962) - Trace elements in feldspars - A review. *Norsk Geol. Tidsskr.*, **42**, 415-454.

HENRIKSEN N. (1969a) - Chemical relations between metabasaltic lavas and metadolerites in the Ivigtut area, South-west Greenland. *Medd. Dansk Geol. Foren.*, **19**, 27-50.

HENRIKSEN N. (1969b) - Boundary relations between precambrian fold belts in the Ivigtut Area, Southwest Greenland. *Geol. Association of Canada, Spec. Paper N. 5*, 143-154.

JENSEN S. B. (1962) - Some dolerite dykes in the southern part of the Godthaab District, West Greenland. *Medd. Grønland*, **169** (4), 3-38.

JENSEN S. B. (1966) - Field work in the Frederikshåb area. *Grønlands Geol. Unders. Rapp.*, **11**, 32-35.

KUNO H. (1960) - High alumina basalt. *J. Petrology*, **1**, 121-145.

KUNO H. (1968) - Differentiation of basalt magmas. Basalts 2, New York: John Wiley and Sons.

LARSEN O. (1966) - K/Ar determinations from Western Greenland. *Grønlands Geol. Unders. Rapp.*, **11**, 57-60.

MACDONALD G. A., KATSURA T. (1964) - Chemical composition of Hawaiian lavas. *J. Petrology*, **5**, 82-133.

MEYROWITZ R. (1963) - A semimicro procedure for the determination of ferrous iron in nonrefractory silicate minerals. *Am. Mineralogist*, **48**, 340-347.

NAUMOV V. A., GURIN P. A. (1967) - Distribution of vanadium, chromium, cobalt, nickel and copper in a differentiated intrusive of palagonite traps of the upper course of the lower Tunguska River. *Geochemistry (USSR), (english transl.)*, **4**, 144-150.

NOCKOLDS S. R., ALLEN R. (1953) - The geochemistry of some igneous series. Geochim. *et Cosmochim. Acta*, **4**, 105-142.

RAGLAND P. C., ROGERS J. J. W., JUSTUS P. S. (1968) - Origin and differentiation of Triassic dolerite magmas, North Carolina, USA. *Contr. Mineral and Petrol.*, **20**, 57-80.

RIVALENTI G., ROSSI A. - The geology and petrology of the Precambrian rocks between Qagssip kangerdluarssua and the inland ice, Frederikshåb district, South West Greenland. Accepted for publication on *Grønlands Geol. Unders. Rapp.* in 1970.

ROBINSON P. T. (1969) - High-titania alkali-olivine basalts of North-Central Oregon, USA. *Contr. Mineral and Petrol.*, **22**, 349-360.

RONOV A. B., MIGDISOV A. A. (1965) - Principal features of the geochemistry of hydrolyzate elements in weathering and sedimentation. *Geochemistry (USSR) (English Transl.)*, **2**, 92-117.

SHAW D. M. (1968) - A review of K-Rb fractionation trends by covariance analysis. *Geochim. et Cosmochim. Acta*, **32**, 573-601.

SIGHINOLFI G. P. (1969) - Determination of some major and trace elements in new standard rock samples by atomic absorption spectroscopy routine analysis. *Atti Soc. Tosc. Sc. Nat., Mem.* Ser. A, **76**, 312-325.

TAYLOR S. R., EMELEUS C. H., EXLEY C. S. (1956) - Some anomalous K/Rb ratios in igneous rocks and their petrological significance. *Geochim. et Cosmochim.* Acta, **10**, 224-229.

WAGER L. R. (1963) - The mechanism of adcumulus growth in the layered series of the Skaergaard intrusion. *Spec. Pap. Miner. Soc. Amer.*, **1**, 1-9.

WAGER L. R., MITCHELL R. L. (1951) - The distribution of trace elements during strong fractionation of basic magma- a further study of the Skaergaard intrusion, East Greenland. *Geochim. et Cosmochim. Acta*, **1**, 129-208.

WALKER F. (1956) - The magnetic properties and differentiation of dolerite sills- a critical discussion. *Am. J. Sci.*, **254**, 433-451.

WATT W. S. (1969) - The coast-parallel dike swarm of Southwest Greenland in relation to the opening of the Labrador Sea. *Can. J. Earth Sci.*, **6**, 340-344.

YODER H. S. jr., TILLEY C. E. (1962) - Origin of basalt magmas: an experimental study of natural and synthetic rock systems. *J. Petrology*, **3**, 342-532.

(*ms. pres. il 9 novembre 1970; ultime bozze il 12 gennaio 1971*)