STRONTIUM ISOTOPES IN KIMBERLITES AND ALKALINE ROCKS

THE ISOTOPIC COMPOSITION OF STRONTIUM IN SOUTH AFRICAN KIMBERLITES AND IN ALKALINE ROCKS OF THE FEN AREA, SOUTH NORWAY

By

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SCOPE AND CONTENTS:

The thesis discusses the petrology and geochemistry of kimberlite and its relation to other rock types. The genesis of diamond is discussed. Strontium isotopic studies are used to investigate the petrogenesis of kimberlite and its relation to the crust-mantle system, and to investigate possible genetic processes involved in the generation of certain varieties of alkaline rock and their relation to carbonatite at the Fen Complex.

ABSTRACT

A review of the petrography of kimberlite is given and a new definition of kimberlite based upon petrographical criteria is proposed. The trace element and stable isotope geochemistry of kimberlite is reviewed. The relation of kimberlite to meimechite, melilitite, carbonatite, basalt and potassic lavas is discussed in detail and it is concluded that kimberlite is not closely related to any of these rocks. A discussion of the genesis of diamond is presented and it is concluded that diamond may be formed by metastable processes over a wide range of temperature and pressure, and may therefore not be useful in the delineation of the depths of formation of kimberlite magmas. Recent experimental work on synthetic systems is discussed in relation to the petrology of kimberlite.

Strontium isotopic studies of kimberlites have revealed no significant differences in the whole rock $^{87}Sr/^{86}Sr$ ratios of fissure and pipe kimberlites. Kimberlites from the Swartruggens fissure (calcareous micaceous kimberlite) have $^{87}Sr/^{86}Sr$ ratios of from 0.709 to 0.716, whilst kimberlite from the Wesselton pipe has $^{87}Sr/^{86}Sr$ ratios of from 0.708 to 0.715. Other kimberlites range in $^{87}Sr/^{86}Sr$

ratio from 0.706 to 0.715. The ratios are uncorrected for geological age but all the samples are considered to be late Cretaceous to early Tertiary and thus the ratios are approximately initial ratios. The $^{87}Sr/^{86}Sr$ ratio of the MIT $SrCO_3$ standard averaged 0.7083 ± 0.0003 during the period of the investigation. All the kimberlite samples analysed were fresh and free as far as could be ascertained from xenoliths of country rock. Any alteration present was solely of a deuteric nature. The $^{87}Sr/^{86}Sr$ ratios bear no relation to the Rb or Sr content of individual kimberlite bodies. The Rb/Sr ratios of olivine rich kimberlite (basaltic) range from 0.005 to 0.11, those of micaceous kimberlites from 0.06 to 0.24. The high initial ratios are not considered to be due to bulk assimilation of granitic material in either a kimberlitic or carbonatitic magma. Rb-Sr data derived from garnet peridotites and eclogite xenoliths in kimberlite are not compatible with production of kimberlite by eclogite fractionation from a melt derived from garnet lherzolite. The Sr isotopic composition of kimberlite can be interpreted in terms of the partial melting of garnet mica peridotite which is either isotopically heterogeneous or homogeneous. The isotopic composition of liquids formed by the partial melting of this rock can be modified by two processes (i) gross contamination with material of low $^{87}Sr/^{86}Sr$ ratio and (ii) by the selective diffusion of material of high $^{87}Sr/^{86}Sr$ ratio into kimberlitic fluids.

The isotopic composition of Sr and the abundances of Rb and Sr have been determined in the alkaline rocks of the Fen complex. The $^{87}Sr/^{86}Sr$ ratios range from as low as 0.703 in carbonatite (søvite) to as high as 0.710 in rauhaugite. The whole rock analyses do not plot on a Nicolaysen diagram as an isochron. Calculation of the initial isotopic composition of strontium in the rocks at the time of intrusion of the complex, approximately 550 m.y. ago shows that the rocks are not simply related as the differentiation products of a single magma as they do not possess similar initial ratios. The lowest initial ratio is seen in the søvites and it is concluded that this rock must have been the parent magma from which the other rocks of the complex were derived. Analysis of the data in terms of the production of hybrid rocks by the bulk assimilation of granite gneiss in carbonatite shows that this process is inadequate to account for the Rb/Sr ratios observed. It is envisaged that selective concentration of granitic Sr of high $^{87}Sr/^{86}Sr$ ratio together with loss or gain of variable amounts of Rb has taken place. The process is closely connected with the fenitisation observed at the margins of the complex and is of a metasomatic nature. Thus, the genesis of rocks of the melteigite-ijolite-urtite series and the pyroxene-søvite series in this complex must be considered as a rheomorphic process. The $^{87}Sr/^{86}Sr$ ratios observed in rødberg and rauhaugite can be explained in terms of the metasomatic alteration of damtjernite.

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CHAPTER ONE

THE PETROGRAPHIC NATURE OF KIMBERLITE

The term kimberlite was introduced into petrological literature by Henry Carvill Lewis (1887, 1888) as a name for the porphyritic peridotite which is the source rock of diamonds found at Kimberley, South Africa. Lewis noted the presence of olivine, serpentine, biotite, bronzite, chrome diopside, pyrope and ilmenite in the rock.

Prior to the introduction of Lewis's term a similar rock had been discovered at Ison Creek, Elliot Co., East Kentucky, by A.R. Crandall. This rock was described by Diller (1885, 1886, 1888) as a peridotite. The mineral assemblage of this rock closely resembled that of Lewis's kimberlite although diamonds were not found. Later investigations (Crandall 1910, Koenig 1956) have verified that the Ison Creek rock is a kimberlite.

In 1892 Diller described a rock from West Kentucky which he termed mica peridotite. The rock consisted of biotite, serpentinised olivine, perovskite and lesser amounts of apatite, talc, magnetite, chlorite and calcite.

Since the publication of these descriptions the terms kimberlite and mica peridotite have become virtually synonymous - particularly in North America. Because of this usage of the terms, definitions of kimberlite existing in petrological literature are frequently inaccurate and often misleading, as the following examples illustrate:

1. American Geological Institute Glossary of Geology, 1960

> "A variety of mica peridotite consisting essentially of olivine, phlogopite and subordinate melilite, with minor pyroxene, apatite, perovskite and opaque oxides. Some examples contain diamonds."

2. Williams, Turner and Gilbert (1954, p. 79-80) regard mica peridotite and kimberlite as being synonymous and quote Shand (1934) in saying

> "most of the blue ground in the diamond pipes of South Africa is a breccia crowded with xenoliths in a ground mass of serpentine, carbonates, olivine, pyroxene, garnet, ilmenite, perovskite and chromite ...... the primary constituents of kimberlite appear to be olivine, serpentine, biotite, ilmenite and perovskite and the abundant carbonates seem to have been formed by the replacement of vanished melilite."

3. Moorhouse (1959, p. 321):

> "the principal mineral is olivine (usually altered to serpentine), bronzite, chrome diopside, phlogopite, perovskite, pyrope, ilmenite, chromite, apatite, magnetite and many other minerals are found. These minerals occur in a ground mass of serpentine and calcite. Melilite has been reported from some American kimberlites and has been suspected in others."

4. Dawson (1967a, p. 242):

> "kimberlite may be defined as a serpentinised and carbonated mica peridotite of porphyritic texture, containing nodules of ultrabasic rock types characterised by such high pressure minerals as pyrope and jadeitic diopside; it may or may not contain diamond. It occurs in diatremes, dykes, veins and sills of very limited size."

The diversity of the definitions is in part due to the variability of kimberlite itself both in mineralogical and geological aspects; in fact, many definitions and classifications of kimberlite are based upon textural characteristics. Thus Lewis (1887, 1888) recognised kimberlite, kimberlite breccia and kimberlite tuff. The present author considers that many of these textural features are of little use in a petrological definition of kimberlite as they are features which are imposed upon the rock during the later stages of emplacement and thus are merely morphological features of no petrogenetic significance. The superficiality of the textural and structural features can be recognised when it is realised that the textural type of kimberlite seen in any given occurrence depends upon the extent of erosion. In Tanzania where erosion has been slight, one can observe a complete gradation down a kimberlite pipe from lacustrine kimberlite tuffs to aeolian kimberlite tuffs, kimberlite breccias and massive (hardebanke) kimberlite (Edwards and Howkins 1966). Other regions such as South Africa have suffered sufficient erosion for the upper tuffaceous beds to be removed. The only textural features which are of some diagnostic value are the characteristic rounded phenocrysts (Fig. 1) seen in many kimberlites. These textures are produced during the transport of kimberlite to the surface of the earth by a fluid media. The process is termed fluidisation (Reynolds 1954) and the rounding of the phenocrysts is attributed to attrition during transport. Whilst such fluidisation textures are common in kimberlites, it should be noted that such features are not unique to kimberlites but are found in a number of diatremes and volcanic necks which contain rocks of widely differing composition (Shoemaker et al., 1962, Coe 1966). The development of fluidisation textures is thus typical of very gas-rich magmas irregardless of their composition.

For petrological purposes the massive kimberlite found in the lower parts of pipes and in fissures provides the best material for study as it contains relatively few country rock xenoliths and is often quite fresh and unbrecciated. Even so, mineralogical variation within such massive kimberlite is extensive and "basaltic" and "micaceous" varieties have been described (Wagner 1914) depending upon the amount of phlogopite present. Use of term basaltic is misleading and incorrect as feldspar is not present in the rocks. The term should be discarded and "basaltic kimberlites" should be referred to as kimberlites.

Detailed petrographic studies of kimberlite have been undertaken by Wagner (1914), Verhoogen (1938), Williams (1932), Holmes (1936), Dawson (1962), Smirnov (1959) and Mannard (1962). From these works and from the writer's own observations, the following salient features of kimberlite petrography have been gleaned. The nature of kimberlite is such that the phenocrysts are much more amenable for study than the groundmass and consequently, all studies are biased in this direction. Kimberlites contain a wide variety of minerals of both primary and secondary origin, however only those minerals which are essential or are of petrogenetic importance are discussed below.

Olivine

Olivine is by far the most important mineral found in kimberlites. It occurs in two generations, as large (up to 2 cm.) phenocrysts and as smaller crystals in the groundmass. The phenocrysts are often well rounded (Fig. 2) or elongate, corroded and embayed and exhibit undulatory extinction. The rounding of the phenocrysts (Figs. 1 and 2) is characteristic of transport in a fluidised system (see above). Many of the phenocrysts are surprisingly resistant to alteration (in marked contrast to the groundmass olivine), serpentinisation being limited to replacement along cracks or to the development of serpentine and magnetite rims (Figs. 2 and 3). The interior serpentinisation is generally not associated with much magnetite and the magnetite-rich rims indicate corrosion of the phenocrysts by the more iron-rich fluid which eventually formed the groundmass. Lee and Lawrence (1968) have found that the groundmass olivine is richer in iron than the phenocrystal olivine.

The small groundmass olivines are often fairly euhedral (Fig. 2) and are generally completely replaced by serpentine, bowlingite, magnetite and calcite. The composition of olivine found in kimberlites is compared with that of olivine in other basic and ultrabasic rocks in Table 1. The data indicate that the kimberlite olivines are not outstandingly different in composition from those found in some early

Figures 1 to 6. Petrography of some kimberlites.

Fig. 1. Doornkloof kimberlite. The rounding of the xenoliths and phenocrysts is generally attributed to fluidisation. (X3)

Fig. 2. Wesselton kimberlite. Rounded fresh first generation olivines are set in a groundmass of euhedral to subhedral second generation olivine together with serpentine, magnetite, calcite, perovskite and apatite. The large olivine crystals are surrounded by reaction rims of magnetite. (X6)

Fig. 3. Wesselton kimberlite. Relatively fresh olivines with reaction rims of serpentine and magnetite. (X20)

Fig. 4. Swartruggens kimberlite. Distorted phlogopite laths and large rounded phenocrysts of a mineral which has been completely replaced by calcite, dolomite and serpentine (? olivine) set in a groundmass of second generation phlogopite together with calcite, chlorite, magnetite, perovskite and apatite. The dark streaks seen within the phlogopite phenocrysts are a bright green Cr-rich chlorite (kammerite). (X5)

Fig. 5. Premier kimberlite. A highly altered (blue ground) kimberlite. Note the distorted micas now altered to vermiculite and the rounded garnet phenocrysts surrounded by dark kelyphitic rims. The groundmass is composed of completely serpentinised olivine. (X5)

Fig. 6. Swartruggens kimberlite. Basal section of phenocrystal phlogopite showing apparent crystallographically controlled replacement by calcite (and dolomite ?). The carbonate is iron stained. Such replacement textures are very common in this kimberlite. Thin sections cut normal to the basal section of phlogopite do not show the orientated intergrowth. Groundmass phlogopites are often completely replaced by calcite. (X100)

Fig 1

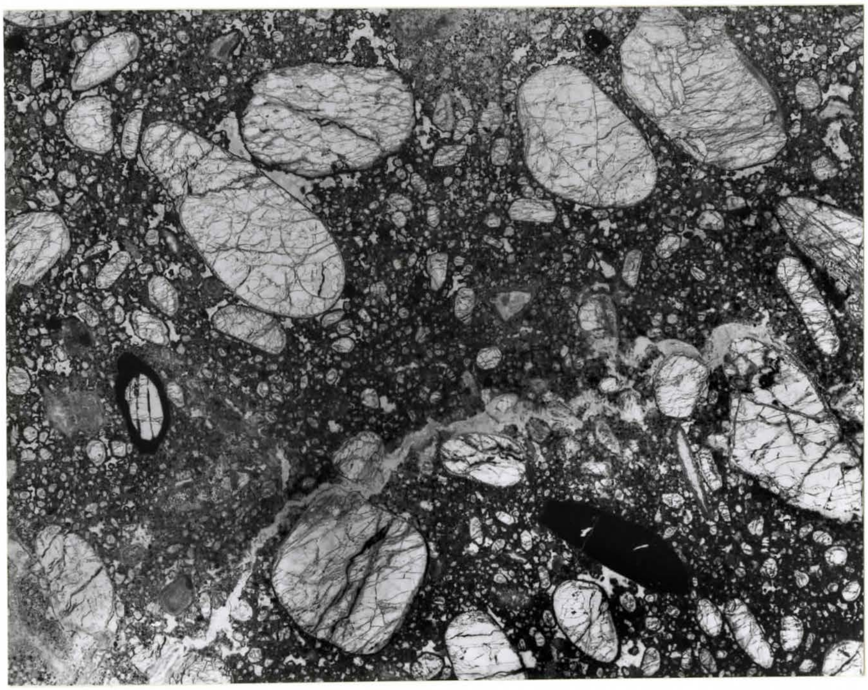


Fig 2

Fig 3

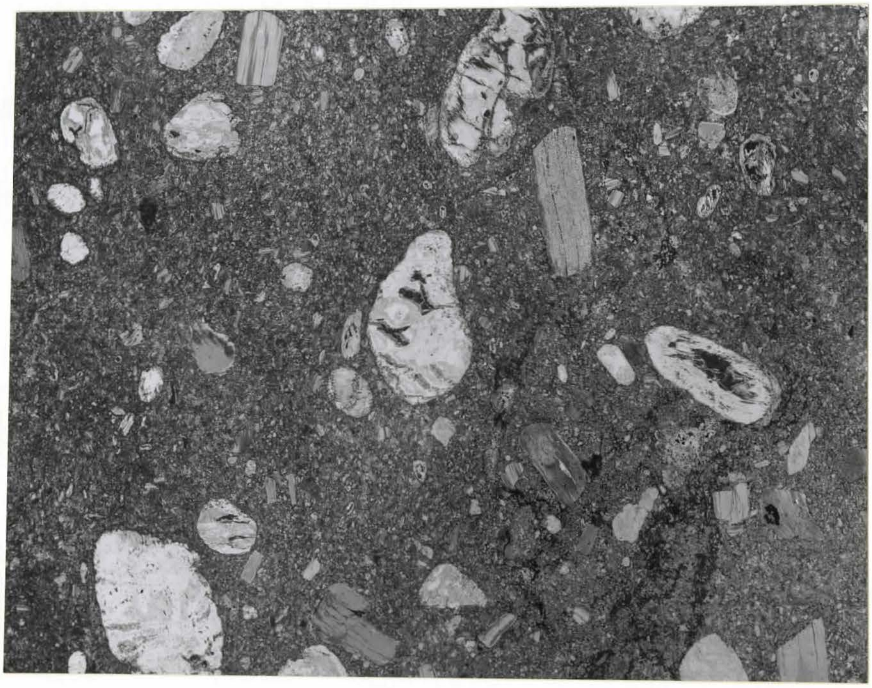


Fig 4

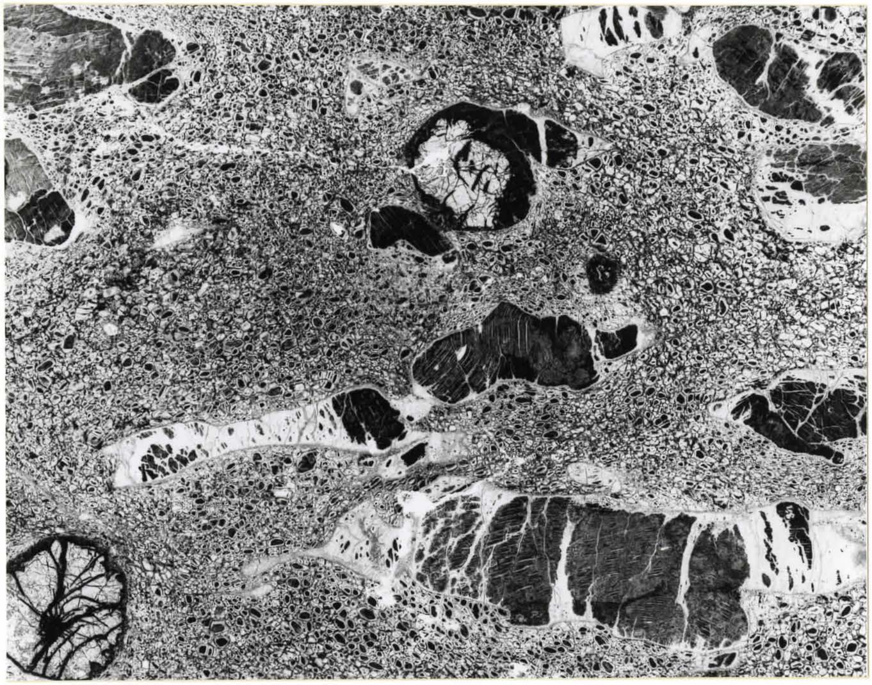


Fig 5

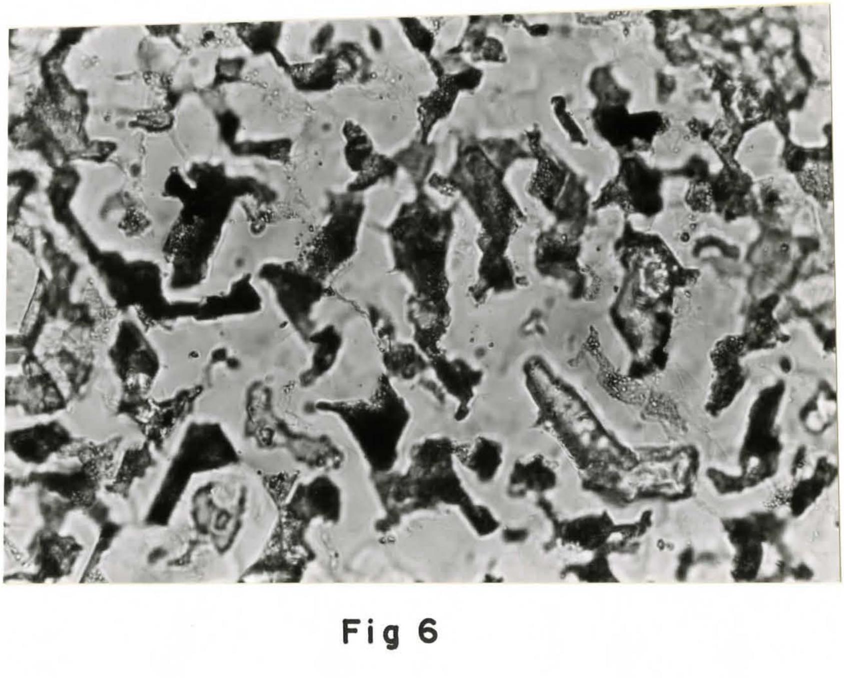


Fig 6

cumulate rocks, ultramafic nodules or alpine peridotites.

Table 1

Rock Type	Olivine %Fo	Reference
Kimberlite, Canada, Phenocrysts	93-94	Lee and Lawrence (1968)
Kimberlite, Canada. Groundmass	82-83	Lee and Lawrence (1968)
Kimberlite, Canada.	85	Watson (1967)
Kimberlite, Tanzania.	90	Mannard (1962)
Kimberlite, Tanzania.	91	Fozzard (1956)
Kimberlite, U.S.A.	91-93	Balk and Sun (1954)
Ultramafic cumulate, Stillwater.	90-80	Jackson (1960), Jess (1960)
Ultramafic cumulate, Great Dyke.	94-86	Hess (1950), Worst (1958,1960)
Ultramafic cumulate, Bushveld.	89-86	Jackson (1967)
Differentiated basic sills.	85-71	Drever and Johnston (1967a)
Picritic sills.	90-88	Drever and Johnston (1967b)
Ultrabasic pillow lavas, Cyprus.	93-92	Gass (1958)
Zoned ultramafic complexes.	85-78	Irvine (1967)
Ultramafic nodules.	90.5	Ross, Foster & Myers (1954)
Alkaline complex dunites.	90	Upton (1967)
High temperature peridotite.	90	Green (1964)
Alpine type peridotites.	94-88	Challis and Lauder (1966)

Other orthosilicates which have been reported in kimberlite are monticellite (Wagner 1914, Dawson 1962, Janse 1963, 1964, Nikishov 1966), calcic olivine (Verhoogen 1938), tiano-clinohumite (Balk and Sun 1954) and titan-olivine (Voshrensenskaya et al., 1965).

Phlogopite

Phlogopite, like olivine, occurs in two generations. The content may vary from as little as 1% up to as much as 80% in some extreme micaceous types. The phlogopite phenocrysts are corroded, rounded and bleached and are often highly distorted (Figs. 4 and 5). In many cases they have been altered to a bright green chlorite (Fig. 4) which is in the Swartruggens fissure kimberlite, a chromium-rich kammerite. Alteration to vermiculite (vaalite) is also common. The margins of the crystals are often rimmed by small magnetite crystals. Compositional zoning is quite commonplace. The phlogopite is weakly pleochroic, some kimberlites being characterised by phlogopite with a normal pleochroic scheme ($Z > X = Y$) whilst others are typified by reversed pleochroic schemes ($X > Y = Z$). Reversed and normal pleochroism can be found within the same zoned crystal in some cases (Watson 1967). The occurrence of mica with reversed pleochroism is typical of alkaline rocks (Hogarth 1964, Von Eckermann 1948, Singewald and Milton 1930, Boettcher 1967). The groundmass phlogopite occurs as small laths and does not have reaction rims of magnetite. Both generations of mica in some calcareous kimberlites are replaced by calcite. Fig. 6 shows an unusual crystallographically controlled replacement of phlogopite by calcite in the Swartruggens kimberlite.

Dawson (1962) has described olivines rimmed by phlogopite and it has been postulated that a reaction has taken place between the olivine and the magma. Similar reactions between olivine and phlogopite have been observed in some potassic volcanic rocks (Holmes 1936, Wade and Prider 1940, Williams 1936) and in lamprophyres (Mukherjee 1961). The reaction relationship has also been postulated on the basis of experimental work by Luth (1967).

Ilmenite

Large ilmenite grains up to 5 cm. in diameter are one of the most characteristic phenocrysts of many kimberlites. The grains are rounded and pitted and generally covered with a coat of leucoxene. Some grains have reacted with the carbonate-rich fluid which formed the groundmass to produce rims of perovskite. Broken ilmenite grains exhibit a very distinctive black glossy lustre which seems to be typical only of ilmenites which contain a high percentage of magnesium. The magnesium content of ilmenite has been investigated by Smirnov (1959), Mannard (1962), Besson (1967) and Lovering and Widdowson (1968). The results of these investigations show that ilmenite from kimberlite contains over 30% of the geikielite ($MgTiO_3$) molecule and up to 10% of hematite molecule. Although exsolved inclusions of titano-magnetite have been reported in one occurrence (Grantham and Allen 1960), most kimberlite ilmenites appear to be homogeneous. Table 2 shows the range in Mg0 content of ilmenites from various environments (Lovering and Widdowson 1967).

Table 2

	MgO%
Basic igneous rocks	0.46-3.27
Inclusions in basic pipes	3.51-4.60
High grade metamorphic rocks	1.0
Kimberlites	7.0-12.0

Kimberlite ilmenite is also reported to be enriched in niobium (0.1-0.3% Nb_2O_5) compared to other ilmenites (Mannard 1962, Deans 1964).

Garnet

Garnet is an important phenocrystal mineral in kimberlite and is sufficiently distinctive that it is employed as an indicator mineral in kimberlite prospecting programs. Garnets range in size from crystals of microscopic dimensions to crystals several centimeters in diameter. Many are rounded and exhibit a wide range of colour including orange, pink, purple and various shades of red. They are compositionally distinctive in being rich in the pyrope molecule and in chromium

(0.3-4.0% Cr_2O_3, Smirnov 1959). In some cases the chromium content is so high that the garnets must be described in terms of the hanleite molecule ($Mg_3Cr_2Si_3O_{12}$) as insufficient calcium is present to accommodate all the chromium as the uvarovite molecule (Nixon et al., 1963).

Nixon et al. (1963) consider that three groups of garnet are present in the Lesotho kimberlites, these being pyrope, chrome-pyrope and pyrope-almandine. Similar groupings can be seen in Siberian kimberlites (Smirnov 1959, Milashev 1958). Mannard (1962) has grouped garnets in Tanzanian kimberlites into kimberlitic garnets which correspond to chrome-pyrope and pyrope, and into eclogitic garnets which correspond to pyrope-almandine garnets.

Pyrope garnets with a Cr_2O_3 content greater than 0.5%wt. occur in only three environments; as phenocrysts in kimberlite, in garnet peridotite nodules in kimberlites and in garnet peridotite lenses in orogenic regions (O'Hara and Mercy 1966). It is possible that the chrome-pyrope phenocrysts are in fact derived from fragmented garnet peridotite nodules. Whether these nodules are cognate xenoliths or are unconnected with kimberlite genesis is not yet known, consequently, many geologists regard the garnets as xenocrystal. If however kimberlite forms at very great depth in the mantle,garnet may be a true phenocryst if it is a stable phase on the liquidus at those depths (see, for example, Green and Ringwood 1967, O'Hara and Yoder 1967).

The pyrope-almandine garnets correspond closely with the garnets found in eclogite xenoliths. A xenocrystal or phenocrystal origin is again possible. The garnets associated with eclogite found in kimberlite are in general highly magnesian when compared to eclogite garnet found in other (mainly metamorphic) environments (Colemann et al., 1965). Recent studies by Rickwood et al. (1968) have indicated that the spread in garnet composition of eclogite garnet found in kimberlites is greater than that proposed by Colemann et al. (1965), and that grossular-rich garnets are quite common, although the dominant garnet type remains pyrope-almandine. The pyrope-almandine garnets are low in Cr and other trace elements relative to the pyropes and chrome pyropes (Mercy and O'Hara 1967) indicating formation under very different conditions. Garnets in kimberlite are frequently surrounded by a rim of kelyphite (Fig. 5) which consists of a mixture of spinel, enstatite, hornblende, mica and chlorite (Nixon et al., 1963). The kelyphite is a reaction product formed between garnet and the transporting fluid.

Pyroxene

Pyroxene is not a very characteristic mineral of kimberlite and in many cases may represent fragmented ultrabasic xenoliths. Enstatite is fairly common as nodular aggregates in South African kimberlites (Williams 1932) but is rare in Siberian kimberlites (Smirnov 1959). The clinopyroxenes include bottle-green diopside, bright green chrome diopside, augite and omphacite. The omphacite is possibly derived from fragmented eclogite xenoliths. The proportions of enstatite to diopside have been found to vary in different kimberlite provinces. In Tanzania and the Congo, diopside predominates over enstatite (Verhoogan 1938, Mannard 1962), whilst in Siberia the reverse is true (Smirnov 1959).

The groundmass of kimberlites is very fine grained and is thus not very amenable for study. However, investigations have shown it to consist of a complex mixture of calcite, serpentine and magnetite together with a host of accessory minerals. Many of the groundmass minerals are secondary in nature and represent the deuteric alteration products of primary phases such as olivine. It should be noted though that unaltered primary minerals crystallise in the groundmass. Some of the more important constituents of the groundmass are:

Serpentine which occurs as pseudomorphs after olivine. It can be found rarely as small laths of (?) primary origin (Watson 1967). Serpentine is one of the most abundant minerals in kimberlite and is generally a pale green antigorite. Smirnov (1959) has shown the serpentine to be highly magnesian and to contain appreciable amounts of nickel (e.g. 0.2%).

Calcite is a common mineral in kimberlite and in some cases can form over 50% of the rock. Such kimberlites should be termed calcareous kimberlites. The calcite occurs as anhedral grains which often contain euhedral crystals of augite, olivine, phlogopite, perovskite, magnetite and apatite. Such textural evidence is interpreted to mean that calcite is a late crystallising primary mineral (Watson 1967) and is not a deuteric alteration product, although calcite can be found replacing earlier ferromagnesian minerals. Replacement of these minerals may have been of a deuteric nature or more likely simply by reaction with the late primary calcite-bearing groundmass fluids. Because of the highly magnesian nature of kimberlite it is probable that many of the "calcites" described from kimberlites are dolomite. This has been found to be true for the Swartruggens kimberlite where the presence of dolomite has been verified by X-ray diffraction studies. In common with carbonatite calcite, kimberlite calcite has been found to be enriched in strontium (e.g. 0.4%SrO in calcite from the Mir pipe, Smirnov 1959).

Magnetite occurs as a product of serpentinisation and also as a primary phase crystallising as small euhedral crystals scattered throughout the groundmass.

Of the host of accessory minerals found in kimberlite (Williams 1932) the most important are perovskite, apatite, zircon, rutile, graphite and diamond.

Although many definitions of kimberlite include the presence of melilite, it must be noted that melilites are exceedingly rare in kimberlites. Carvill Lewis (1887) first mentioned the possibility that melilite might be found in the groundmass of kimberlite and since that time melilite has achieved a status in kimberlite petrography out of all proportion to the available evidence concerning its presence in kimberlites. Melilite has, in fact, only rarely been found in kimberlite, although supposed evidence for its former presence has been presented by several authors. Wagner (1914, p. 46) in describing the Franspoort kimberlite dyke presented the following observations:

> "Calcite is present in the groundmass in minute homogeneous laths the appearance of which suggests that they are pseudomorphs after a lath shaped mineral originally present."

The original lath shaped mineral is presumed to have been melilite. Wagner (1914) also points out that in other specimens of the rock the habit of the calcite was totally different. Williams (1932) likewise finds calcite pseudomorphs after a lath shaped mineral presumed to have been melilite; however, Williams (1932) notes that fresh melilite has not been found in South African kimberlites and that its former presence has only been suspected in a few occurrences, i.e. Kadi, Schuller and Jagersfontein.

In 1934 the "melilite hypothesis" was given further impetus by Shand who considered that the high CaO and calcite content of kimberlites could only have been derived by the breakdown of an original lime-rich mineral, i.e. melilite. It should be noted, however, that during the 1930's petrologists were acrimoniously debating the evidence for and against a magmatic origin for carbonatites and that Shand was one of the chief opponents of the magmatic theory. Hence, Shand was unable to admit the possibility that carbonates found in kimberlite might be of a primary magmatic origin, and thus in accordance with his beliefs, all the carbonate must be of a deuteric nature.

Recently, Frankel (1956) and Watson (1967) have described lath shaped minerals in kimberlite replaced by calcite. Both authors suggest the original presence of melilite but Watson (1967) considers most of the calcite to be primary. The occurrence of fresh melilite has been reported only from one occurrence, in Siberia (Nikishov 1966). No details are available. Williams, Turner and Gilbert (1954) have reported melilite in the Elliot Co. kimberlite but Koenig (1956) considers that the mineral described is not melilite. Optical and X-ray studies of the kimberlites employed in the present study failed to reveal the presence of any melilite.

The above evidence shows that melilite, contrary to many standard definitions of kimberlite, is extremely uncommon and thus should not be regarded as a typical mineral of kimberlites. Evidence for the presence of decomposed melilite is likewise scant and unconvincing. In some of the more calcareous kimberlites examined, e.g. Swartruggens and Doornkloof, tabular phlogopites show a partial conversion to calcite. Similar pseudomorphs have been described from the Monastry kimberlite by Dunham (Sampson 1953). Thus, description of the calcite laths seen in some kimberlites as pseudomorphs after melilite may be erroneous. In addition, the typical decomposition products of melilite, apart from calcite, such as hydrogrossular, xonotlite and cebollite (Christie 1961, Deer et al., 1966) are not found in kimberlites.

It is possible that melilite may have been an important constituent of some kimberlites, particularly the calcareous varieties, because of the general bulk composition of the rocks. Melilite will, however, be confined to the later stages of crystallisation of kimberlite, as it will only crystallise within a low pressure (crustal) environment (Yoder 1968). Melilite may also form by reaction of primary minerals with the calcium-rich transporting fluid, e.g.

$$\text{olivine} \xrightarrow{\text{Ca}} \text{monticellite} \xrightarrow{\text{CaAl}} \text{melilite} \xrightarrow{CO_2H_2O} \text{calcite} + \text{serpentine}$$

Formation of melilite as such a reaction product has been postulated in alnöites (Bowen 1922) and turjaites (Kranck 1928).

From the above comments certain features which appear to be characteristic of kimberlites can be ascertained, thus:

1. Kimberlites are porphyritic rocks with rounded and corroded phenocrysts.
2. Olivine was originally the most abundant mineral in kimberlites.
3. Phlogopite is a major phenocrystal mineral and its pleochroism is that typical of alkaline rocks.
4. Phenocrystal ilmenite is typically magnesium rich.
5. Garnet is typically pyrope and chrome pyrope.
6. Primary calcite is a ubiquitous component of the groundmass.

Although kimberlite is the primary terrestrial source of diamonds, its presence or absence is of little use in a petrographic definition of kimberlite as the majority of kimberlites do not contain diamonds. Likewise, the highly distinctive assemblage of ultrabasic xenoliths found in kimberlite, particularly garnet-peridotites and grosspydites, is not found in all kimberlites. However, if either diamonds or ultrabasic xenoliths are found in a supposed kimberlite, they can be considered as providing strong circumstantial evidence in favour of considering the rock to be a true kimberlite.

The assemblage of magnesian ilmenite and pyrope is considered by the writer to be one of the most distinct and characteristic features of kimberlite. The association can be observed in all the major kimberlite provinces of the world and is sufficiently distinctive that it is generally employed as an indicator of possible diamondiferous regions by mining companies. Several petrologists (James 1965, Artsybasheva 1964) have emphasized the unique association of the assemblage with kimberlite.

A definition of kimberlite proposed by the present writer is:

"Kimberlite is a porphyritic alkalic peridotite containing rounded and corroded phenocrysts of olivine (serpentinised, carbonatised or fresh), phlogopite (fresh or chloritised), magnesian ilmenite, pyrope and chrome-rich pyrope set in a fine grained groundmass composed of second generation olivine and phlogopite together with calcite, dolomite, serpentine, magnetite, chlorite, perovskite and apatite. Diamond and garnet-peridotite xenoliths may or may not occur."

Three varieties of kimberlite can be recognised namely kimberlite (equivalent to basaltic kimberlite), micaceous kimberlite and calcareous kimberlite according to the amounts of mica or carbonate present.

Relationship of kimberlites to mica peridotites and "central complex kimberlites".

Many mica peridotites and the ultrabasic rocks associated with carbonatite complexes have been termed kimberlite (Dawson 1966). A type locality of each of such rocks is examined below and compared with the above definition of kimberlite. It should be realised also that the percentage of mica in many kimberlites is negligible and that such kimberlites bear little relation to mica peridotites which commonly contain over 20% mica (Koenig 1956).

Mica peridotites of Western Kentucky and Southern Illinois, U.S.A.

Approximately fifty dykes occur in this area, including the Flanery dyke which is Diller's (1892) type mica peridotite. The dykes contain abundant phlogopite, very little pyroxene and no feldspar or quartz. Serpentine and calcite have replaced nearly all the olivine and form a large part of the groundmass together with magnetite, ilmenite, perovskite and chlorite. All the dykes are holocrystalline and porphyritic (Koenig 1956). Features which contrast with kimberlites are:

1. Phenocrysts are commonly euhedral, alteration of phenocrystal olivine to serpentine and magnetite is ubiquitous.
2. Magnesian ilmenite is not found.

Von Eckermann (1967) in defining kimberlite relies upon Shand's (1934) definition which implies that melilite was an essential component of all kimberlites, a conclusion at variance with observations as noted above, and stemming largely from Shand's inability to accept a magmatic origin for the calcite found in kimberlite. Pyrope garnet was regarded by Shand (1934) to be a xenocryst. Von Eckermann's (1967) paper summarises the results of his numerous investigations of the Alnö "kimberlite dykes". From this work it is clear that the genesis of the dykes is an intimate part of the genesis of the alkaline rocks in general occurring at Alnö and that they are a late stage relatively shallow level phenomena. Features which can be ascribed to fluidisation are not found and features which are clearly at variance with them being called kimberlite are:

1. They are not always porphyritic and the phenocrysts when present are euhedral.
2. A second generation of olivine crystals is not typical.
3. The mica is biotite, not phlogopite, in many cases.
4. Magnesian ilmenite is not present.
5. Pyrope is not present.
6. Large quantities of aegerine-augite and augite are present.

3. Pyrope garnet is not found. Garnet is very rare in these rocks and is of a yellow green type (? grossular) never seen in kimberlites. In one case garnet appears to be a reaction product formed between olivine and the magma (Clegg 1955). The garnets are always found as groundmass minerals (English and Grogan 1948, Clegg 1955).
4. No garnet peridotite xenoliths or diamond have been found.

   The geological aspects of the dykes (Koenig 1956) and their mineralogy appear to point to a shallow depth of origin with quiet intrusive conditions.

The writer concludes that mica peridotites such as are found in West Kentucky and Southern Illinois cannot be termed kimberlites. Other groups of dyke rocks found in the U.S.A. commonly called either mica peridotite or kimberlite appear in some cases to be true kimberlites, that is, magnesium ilmenite and pyrope are present. Examples include Fayette Co. (Hickock and Mayer 1924), Dixonville (Hoeness and Graber 1926) and some dykes near Ithaca (Martens 1924).

Central Complex kimberlites - Alnö and Fen

Some geologists, notably Von Eckermann (1967), have called ultrabasic rocks which occur within carbonatite complexes, kimberlites. Not all geologists would agree with such a description and James (1965) has termed the rocks phlogopite-serpentinites. Mannard (1962) has also objected to calling the rocks kimberlite.

7. Melilite and its alteration products are common. Fresh Melilite is not abundant but the euhedral lath shape of calcite pseudomorphs and the typical decomposition products of melilite, i. e. calcite and garnet (melanite) indicate that melilite was originally present in considerable quantities.
8. No garnet peridotite xenoliths have been found.

Von Eckermann (1967) has postulated the presence of diamond in an Alnö dyke rock, but the occurrence is as yet unverified.

From the above evidence the writer concludes that the Alnö dykes are not kimberlites and are better petrographically described as alnöites (i. e. an olivine-melilite-clinopyroxene-phlogopite-nepheline rock). Similar ultrabasic rocks occur at Ngualla, Tanzania (James 1958), Rangwa, Kenya (McCall 1963) and in several Russian carbonatite complexes (Heinrich 1966, Tomkieff 1961). Mannard (1962) considers that the Ngualla occurrence is not a kimberlite on the basis of the fact that melanite was found in the rock.

The damtjernite occurrence forming the core of the Fen alkaline complex, Norway, has been considered to be a residual product of a kimberlite magma (Saether 1957). This rock is petrographically quite unlike any known variant of kimberlite and moreover contains little olivine (c. 12%). It consists of phenocrysts of olivine, biotite, amphibole and titanaugite set in a groundmass of biotite, amphibole, calcite, magnetite, pyroxene, nepheline and feldspars. The rocks do not contain pyrope or magnesian ilmenite. Thus damtjernite is quite obviously unrelated to kimberlite, even as a differentiate, and is in fact a lamprophyre. Ultrabasic xenoliths occur in the rock and appear to be cognate xenoliths, no garnet peridotite xenoliths are found. Xenoliths and phenocrysts show the effects of fluidisation indicating that physical conditions prevailing during the intrusion of the damtjernite were similar to those of kimberlite.

CHAPTER TWO

A REVIEW OF THE TRACE ELEMENT AND STABLE ISOTOPE GEOCHEMISTRY OF KIMBERLITE

Major element geochemistry

The major element geochemistry of kimberlite is fairly well known and has been adequately discussed by Dawson (1967b) who concluded that kimberlites, whilst being very ultrabasic, contain unusually high amounts of K_2O, Al_2O_3, TiO_2, CaO, CO_2, P_2O_5, H_2O and SO_3 compared to normal peridotites. Kimberlites have low Fe/Mg ratios but high K/Na and Fe_2O_3/FeO ratios. Whilst kimberlites are dominantly potassic (K>Na) it should be noted that sodic kimberlites (K<Na) are known from the Singida province (Mannard 1962). The high Fe_2O_3/FeO ratio has been ascribed to the conditions of intrusion of kimberlite and to the serpentinisation of the primary minerals. The development of the Fe_2O_3/FeO ratio as a function of the fugacity of CO_2 and O_2 has been discussed by Kennedy and Nordlie (1968).

An important aspect of the major element geochemistry is the extreme variation exhibited by such elements as CaO, K_2O, H_2O and CO_2. This is a consequence of the complete chemical gradation which exists between micaceous kimberlite, calcareous kimberlite and kimberlite. Similar variations are also seen in the trace element content.

The degree of undersaturation of silica in kimberlites is expressed in the CIPW norm by very high olivine, hypersthene, calcite, and magnetite. Some norms also show nepheline, leucite, kaliophyllite, kalsilite and calcium orthosilicate (Dawson 1962).

The chemical composition of some typical kimberlites is shown in Table 3.

Trace Element Geochemistry

The trace element geochemistry of kimberlite is very poorly known. Most of the determinations have been made by emission spectrographic techniques which whilst adequate for trace elements present in relatively high concentrations, e.g. Ni, Cr, Nb, are subject to matrix effects of unknown magnitude and to erratic behaviour in the arc (Gurney et al. 1966). Many of the elements determined occur at concentrations close to the limits of sensitivity of the technique and thus should be regarded only as indications of the true concentration. In addition, large discrepancies exist between individual groups of determinations using the same analytical techniques, e.g. Litinsky (1961) and Dawson (1962), and between determinations of the same element using different analytical techniques, e.g. Burkov and Podporina (1966) and Haskin et al.

Table 3. The major element geochemistry of some kimberlites

	1	2	3	4	5	6	7	8	9
SiO_2	36.32	31.71	33.25	32.7	23.25	29.57	30.19	27.66	27.56
TiO_2	1.25	2.31	2.09	2.1	5.10	1.31	1.46	1.67	1.43
Al_2O_3	4.66	4.72	1.75	3.2	3.15	3.48	2.50	3.23	3.52
Fe_2O_3	6.04	6.68	7.99	3.9	6.98	5.04	6.55	1.49	6.00
FeO	3.74	4.51	2.95	5.8	7.07	2.63	1.65	1.98	1.52
MnO	0.07	0.26	0.16	0.2	0.16	0.11	0.10	0.08	0.13
MgO	26.21	27.45	31.40	31.5	20.81	26.26	31.32	22.05	25.83
CaO	6.63	7.61	5.22	8.1	14.78	11.92	8.25	16.47	13.35
Na_2O	1.02	0.20	0.10	0.5	0.28	0.25	0.28	0.23	0.31
K_2O	1.31	0.75	0.88	2.0	1.16	0.54	0.49	0.23	0.26
H_2O^-	2.45	1.36	0.63	-	1.10	18.65	16.10	20.76	19.25
H_2O^+	7.14	9.17	9.66	3.4	4.87				
CO_2	2.50	3.19	2.82	5.1	10.37	-	-	-	-
P_2O_5	0.72	0.79	0.53	0.4	0.76	0.45	0.76	0.60	0.25
	100.06	100.71	99.43	98.9	99.84	100.21	99.65	96.45	99.41

1. Average of 39 South African kimberlites (Williams 1932)
2. Average of 4 Lesotho kimberlites (Dawson 1962)
3. Sierre Leone kimberlite (Grantham and Allen 1960)
4. Micaceous kimberlite, Ontario, Canada (Lee and Lawrence 1968)
5. Calcareous kimberlite, Bachelor Lake, Quebec (Watson 1955). Average of 3 analyses.
6. Average of 210 Siberian kimberlites (Lebedev 1964)
7. Average of 63 Muna region (Siberia) kimberlites (Lebedev 1964)
8. Average of 13 Alakit region (Siberia) kimberlites (Lebedev 1964)
9. Average of 63 Daaldyn region (Siberia) kimberlites (Lebedev 1964)

(1966). Whether these differences represent actual differencies in the geochemical character of Siberian and African kimberlites or merely reflect errors in the analytical techniques is as yet unknown. A major difficulty in the interpretation of the Russian data is that analytical details are seldom given and information concerning the nature of the kimberlite analysed is extremely rare. As a consequence of these difficulties, it is only possible to outline the geochemistry of kimberlite, the major points of which are discussed below.

Table 4 lists the principal trace element determinations available to the writer. Also included are the average concentrations of trace elements in ultramafic rocks and carbonatites, which may be considered as the two extremes between which the major element chemistry varies. (N.B. No genetic connection with either of these rocks is implied, they serve only to illustrate trace element abundance levels.)

The overall characteristic of the geochemistry, as previously noted by Dawson (1967b) is that two major groups of trace elements are present:

1. Trace elements considered to be typical of ultramafic rocks, e.g. Cr, Co, Ni, Re, Os.
2. Trace elements considered to be typical of alkaline rocks, carbonatites and potassic lavas, e.g. Nb, Zr, Sr, rare earths.

Ultrabasic Geochemistry

Concentrations of Cr, Ni and Co are lower in kimberlites than are found in peridotites. This can be ascribed to the presence of minerals such as calcite which dilute the whole rock data by widely varying amounts. Litinsky's (1961) data for Ni is extremely low and is at marked variance with all the other determinations, and thus must be regarded with some suspicion. The principal Cr, Ni, and Co bearing phases are olivines, garnets and micas. The olivines contain Co and Ni in concentrations similar to those observed in normal peridotites (Nixon et al. 1963). Turekian (1963) has noted the constant covariance of Cr and Ni in a variety of igneous rocks and that this relation is also true for kimberlites. This is remarkable in view of the fact that the principal location of chromium in basic igneous rocks is in chromite and magnetite, whilst in kimberlite the major chromium bearing minerals are olivine, serpentine, ilmenite and garnet (Litinsky 1961, Nixon et al. 1963). Garnets in particular contain very high concentrations of Cr (Meyer 1968, Nixon et al. 1963). Chromite is found in kimberlite but it is a very minor mineral and is insignificant when compared to the amounts found in alpine peridotites or layered ultrabasic rocks.

Table 4. Trace element geochemistry of kimberlites

Elements listed in Table 4 are arranged in order of increasing atomic number (Z). All concentrations are in parts per million (ppm) unless otherwise stated. Data for average ultramafic rocks (UMR) are taken from Goles (1967), Vinogradov (1962) and Ehman and Lovering (1967). Data for average carbonatites (CARB) are from Gold (1966).

Methods

ES	Emission spectrography	AA	Atomic absorption
ESV	Semiquantitative ES	XRF	X-ray fluorescence
CHEM	Chemical Determination	NAA	Neutron activation
COLOR	Colorimetric analysis	ID	Isotope dilution
FP	Flame photometry	HGVD	Hg vapour detection

Sources of Data

1. Burkov and Podporina (1965)
2. Dawson (1962)
3. Lee and Lawrence (1968)
4. Janse (1964)
5. Cherepanov (1966)
6. Agyei (1968)
7. Steuber and Goles (1967)
8. Gangadharam and Aswathanarayana (1969)
9. Litinsky (1961)
10. Bobriyevich et al. (1959)
11. Young et al. (1954)
12. Turekian and Carr (1961)
13. Williams (1932)
14. This work
15. Gurney et al. (1966)
16. Manton and Tatsumoto (1969)
17. Haskin et al. (1966)
18. Kudryavtsev (1964))
19. Fozzard (1956)
20. Burkov and Podporina (1966)
21. Morgan and Lovering (1967)
22. Ehmann and Lovering (1967)
23. Ahrens et al. (1967)
24. Borisenok (1959)

Table 4. Trace Element geochemistry of kimberlites

Z	Range	Mean	Number	Method	Source	UMR	CARB
Li		34	32	FP	1	0.5	15
	<4-50	16	14	ES	2		
	3.5-3.3	3.4	2	CHEM	3		
		20	4	ES	4		
Be		1	38	ES	1	0.2	5
B		149	48	ES	1	20	0
	20-200		2	ESV	3		
		190	226	NAA	5		
		4	1	COLOR	6		
Sc		10	48	ES	1	15	10
	20-30	25	14	ES	2		
		15	4	ES	4		
	11.4-17.8	14	3	NAA	7		
		<20	2	ES	3		
	12.5-27.6	19	5	NAA	8		
V		120	21	CHEM	1	40	105
		170	459	ES	9		
	65-180	120	14	ES	2		
		160	4	ES	4		
		130	2	ES	3		

Z	Range	Mean	Number	Method	Source	UMR	CARB
Cr	950-2000	1439	14	ES	2	2400	102
	100-10000	1500	459	ES	9		
	1500-1600	1550	2	ES	3		
		1000	4	ES	4		
		1250			10		
	690-1720	1200	3	NAA	7		
		875	1	NAA	12		
Co	65-110	77	14	ES	2	110	19
		40	459	ES	9		
	30-80	59	10	COLOR	11		
		50	4	ES	4		
		78	2	ES	3		
	72-91	80	3	NAA	7		
		71	1	NAA	12		
Ni	500-1700	1140	14	ES	2	1500	32
	50-2000	450	459	ES	9		
	900-1500	1130	10		11		
		1048	3	CHEM	13		
		1200	4	ES	4		
		1100	2	ES	3		
		1360			10		
Cu	10-300	100	14	ESV	2	30	88
		60	459	ES	9		
		56	2	ES	3		
	15-110	46	15	AA	14		

Z	Range	Mean	Number	Method	Source	UMR	CARB
Zn	10-100		2	ES	3	30	160
	30-115	81	15	AA	14		
Ga	3-30	9	14	ES	2	5	2.4
	1-10		2	ES	3		
		1	10	ES	24		
Ge		0.5	48	CHEM	1	1	3.3
	0.1-1		2	ES	3		
Rb	10-100		14	ESV	2	~1	52
		11	19	FP	1		
		250	4	ES	4		
	73-135	116	6	ES	15		
		113	1	ID	16		
	103-432	235	5	NAA	8		
	4-265	104	25	ID	14		
Sr		1140	39	FP	1	20	1000-3000
	120-1100	426	13	ES	2		
		600	4	ES	4		
		200	459	ES	9		
	710-760	735	2	ES	3		
		405	1	ES	12		
		2040	1	ID	16		
	274-1883	935	25	ID	14		
Y	30-75	46	14	ES	2	5	114
		40	4	ES	4		
	4.9-12.9		3	NAA	17		

Z	Range	Mean	Number	Method	Source	UMR	CARB
Zr	300-700	445	14	ES	2	30	461
		200	459	ES	9		
		97	53	CHEM	1		
		250	2	ES	3		
		190	4	ES	4		
Nb	n. d. -500	70	459	ES	9	1	Nb+Ta 560
	130-400	240	14	ES	2		
		160	57	CHEM	1		
		200	4	ES	4		
	210-220	215	2	ES	3		
	55-160				18		
	15-590	180	17	CHEM	19		
Mo	3-12		14	ES	2	0.2	64
	n. d. -0.5		2	ES	3		
	1-2		15	AA	14		
Ag	0.1-1		2	ES	3	0.05	3.9
Sn	1-10		2	ES	3	0.5	2.5
Cs	4.2-8.0	6	5	ES	15	0.1	0
	1.0-34.8	13	5	NAA	8		
Ba	130-2600	740	14	ES	2	1	4500
	1900-2000	1950	2	ES	3		
		100	4	ES	4		
La	100-650	357	14	ES	2		
		150	2	ESV	3		
	15-129	46	24	XRF	20		

Z	Range	Mean	Number	Method	Source	UMR	CARB
Ce	46-273	112	24	XRF	20		
	72, 510	291	2	NAA	17		
Pr	3.4-26.7	12	24	XRF	20		
	6.6-36	17	3	NAA	17		
Nd	10.5-88.5	42	24	XRF	20		
	24-134	60	3	NAA	17		
Sm	1.9-13.8	6	24	XRF	20		
	5-6-11.6	8	3	NAA	17		
Eu	0.09-1.66	0.6	23	XRF	20		
	0.28-2.0	1.2	3	NAA	17		
Gd	1.04-8.88	3.6	24	XRF	20		
	5.5-8.9	6.5	3	NAA	17		
Tb	0.13-1.1	0.5	11	XRF	20		
		0.58	1	NAA	17		
Dy	0.61-2.74	1.5	23	XRF	20		
Ho	0.24-0.78	0.4	5	XRF	20		
	0.63-0.67	0.65	2	NAA	17		
Er	0.17-1.47	0.65	10	XRF	20		
	0.87-1.38	1.12	2	NAA	17		
Tm		0.22	2	NAA	17		
Yb	0.39-3.37	1.07	16	XRF	20		
	0.96-1.20	1.11	3	NAA	17		
Lu	0.16-0.19	0.17	2	NAA	17		
Ta		8.6	16	CHEM	1		

Z	Range	Mean	Number	Method	Source	UMR	CARB
Re		0.069 ppb	1	NAA	21		
Os		1.34 ppb	1	NAA	21		
Hg		200 ppb	1	NAA	22	4 ppb	
	10-70 ppb	45 ppb	14	HSVD	14		
Pb	<3-20		14	ESV	2	0.05	27
		30	4	ES	4		
	5-50		2	ES	3		
	60-120	77	14	AA	14		
		37	1		16		
Th	8.1-39.8				23	0.06	649
	12.3-26.3	19.7	5	NAA	8		
		30	1	?	16		
U	0.9-5.0				23	0.02	57
	0.48-0.77	0.61	5	NAA	8		
		2.5	1	?	16		

Morgan and Lovering (1967) have shown that kimberlite, in common with peridotite and dunite, possesses low Re and high Os concentrations relative to other igneous rocks.

The concentrations of Cr, Ni, Co, Re, Os in kimberlite whilst being akin to those of alpine peridotites and accumulate peridotites, are very different to the concentrations of these elements found in peridotites associated with carbonatite complexes, which are depleted in these elements (Ducellier 1963, Gerasimovskii and Belyayev 1963) and which have evidently been formed by very different processes.

Alkaline Geochemistry

Table 4 shows that kimberlites are enriched in Rb, Li, Cs, Zr, Nb, Ba, Sr, Y, rare earths, Th and U relative to normal peridotites. Some of these elements reflect the variations seen in the major element geochemistry, e.g. Rb and Ba with K (mica) and Sr with Ca (calcite). The trace element assemblage is similar to that seen in carbonatites, potassic lavas and a wide variety of alkaline rocks. The similarity of the trace element assemblage between kimberlite and carbonatite has been used as an argument for genetically relating the two rocks, however such arguments are spurious when based upon similarities alone, as any of the other "similar rocks" could equally well be used. Two points must also be borne in mind when considering the similar geochemistry of the rocks.

Firstly, the trace element assemblage is of the miascitic type, i.e. high Nb content, lack of zirconium silicates, rare earth, Be and Li minerals. The development of either a miascitic or agpaiitic assemblage appears to depend upon the dominant volatile species present; miascitic assemblages being found in CO_2-rich environments and agpaiitic in Cl, F and H_2O-rich environments (Heinrich 1966). Transport of certain elements as carbonate complexes, e.g. Nb (Aleksandrov 1967), rare earths (Kosterin 1959), U (Naumov 1962, Hostetler and Garrels (1962) probably plays a dominant role in the development of the miascitic assemblage. Hence, the development of any given trace element assemblage would appear, apart from availability of elements, to be very dependent upon the volatile species present. Thus any two magmas not necessarily genetically related might develop similar trace element assemblages if they contain the same dominant volatile. The abundance of CO_2 in carbonatites and kimberlites is thus probably the cause of the development of the similar trace element assemblages.

Secondly, it should be noted that some of the characteristic trace elements in kimberlite, e.g. Sr, Nb, Zr are present in concentrations similar to those found in kimberlites, in certain alkali basalt occurrences quite unconnected with carbonatites, CO_2-rich systems or continental magmatism, e.g. Tristan da Cunha, Marquesas, Hawaii (Baker et al. 1964, Chao and Fleischer 1960, Nockolds and Allen, 1954).

These two points thus illustrate the difficulties inherent in considering "similar" trace element assemblages, as the assemblages may be the result of two or more processes acting independently or acting together to varying degrees.

Ba and Sr

Ba and Sr abundances are not as high as those found in carbonatites (Gold 1966) or potassic volcanics (Higazy 1954, Carmichael 1967). Ba is primarily located in phlogopite, as micaceous kimberlites are enriched in Ba relative to kimberlites (Dawson 1962). Sr is primarily concentrated in the carbonates and in perovskite. In all kimberlites so far examined it has been found that Ba/Sr ratios are greater than 1. This is in contrast to carbonatites (Gold 1966) and basalts (Nockolds and Allen 1954, 1956) where Ba/Sr ratios are less than 1. Verwoerd (1966) however considers that although Sr is more abundant than Ba in carbonatites, there is no regularity in the Sr/Ba ratio for any single occurrence or type of carbonatite in general. In granitic rocks, as a consequence of the presence of potassium feldspar, Ba/Sr ratios are greater than 1. This is of importance if kimberlites are derived by mixing carbonatite and granitic material as proposed by Dawson (1966).

Nb/Ta ratios

Although data are scant, Nb/Ta whole rock ratios appear to be low, approximately 20 (Burkov and Podporina 1965), and quite unlike those of carbonatites (10-10000, Heinrich 1966). The major Nb-bearing minerals in kimberlite are ilmenite (Deans 1964, Mannard 1962) and perovskite (Grantham and Allen 1960). Unfortunately no mineral Nb/Ta data are available although differences in Nb/Ta ratio can be expected as ilmenite is a phenocrystal mineral and perovskite is a groundmass mineral.

Th/U ratios

Th/U ratios are in general greater than one. The ratios are higher than usually found in igneous rocks, e.g. 8-9 (Ahrens et al. 1967), 25-34 (Gangadharam and Aswathanarayana 1969), 12 (Manton and Tatsumoto 1969). The average Th/U ratio in basic igneous rocks is 3.0 and in acidic rocks 4.3 (Clark et al. 1966). High Th/U ratios are found only in allanite (7-200) and monazite (50-60) (Clark et al. 1966). The high Th/U ratios of kimberlite place considerable restrictions upon mixing processes involving carbonatite and granite as proposed by Dawson (1966) and upon the degree of assimilation of granitic material by a kimberlitic magma. Addition of crustal material to either carbonatite (Th/U ratio c. 11) or kimberlite would merely lower the Th/U of the hybrid rock. If it is considered that assimilation of crustal material has played a significant role in the development of kimberlite, then the original "kimberlitic magma" must have possessed an even higher Th/U than seen in kimberlites.

Further studies must be carried out to determine the exact locations of Th and U in the minerals of kimberlite and as to whether or not small amounts of rare earth minerals are present or not. The Th/U ratio of zircon which is a common accessory mineral in kimberlite cannot account for the Th/U ratio of the whole rock as it possesses a low (0.23-0.70) Th/U ratio (Ahrens et al. 1967) and is similar to the Th/U ratio of zircons found in granitic rocks and pegmatites.

K/Rb ratios

Six K/Rb ratios determined by Gurney et al. (1966) showed little variation and all lay within the "main trend" of K/Rb ratios as defined by Shaw (1968). The average of the determinations was 246. In contrast, five K/Rb ratios determined by Gangadharam and Aswathanarayana (1969) varied from 140-602 but averaged 256. The K/Rb ratios to judge from the limited data available are not those typical of late differentiates, i.e. K/Rb<100 (Shaw 1968) as proposed by Dawson (1966) on the basis of visual estimates of Rb concentrations.

K/Cs ratios

Six K/Cs ratios determined by Gurney et al. (1966) are similar to the crustal average ranging from 4,400-7,100 (average 5,400). Gurney et al. (1966) state that their Cs determinations are semi-quantitative only, due to the erratic behaviour of kimberlite in the arc. This could explain the lack of agreement with Gangadharam and Aswathanarayana's (1969) neutron activation data which shows the K/Cs ratio of five kimberlites to range from 81.0-6198 and to average 1630. This average is extremely low and is similar to that found in eclogite nodules in kimberlite (Gurney et al. 1966).

Ga/Al ratios

Dawson (1962) has stated that the Ga/Al ratios of kimberlite are typically those of late differentiates. Values of the Ga/Al ratio ratio given by Dawson (1962) range from 1.85×10^{-4} to 4.16×10^{-4} and average 3.6×10^{-4}. The gallium concentrations are low (7 ppm) and very near the sensitivity limit of the technique (3 ppm), and thus can be regarded as approximations only of the true gallium content. Similar considerations must also be taken into account when drawing conclusions from Borisenok's (1959) data, which indicates a Ga/Al ratio of 1.0×10^{-4} for Yakutian kimberlites, a value which is very similar to that seen in other ultrabasic rocks (c. 1.1×10^{-4}, Borisenok 1959). In conclusion, it can be said that Ga/Al ratios of kimberlites are too imprecisely known to state categorically that they are typical of late differentiates.

Rare Earth Elements

Figs. 7-10 illustrate the rare earth element (REE) distribution patterns found in some African and Russian kimberlites and indicate that kimberlites are enriched in total REE relative to crustal rocks and that they are preferentially enriched in the light REE. The major REE-bearing phase in kimberlite is undoubtedly calcite (and dolomite), substantial amounts of REE also probably occur in perovskite and apatite. The REE distribution patterns are similar to those observed in many types of rocks but are complementary to those found in high temperature peridotites which are the only peridotites studied in any detail (Haskin et al. 1966). Studies of the distribution patterns of REE in the phenocrystal minerals of kimberlite such as olivine and garnet would be of interest in this connection.

Some of patterns seen in Figs. 7-10 show prominent negative europium (Eu) anomalies. Such anomalies in basaltic rocks are generally due to the removal at some stage in the rocks evolution of plagioclse or potassium feldspar, minerals which preferentially concentrate Eu. Such a mechanism cannot be invoked to explain the kimberlite Eu anomalies as feldspar plays no role in kimberlite petrology and is not a stable phase at the depths of generation of kimberlite magmas. The

Figs. 7-10. Distribution patterns of rare earth elements in kimberlites relative to chondrites and shales.

All concentrations are normalised to Yb=1. Plots are derived by dividing concentrations of individual elements in the kimberlite by the concentration of corresponding elements in chondritic meteorites (Haskin et al. 1966). The resulting ratios are plotted on a logarithmic scale against ionic radius. Kimberlite rare earth distributions are shown as dashed lines which indicate the degree of fractionation relative to the meteoritic standard (solid horizontal line). The curved solid line illustrates rare earth distributions in a composite shale (Haskin et al. 1966) which is an estimate of rare earth distributions in the crust relative to chondrites.

Fig. 7. Rare earth distributions in some African kimberlites. Data from Haskin et al. (1966).

Fig. 8. Rare earth distributions in the East and West Udachnaya pipe, a composite intrusion in Siberia. Burkov and Podporina (1966).

Fig. 9. Rare earth distributions in the Zarnitsa pipe. Burkov and Podporina (1966).

Fig. 10. Rare earth distributions in the Mir pipe. Burkov and Podporina (1966).

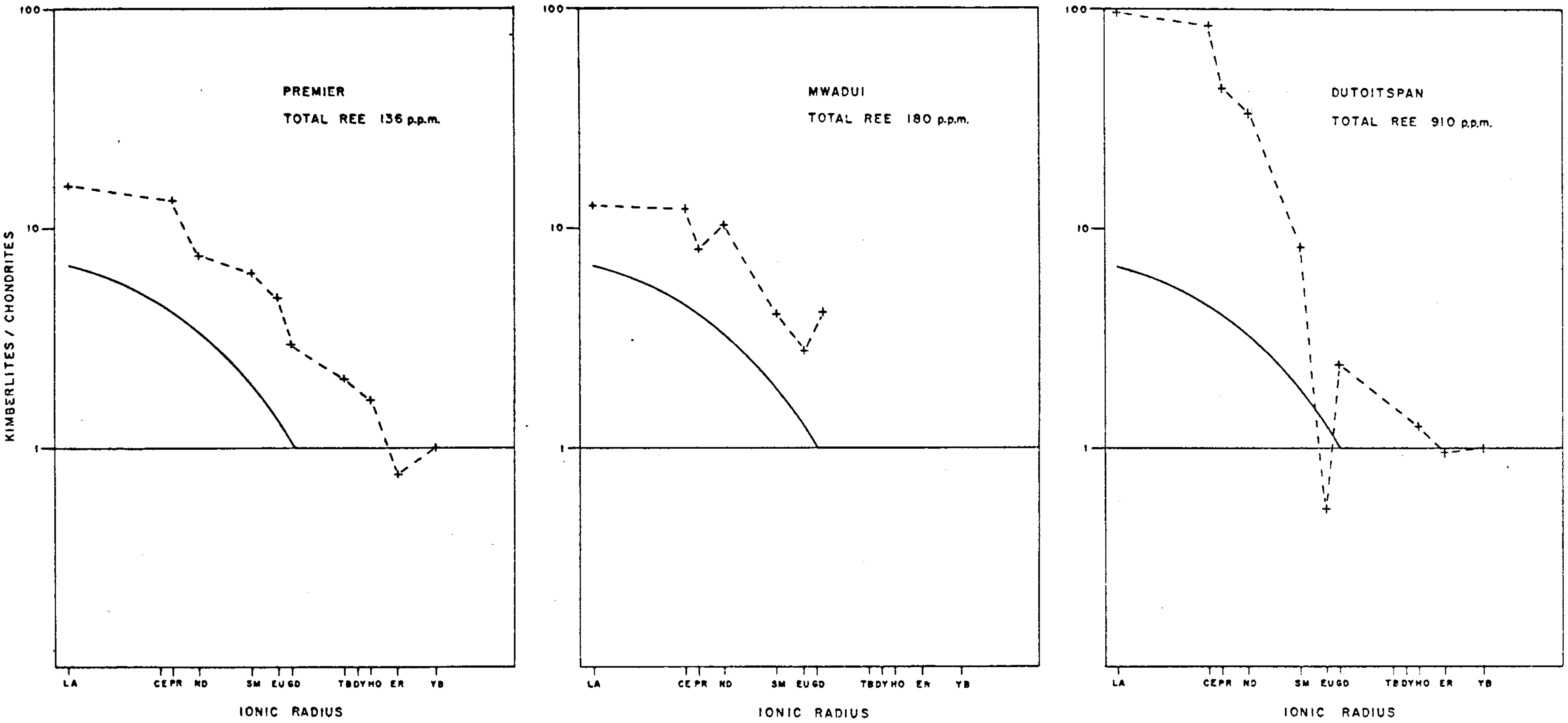


Fig. 7. Rare earth distributions in some African kimberlites.

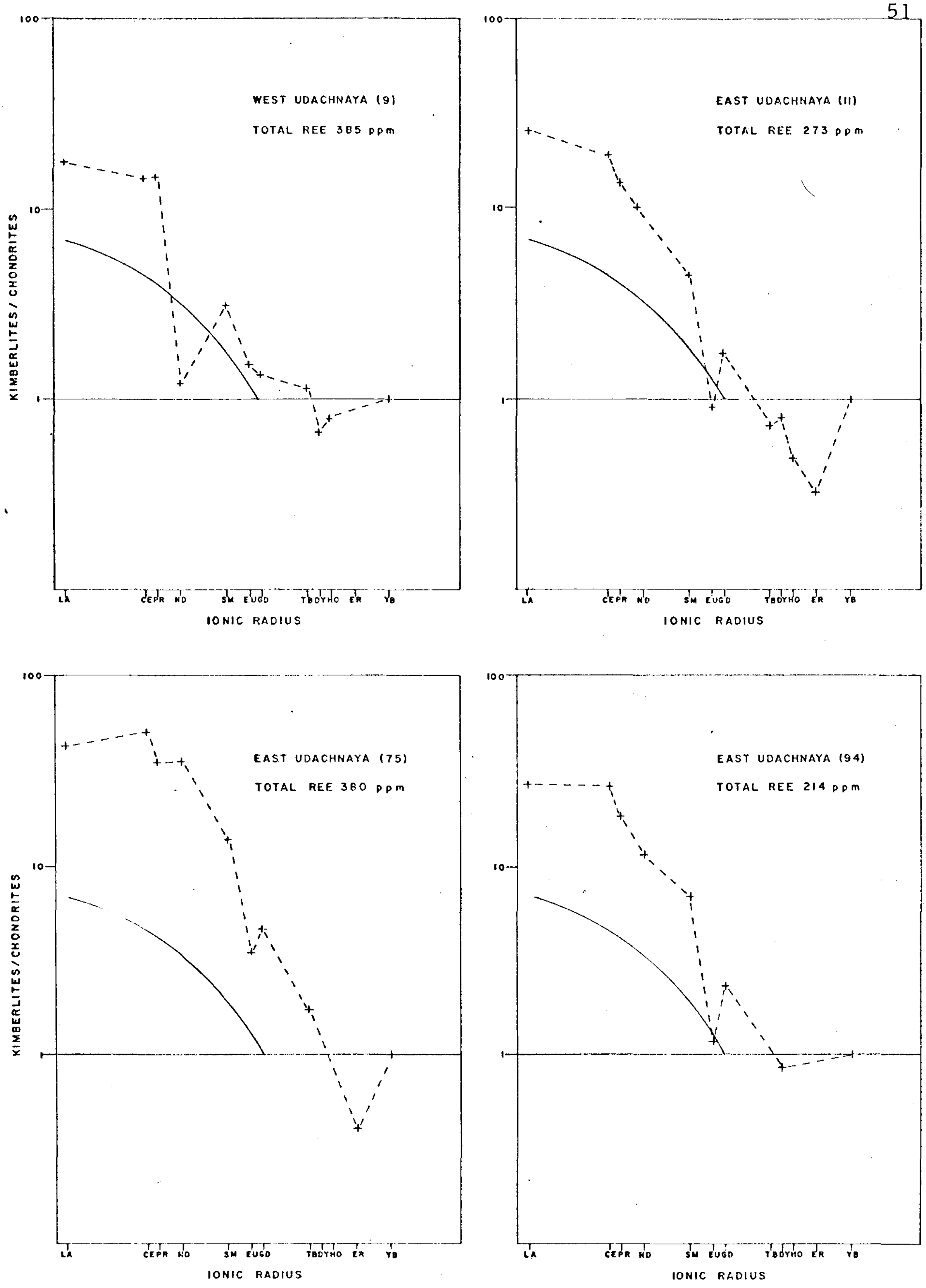


Fig. 8. Rare earth distributions in the East and West Udachnaya pipe, a composite intrusion in Siberia.

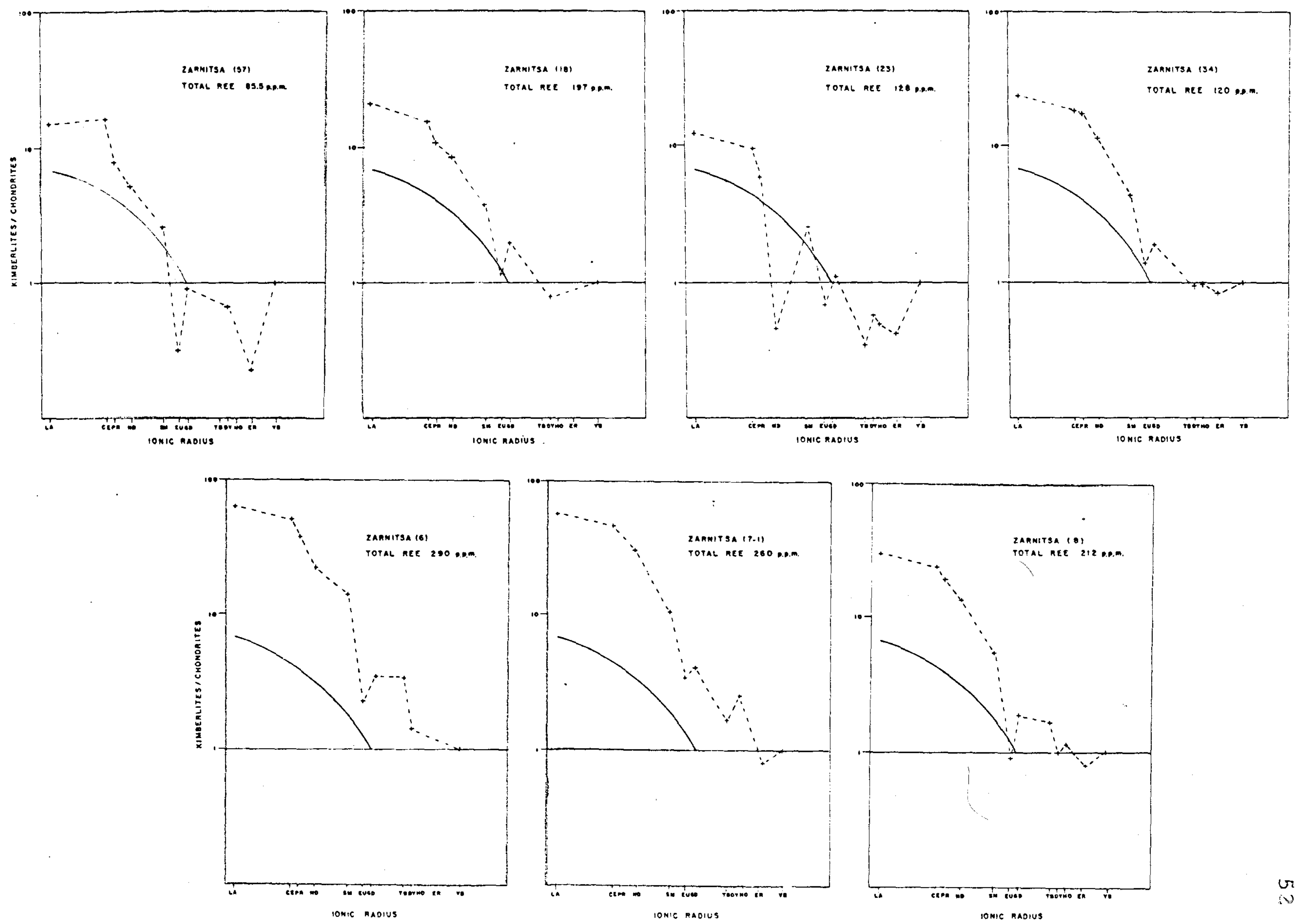


Fig. 9. Rare earth distributions in the Zarnitsa pipe.

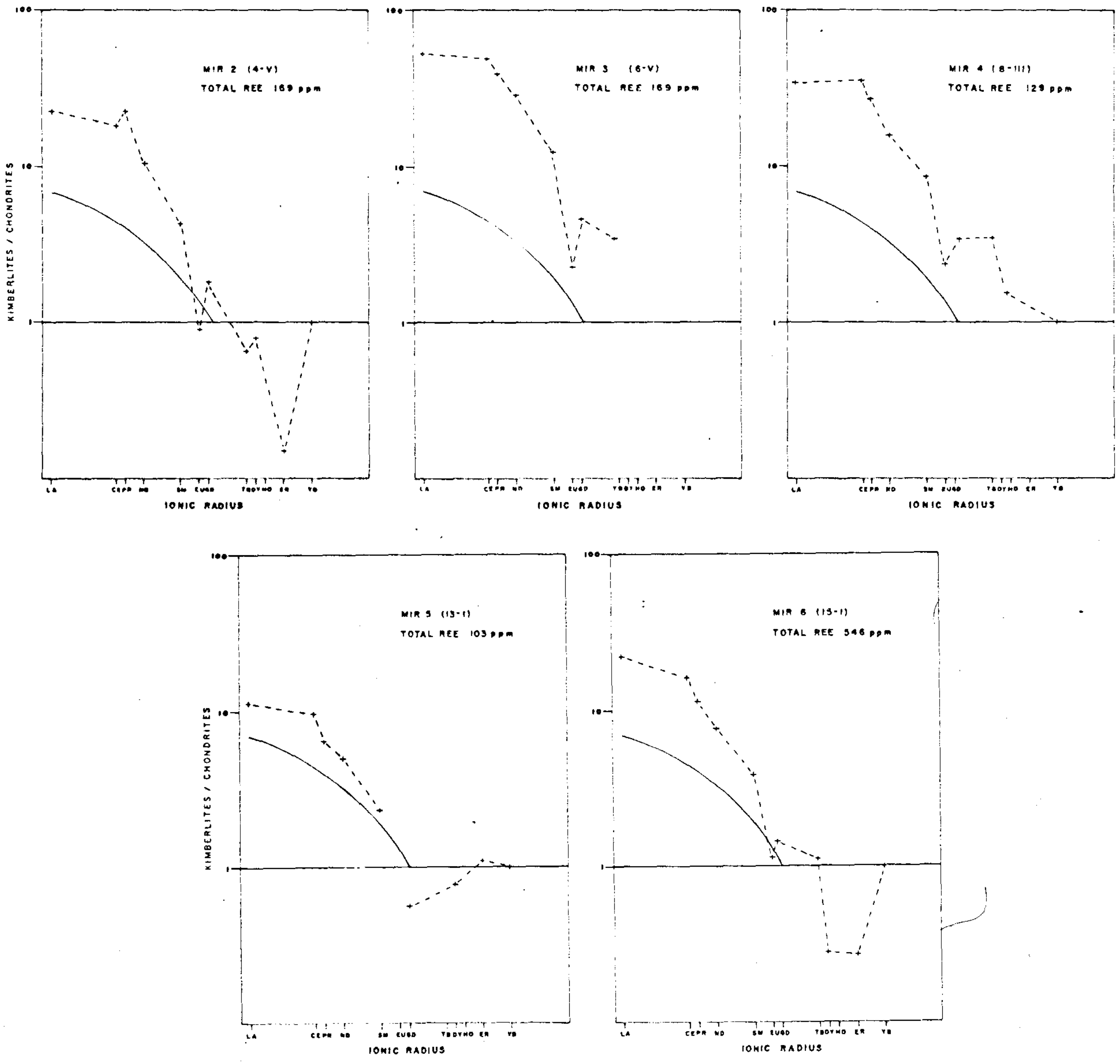


Fig. 10. Rare earth distributions in the Mir pipe.

Eu anomaly must be caused by the subtraction of some other Eu-rich mineral or be due to variations in the oxidation state of Eu. The latter possibility would seem the more likely as conditions at the site of kimberlite genesis as deduced by Kennedy and Nordlie (1968) are highly reducing and thus favourable for Eu^{+2} formation,and because no other common rock forming mineral or mineral in kimberlite is yet known to concentrate Eu in a manner analogous to the feldspars.

It should be borne in mind also that the data of Burkov and Podprina (1966) was obtained by X-ray spectrographic techniques working at the limits of sensitivity for the heavy REE, and even though the presence of Eu anomalies is supported by neutron activation data (Haskin et al. 1966) that much further work is required to definitely establish the presence of the Eu anomalies.

Boron (B)

The B content of kimberlite has been determined by Cherepanov (1967) who concluded that these rocks are anomalously enriched in B (190 ppm) compared to other ultrabasic rocks (20 ppm). The high B content is attributed to degassing of the earth's mantle at the site of kimberlite formation. Similar high B concentrations have been recorded by Burkov and Podporina (1965) but Agyei (1968) found a very low B content (4 ppm) in the Swartruggens kimberlite, a value which is not significantly different from the B content of basalt (2 ppm) as determined by Agyei (1968).

Cu, Zn, Pb and Mo abundances

Table 5 presents new data for Cu, Zn, Pb and Mo in kimberlite. The data for Cu are in agreement with the earlier data of Litinsky (1959) and Lee and Lawrence (1968) and indicate that kimberlites are slightly enriched in Cu relative to other ultramafic rocks but contain less than the average carbonatite. Gerasimovskii and Belyayev (1963) have pointed out that high copper contents are characteristic of alkaline ultramafic rocks associated with carbonatite complexes.

Only Lee and Lawrence (1968) have given semi-quantitative data for Zn in kimberlite. The average of the Zn determinations given in Table 5 is 81 ppm and falls within Lee and Lawrence's (1968) estimated range of Zn concentrations (10-100 ppm). The Zn content of kimberlite is greater than the average Zn content of ultramafic rocks.

Previous data for Pb are very varied and not in agreement with the average of 77 ppm found in the present work. All the data, however, indicate greater Pb concentrations in kimberlite than in the average ultramafic rock or carbonatites.

Table 5. Abundances of Cu, Zn, Pb, Mo and Hg in some kimberlites

No.	Sample	Cu	Zn	Pb	Mo	Hg
1	Swartruggens	50	115	100	~1	40
3	Swartruggens	50	95	120	~1	40
6	Swartruggens	40	100	80	~1	40
7	Swartruggens	30	90	90	~1	60
8	Swartruggens	30	90	70	~1	60
9	Swartruggens	35	90	80	~2	60
10	Wesselton	45	75	70	~1	30
11	Wesselton	50	75	70	~1	10
20	Premier	60	55	70	~1	50
21	Premier	40	65	70	n.d.	50
22	Premier	15	30	70	n.d.	40
23	Monastry	110	105	70	n.d.	30
24	Dutoitspan	60	85	70	n.d.	1670
25	Bultfontein	40	80	60	n.d.	70
26	Doornkloof	40	70	70	~1	60

Cu, Zn, Pb and Mo (ppm) determined by atomic absorption, Hg (ppb) by mercury vapour detection. (Analysts - Rocky Mountain Geochemical Co.)

The Mo data provide only indications of the true Mo concentration as they lie at the limits of detection of the technique (1 ppm). They do however serve to illustrate that kimberlites are not rich in Mo, an element which concentrates in the last stages of differentiation. Mo contents of carbonatites are much higher than those of kimberlite.

Mercury (Hg)

Ehman and Lovering (1967) have found that the Hg content of a South African kimberlite (200 ppb) is about ten times that of basaltic rocks and is also higher than granitic rocks (40 ppb). Ultramafic inclusions within the kimberlite were found to contain even higher Hg contents (780-1230 ppb). Hg determinations in the present work (Table 5) confirmed the relatively high concentrations of Hg, however, with the exception of the Dutoitspan sample, concentrations of Hg were much lower than those found by Ehman and Lovering (1957) ranging from 10-70 ppb and averaging 45 ppb. The abnormally high Dutoitspan value could be due to contamination with laboratory Hg which is always a significant problem in Hg analysis, but the sample was processed at the same time as the other samples and in exactly the same manner.

Very little is known of the geochemistry of Hg in rocks and no extensive determinations of Hg in ultramafic rocks have been reported. Data for two carbonatites from the Fen complex obtained by the same method as used for the kimberlites indicated negligible Hg. Russian data for the alkaline rocks of the Lovozero massif indicate Hg contents of 180-400 ppb (Aidiyan 1967) and in lamprophyres 3000-7000 ppb. (Dvornikov 1965). The accuracy of the Russian data is unknown but Aidiyan (1965) reports Hg concentrations in basaltic rocks which are about twice as great as those determined by Ehman and Lovering (1967). Allowing for this, it would appear that alkaline rocks are enriched in Hg relative to basalts, carbonatites and kimberlites.

Stable Isotope Geochemistry

Carbon

Stable isotope studies of kimberlite have largely been confined to the study of carbon. Kimberlites contain a number of carbon-bearing minerals, e.g. calcite, dolomite, graphite, diamond, moissanite and bituminous material. A summary of the results of several investigations is shown in Table 6. The data prompt the following conclusions:

The relatively heavy isotopic composition of carbon in diamond and the carbonated phases shows that these phases are not genetically related either to the carbonates of the enclosing rocks (limestones) or to the bitumens occurring in the kimberlite. The bitumens are generally regarded as being derived from the sedimentary country rock during the intrusion of the kimberlite.

The isotopic analyses of diamonds from different parts of the world show that they all have essentially the same isotopic composition. This, according to Vinogradov et al. (1965, 1967), indicates identical conditions of formation from an identical source of carbon.

The isotopic composition of carbon in the carbonate phases is very similar to that of carbonatites and their associated alkaline rocks (Deines 1967, Taylor et al. 1967, Vinogradov et al. 1967).

If diamonds form from the same source of carbon as do the carbonates, then it can be expected that if isotopic equilibrium prevails, diamonds and carbonates will have similar isotopic compoditions. This would seem to be the case to judge from the data in Table 6, but data for co-existing diamond and calcite are required before any definite conclusions can be drawn. It is suggested in Chapter 4 that diamonds form by reduction processes involving carbon dioxide, this gas is also assumed to be the source of carbon in the carbonates and hence should possess a similar isotopic composition to diamond and carbonate. Unfortunately no analyses are available of the isotopic composition of carbon in fluid inclusions in diamond but studies by Taylor et al. (1967) of the composition of carbon dioxide from springs in the Laacher See area indicate that the carbon dioxide was in approximate isotopic equilibrium with carbonatite at high temperatures.

There is also the possibility that isotopic fractionation occurs during the formation of diamond. Laboratory studies are inconclusive as Vinogradov et al. (1965) consider that isotopic fractionation does not occur during the formation of synthetic diamond from graphite, whilst Hoening (1961) finds a degree of fractionation within his experimental error and Cannon (1962) finds definite evidence of fractionation. As the formation of diamond may not be simple phase transformation and involve various gaseous components, it may be that some isotopic fractionation occurs. In accordance with the general principles of stable isotope fractionation it can be expected that the amount of fractionation occurring at high temperatures is slight. If any fractionation between diamond and co-existing phases is to be detected it should be searched for in diamonds which might have formed by metastable processes at low temperatures. Bottinga (1969) has investigated the fractionation of carbon isotopes between graphite, diamond and carbon dioxide at various temperatures. It was found that the maximum fractionation between carbon dioxide and either of the solid phases occurred at very low temperatures (100-240°C).

Table 6. Isotopic composition of carbon in diamonds, kimberlites, igneous rocks and carbonaceous chondrites

Sample	δC^{13}‰	Source
Diamonds	- 5.6 to - 8.8	1
Diamonds	- 1.9 to - 9.7	2
Carbonates in kimberlite	- 5.6 to - 7.9	1
Calcite vein in kimberlite	- 5.3	3
Moissanite in kimberlite	-25.3	1
Carbonado	-28.0	1
Graphite, ultramafic inclusion	- 7.8	1
Graphite, pyrope peridotite	- 5.9	1
Limestones and bitumens, Yakutia	- 3.0 to -25.3	1
Marine limestones	- 4.0 to + 4.0	3,7
Dixonville dyke	+12.0 to +24.8	5
Carbonatites	- 3.0 to - 7.0	1,5,6
Alkaline rocks	- 1.0 to - 7.0	5
Basalts	- 9.0 to -27.0	1,3
Types I and II carbonaceous chondrites	- 3.7 to 11.4	1,4

$$\delta C^{13} = \left(\frac{\left[{}^{13}C/{}^{12}C\right] \text{ sample}}{\left[{}^{13}C/{}^{12}C\right] \text{ standard}} - 1 \right) \times 10^{3} \text{ per mil (‰)}$$

All data are relative to the Chicago Pee Dee belemnite standard.

1. Vinogradov et al. (1965, 1967)
2. Wickmann (1956)
3. Baertschi (1957)
4. Boato (1954)
5. Deines (1967, 1968)
6. Taylor et al. (1967)
7. Craig (1953)

The graphite found in the ultramafic nodules is probably in isotopic equilibrium with the diamond and carbonates in the host kimberlite.

Vinogradov et al. (1965, 1967) have noted the similarity in isotopic composition of diamond and Types I and II carbonaceous chondrites,and have assumed that the diamond carbon was derived from carbon-rich mantle rocks formed from the meteoritic material. The assumption that the mantle is composed of material equivalent in composition to carbonaceous chondrites,is open to question. Moreover, the isotopic composition of carbon in the carbonaceous chondrites is not uniform, e.g. graphite δC^{13} in Orgeuil is -11‰ and carbonate is +60‰ (Clayton 1963, Deines 1968).

The light nature of the carbon in moissanite (SiC) and carbonado shows that they were not derived from the same sources of carbon as diamond. They may represent carbon derived from the country rocks which was introduced into the kimberlite during intrusion and which was pyrometamorphosed into its present condition.

Deines (1967, 1968) has determined the isotopic composition of carbon in carbonates from the Dixonville kimberlite dyke, Pennsylvania. Calcite inclusions in the dyke contain the heaviest terrestrial carbon known and range in δC^{13} from +12 to +24.8‰. The carbon is heaviest at the centre of the dyke and the variation is considered to be due to isotopic exchange with light carbon introduced into the dyke from the country rock during intrusion. Deines (1968) considers that the heavy carbon is derived from the mantle. The carbon is intermediate in isotopic composition between the extreme meteorite values and the values which are generally taken to be representative of primary mantle carbon, i. e. carbonatite and diamond carbon. The discovery of this heavy carbon prompts the question as to whether or not most of the carbon seen in carbonatites and kimberlites has been altered by exchange reactions with crustal rock carbon.

Oxygen

Deines (1967, 1968) found that the isotopic composition of oxygen in the Dixonville dyke ranged from δO^{18} +17 to +23‰ (relative to SMOW) and that a strong correlation with the carbon isotopic composition existed. As with the carbon, oxygen was found to be heaviest at the centre of the dyke.

Sheppard and Epstein (1968) found that phlogopite xenocrysts in kimberlite exhibited δO^{18} values ranging from +6.0 to +7.4‰ and that calcites coexisting with phlogopite from Bachelor Lake ranged in δO^{18} from +8.5 to +10.4‰.

Extensive equilibration of kimberlite with meteoritic water would not seem to have played a role in the deuteric alteration as this would be expected to have produced lower concentrations of O^{18} than are observed.

Hydrogen

D/H ratios for phlogopites reported by Sheppard and Epstein (1968) range from δD -50 to -73‰ (relative to SMOW) and are similar to the δD values reported for most other ultrabasic rocks. The Bachelor Lake phlogopite has a δD of -92‰. Sheppard and Epstein (1968) consider that this kimberlite has been affected by alteration processes but that there is no evidence for general large scale exchange with meteoritic waters.

Boron

Table 7 shows the isotopic composition of boron in kimberlites and basalts.

The phlogopite data of Sheppard and Epstein (1968) lies within the range of δO^{18} values reported for most other ultrabasic rocks, whilst the Bachelor Lake calcite is slightly enriched in O^{18} relative to these rocks and to most other common igneous rocks (δO^{18};+5.5 to +7.0‰, Taylor 1968). Deines' (1967, 1968) data are significantly different from all other δO^{18} values for terrestrial rocks and are very enriched in O^{18}. Taylor (1968) has discussed the question of O^{18} enrichment in magmas and has concluded that enrichment can be brought about by equilibrium magmatic differentiation, by assimilation of material rich in heavy O^{18}, e.g. sediments, by exchange with deuteric aqueous fluids or by exchange with adjacent metamorphic waters. Of these processes only two are likely to play any role in the development of kimberlite δO^{18} values.

Assimilation of sialic crust is a possible mechanism for increasing δO^{18} values but the amounts required are such that the kimberlite would have been destroyed. Deuteric alteration of minerals in kimberlite is typically observed and this process could have been instrumental in bringing about the observed δO^{18} values. O^{18} enrichment could also have occurred at the second boiling point of kimberlite magma when carbon dioxide and water were rapidly removed from the magma.

Table 7

	B^{11}/B^{10}	δB^{11} ‰	
Yakutian kimberlite	4.115	+28.7	Cherepanov(1967)
Picritic basalt	4.060	+15.0	"
Porphyritic basalt	3.972	- 7.0	"
Swartruggens kimberlite	4.041	+10.3	Agyei (1968)
Hawaiian basalt	4.031	+ 7.8	"

$$\delta B^{11} = \frac{B^{11}/B^{10}}{4} - 1 \times 10^{3} \text{ per mil (‰)}.$$

Cherepanov (1967) considers that kimberlites are enriched in heavy boron relative to basalts and that the enrichment is due to distillation of gases during the process of mantle degassing. Cherepanov (1967) also assumes that a δB^{11} gradient exists in the crust and mantle, and that the boron in kimberlite and basalt was derived from the same source. Concentration of B^{11} in kimberlite relative to basalt is untenable in terms of the Rayleigh fractionation model, which predicts that the lighter isotopes will be enriched in gaseous phases during fractional distillation. Some other process for the enrichment of heavy boron in kimberlite should be searched for; it may be that if Cherepanov's (1967) data is valid, the boron in kimberlite is a residual phase left behind after degassing has occurred.

The δB^{11} values of Agyei (1968) are in sharp contrast to Cherepanov's (1967) data. Agyei (1968) considers that boron does not show any significant variation in its isotopic composition in terrestrial rocks and meteorites, only sea water has been shown to possess anomalous δB^{11} values (+52 to +60‰).

Once again a discrepancy between Russian and Western data is evident. The anomaly may be due to the different processes used to prepare the samples, the Russian work utilising methyl borate distillation (Shergina and Kaminskaya 1963) and Agyei (1968) using cyclic pyrohydrolysis. Both groups claim that isotopic fractionation does not occur during the boron extractions.

Conclusion

It is concluded from the above survey that the geochemistry of kimberlite is inadequately characterised. Much further data is required to define such parameters as K/Rb, Ga/Al, Th/U ratios, rare earth distribution patterns and the presence or absence of anomalous boron and mercury concentrations. More determinations by techniques which are relatively insensitive to matrix effects, such as neutron activation and isotope dilution, are required.

The discrepancies which exist between Russian and Western work can only be resolved by the use of an interlaboratory kimberlite standard.

In the field of isotope geochemistry much further work is required on the isotopic composition of carbon and oxygen in co-existing mineral phases. Isotopic studies of boron, nitrogen, water and carbon dioxide included in diamond would be of great value in characterising the isotopic composition of the fluid from which diamond grew.

CHAPTER THREE

POSSIBLE RELATIVES OF KIMBERLITE IN TIME AND SPACE

Kimberlite Lavas

The majority of kimberlites occur as pipes and dykes, the surface manifestation of such intrusives being pyroclastic deposits of the type described by Edwards and Howkins (1966). Possible extrusive equivalents (lavas) of kimberlite have been described from two localities, Igwisi and Meimecha-Kotui, but it should be emphasized that no kimberlite lava of a definite extrusive origin is known.

Three volcanic cones comprise the Igwisi Hills in Tanzania. The lavas are vesicular and are composed of phenocrysts of fresh olivine (21%, Fo. 93) set in a groundmass of glass and its alteration products, calcite, magnetite and perovskite. Inclusions of iron oxides, phlogopite and monticellite (?) occur in the olivines. Calcite pseudomorphs after an unknown tabular mineral, considered to be phlogopite by Dunham (Sampson 1953) or portlandite (Bassett 1954) occur in some varieties. Dunham considered the rocks to be kimberlites but Sampson (1953) and Bassett (1954) were of the opinion that they were not kimberlites but were derived by the mixing of peridotite and fused limestones. Fozzard (1956) stated that the rocks were probably the surface manifestation of a kimberlite type fissure at depth.

The Meimecha-Kotui district of Siberia is composed of an extensive series of intrusive alkaline and ultrabasic rocks together with a few carbonatites and kimberlites (Makhlayev and Surina 1963, Davidson 1964, 1967a). Accompanying the intrusive rocks are a thick series of lavas and tuffs of an alkaline ultrabasic rock termed meimechite. This rock consists of magnesian olivine, serpentine and phlogopite set in a black glassy groundmass together with perovskite and amygdales filled with calcite and serpentine (Moore and Sheinman 1946). Krutoyarski (1958) considers that the meimechite resembles the Siberian micaceous kimberlites.

Table 8 shows that the Igwisis lavas bear little chemical relation to kimberlite being very low in silica and high in alumina. Even the most silica deficient calcareous kimberlites contain far less alumina than the Igwisi lavas. The Igwisi lavas are, in addition, sodic and poor in alkalies. Table 8 also shows that the meimechite, apart from being sodic, is very similar in composition to kimberlite. Cherepanov (1967) has found that boron is highly enriched in kimberlite and meimechite (90 ppm) relative to other ultrabasic rocks and

Table 8. Composition of kimberlite, meimechite and Igwisi Lavas

	1	2	3	4	5	6
SiO_2	27.81	88.98	19.64	18.0	13.3	36.76
TiO_2	1.63	1.36	1.72	3.65	2.03	1.24
Al_2O_3	3.40	4.34	1.27	11.7	8.98	2.27
Cr_2O_3	0.13	-	-	-	-	0.31
Fe_2O_3	5.40	5.73	9.0	7.4	2.94	7.35
FeO	2.82	4.61	2.70	2.2	2.15	5.37
MnO	0.12	0.07	0.47	0.22	0.18	0.15
NiO	0.14	-	-	-	-	0.16
MgO	25.53	34.83	22.17	23.2	13.78	33.24
CaO	12.21	7.57	20.16	16.7	29.63	4.10
Na_2O	0.33	0.38	tr	-	0.16	0.69
K_2O	0.66	1.17	tr	-	0.03	0.40
P_2O_5	0.50	0.97	1.14	-	-	0.19
H_2O^+	-		4.64	9.0	-	7.20
CO_2	-		15.84	8.6	17.1	0.71

1. Yakutian kimberlites. 339 analyses from 107 intrusions. Bobrievich et al. (1964).
2. Average kimberlite (Nockolds 1954).
3. "Carbonatitic" kimberlite (Williams 1932).
4. Igwisi Lava DNS 335 (Sampson 1953).
5. Igwisi Lava DNS 341 (Sampson 1953).
6. Meimechite. 10 analyses (Davidson 1967).

basalts (e.g. 1-5 ppm, Vinogradov 1962). Agyei (1968), however, indicates only a slight enrichment of boron in the Swartruggens kimberlite (4 ppm) relative to basalt (2 ppm).

The composition of the Igwisi rocks indicates that they are in all probability not extrusive kimberlites. Pyrope, chrome diopside, magnesian ilmenite and ultrabasic xenoliths have not been found either in the Igwisis lavas or meimechite. Davidson (1967a) considers that meimechite lavas and tuffs lacking such high pressure minerals are primary unadulterated kimberlite material,which reached the surface as a magma of direct mantle origin or was formed by the refusion in depth of pre-existing kimberlite. Such conclusions are based upon the belief that garnets, ultrabasic xenoliths and even diamonds are either crustal xenoliths or are minerals which crystallised in a low pressure environment. Such beliefs are contrary with experimental studies of mineral stability fields and with direct observation of magmas such as the Hawaiian lavas,which are known to have commenced crystallisation at high levels in the mantle and in the lower crust. If a meimechite not containing the high pressure minerals were intruded into a crustal environment and underwent a period of crystallisation, then crystallisation of minerals such as olivine, pyroxene and even feldspar (which can be expected to be a liquidus phase at shallow depths) would modify the meimechite composition by fractional crystallisation and gravitative differentiation to bulk compositions far removed from that of kimberlite. At no time would pyrope garnet, garnet peridotite or eclogite nodules form. Hence, crystallisation of a kimberlite from a meimechite at shallow depths cannot account for the mineralogy of kimberlite. Refusion at depth of pre-existing kimberlite to give a liquid of kimberlitic composition (i.e. meimechite) is very unlikely as in toto melting would be required. Melting experiments, at one atmosphere pressure, have demonstrated that meimechite melts over a wider range of temperature (975-1425°C) than does kimberlite (1175-1475°C) (Bazilevskii and Ukhanov 1967), thus meimechite is unlikely to be a melting product of kimberlite.

The present writer feels that the above evidence and the lack of high pressure phases in meimechite, even though the rock is compositionally similar to kimberlite, is decisive evidence against the rock being a kimberlite lava. Much further work is required to elucidate the relation, if any, between meimechite and kimberlite. The scarcity of meimechite in other kimberlite provinces indicates that its development is possibly purely local and that it represents merely an extreme facies of the Maimecha-Kotui activity.

Relation to melilitites (melilite basalts)

It is often ascerted in petrological literature that kimberlites are closely related to and possibly derived from melilitites. This asςertion is founded upon remarkably little geological evidence. The basis of the "melilitite hypothesis" lies in the supposed former presence of melilite in some kimberlites and upon the occurrence in South Africa of pipes of melilitite and nepheline-melilitite. Melilite has been shown in Chapter One to be of little importance in kimberlite petrography, which should not be the case if there were a close relation to melilitites. The influence of Shand (1934) and his theory of non-magmetic carbonate have also been mentioned.

In South Africa there exists an area of melilitite activity stretching from Heidelberg (Cape Province) past Sutherland to the western edge of the Bushmanland Plateau (Truter 1949). A few kimberlites can be found within this region but the main body of kimberlite activity lies far to the north-east, as illustrated by the maps of Verwoerd (1966), Bardet (1964) and Wagner (1914), where melilitite is unknown. The volume of kimberlite in the South African province undoubtedly exceeds that of melilitite. Other kimberlite provinces either lack melilitites altogether, e.g. Tanzania, or contain only sporadic occurrences, e.g. Siberia.

The relation of kimberlite to melilitite was largely advanced by Taljaard (1936), a student of S. J Shand, who presented the following evidence in an attempt to support his theory:

1. Reuning (1932) mentions the presence of kimberlite, though in a transported state in an area of Bushmanland where many occurrences of nepheline-melilitite are found.
2. At Kopieskraal, West Bushmanland, there are found on the plains boulders of melilitite, tuffaceous surface limestone, milky chert and "boulders of a rock locally called kimberlite" (Taljaard 1936, p. 300).
3. At Sutherland the same "kimberlitic" material as that found with the Kopieskraal melilitite is present (Taljaard 1936, p. 312).
4. In thin sections of the Kopieskraal and Sutherland "kimberlite" Taljaard (1936, p. 314) saw only "a melilite basalt in an advanced stage of alteration".
5. Calculations are presented to derive a rock of kimberlite composition from a melilitite by hydrothermal alteration.

In no case does Taljaard (1936) describe an intrusion containing both melilitite and kimberlite. Taljaard's (1936) evidence for the association of kimberlite and melilitite is built solely upon the presence of loose boulders of rock, a rock which he himself terms altered melilite basalt. The field evidence is thus insufficient to allow one to state that kimberlites are hydrothermally altered melilitite.

Mineralogically and texturally kimberlite and melilitite are very different, moreover the melilitites do not contain high pressure minerals or ultrabasic xenoliths and frequently contain nepheline, a mineral never found in kimberlites. Morphological similarities of intrusions, e. g. occurrence as pipes,does not imply a genetic relation nor does the fact that melilitites and kimberlites belong to the same cycle of magmatic activity (Staritsky 1963), as melilitites can develop in areas devoid of kimberlite activity, e. g. Eiffel, Swabia, Hawaii.

Of great importance in connection with the "melilitite hypothesis" is the occurrence of two intrusions where a close geological relation between melilitite and kimberlite appears to exist.

At Mukrob, in South West Africa, there occurs a dyke containing phenocrysts of olivine and a lath shaped mineral (? melilite now replaced by calcite set in a calcitic matrix. Texturally the rock is similar to olivine melilitites described from Swabia and South Africa (Frankel 1956). The rock contains magnesian ilmenite and a number of ultrabasic xenoliths, e. g. eclogite garnet-ilmenite rock and enstatite peridotite. Frankel (1956) considers "that this rock represents a portion of the magma of ultrabasic character which gives rise to kimberlite".

From Siberia, Ukhanov (1963) has described a kimberlite breccia pipe, Bargydamalakh, which contains a core of olivine-monticellite-melilitite. Ukhanov (1963) considers that the chemistry and petrology of the two rocks indicates a direct genetic connection and that the kimberlites of the Anabar region were originally melilite-bearing rocks. Ukhanov (1963) does not extend this conclusion to all varieties of Yakutian kimberlite.

These occurrences lend some credence to the "melilitite hypothesis" but do not provide proof, as they are not typical of either kimberlite or melilitite provinces.

Von Eckermann's (1961) proposal that the Alnö "kimberlites" are derived from melilitites is invalid as a general explanation for true kimberlites, as it was shown in Chapter I that the "kimberlites" found at Alnö are in reality lamprophyres (alnöites).

In conclusion, the present writer considers that there is as yet insufficient geological evidence to support any theory postulating a close genetic relationship between melilitites and kimberlites.

Kimberlites and carbonatites

It has been proposed that kimberlites are genetically related to carbonatites in two possible ways, either carbonatite is an extreme differentiate of kimberlite (Saether 1957, Garson 1962, 1965, King and

Sutherland 1960) or kimberlite is the hybrid reaction product of the assimilation of crustal material in a carbonatite magma (Von Eckermann 1961, Dawson 1966, 1967). In either case, the proponents of the hypothesis rely heavily upon the presence of supposed kimberlites within alkaline rock-carbonatite complexes.

It can also be said that kimberlite and carbonatite may represent different fractions of a magma of less extreme composition, which differentiates within the mantle. This type of genetic relationship is not considered in the discussion below as the adherents of the kimberlite-carbonatite hypothesis do not define genetic relations in this wider and possibly more correct sense, but in the sense that either kimberlite or carbonatite are very closely related either one being the immediate parent of the other with differentiation taking place in a crustal environment.

The close genetic links between kimberlite and carbonatite have been proposed largely on the basis of the following evidence:

1. Kimberlites are closely associated in time and space with carbonatites or with rock types found in carbonatite complexes (Davidson 1964, Dawson 1966).
2. A complete chemical gradation is said to exist between kimberlite and carbonatite (Dawson 1966).

3. Kimberlites and carbonatites are similar geochemically being enriched in Nb, Ba, Sr, Zr, REE, etc.
4. Kimberlites are found within some carbonatite complexes, e.g. Alnö (Von Eckermann 1961, 1967), Fen (Saether 1957), Ngualla (James 1958), Tundulu (Garson 1965).
5. Kimberlites are rich in calcite and dolomite and experimental studies have shown these minerals need not be alteration products (Franz 1965, Wyllie 1966). Thus, the calcite in kimberlite is thought to be a magmatic calcite and to be similar to the carbonatite calcite.
6. De Sousa Machado (1958) has shown that the carbonatite activity along the Lucapa graben in Angola is replaced to the north-east by kimberlite activity of the same age of Bakwanga (Congo).
7. Late stage carbonate dykes cut the Premier kimberlite (Daly 1925).
8. Dawson (1964) has reported carbonatite tuff cones in northern Tanzania which contain xenoliths of lherzolite, harzburgite and garnet-mica-peridotite. The garnet-mica-peridotite xenoliths contain chrome diopside and pyrope. The xenolith suite is identical to that found within kimberlites.

9. Allen and Deans (1965) have described alnöite and ankaratrite from the Soloman Islands containing ultrabasic inclusions, pyrope, chrome diopside and magnesian ilmenite.

10. Moissanite (SiC) has been found to occur rarely in both kimberlite and carbonatite (Davidson 1964).

Examining the evidence in greater detail, it can be seen that the association of kimberlite and carbonatite is in actuality not as intimate as supposed, and that the two types of activity are tectonically and geographically (30-60 km.) separated (Bardet 1964, James 1965, Verwoerd 1966). Generally kimberlites are confined to the uplifted centres of continental platforms and are often related to large scale structural features, e.g. deep fracture zones, disjunctive zones, lineaments, etc., (Arsenyev 1961, Gonshakova et al. 1964, Lebedev 1964, Crocket and Mason 1968). In contrast, carbonatites and the associated alkaline rocks occur in the peripheral parts of the shield areas or are closely related to large scale rift structures (James 1965, Ginzburg 1962, Heinrich 1966). The occurrence of kimberlite at the north-eastern end of the Lucapa graben is anomalous and according to Dawson (1964) represents a case of a kimberlite intruded into a graben which has resulted from the excessive dilation of an upwarped area. No decisive evidence can be found which indicates a genetic relation to the Angolan carbonatites, a similar age does not imply a genetic relation and it seems that the two types of activity have merely exploited the same zones of crustal weakness.

Whilst kimberlite and carbonatite are both manifestations of continental magmatic activity and are often a part of the same magmatic cycle (Staritsky 1963, Bardet 1964), it should be realised that many other types of magmatic are contemporaneous, the most important and abundant of these being basaltic.

A variation diagram has been presented by Dawson (1966, Fig. 1, p. 2) as evidence for the complete chemical gradation between kimberlite and carbonatite. Trends deduced by plotting rocks on such diagrams are artificial, because most rock types can be characterised by the ten oxides employed by Dawson (1966) as co-ordinates and as a consequence of this a complete chemical gradation can be shown to exist between any given rock types if enough selectivity is employed in the choice of analyses. A diagram of this type demonstrates true chemical gradations only for a consanguinious series of rocks. The analyses of South African kimberlites and Swedish carbonatites and alnöites plotted by Dawson (1966) do not represent such a consanguinious series and hence do not demonstrate a complete chemical gradation between kimberlites and carbonatites, which has been produced by differentiation processes.

The peculiar geochemistry of carbonatites and kimberlites is shared by many other rock types, e.g. katungites, wolgidites, jumillites, and nepheline syenites all of which do not show any obvious geological relation to occurrences of kimberlite. The similar geochemistry does not imply a genetic connection unless all the rocks of such geochemistry are genetically related. The question of comparing rocks of similar geochemistry has been discussed in Chapter 2 and it has been concluded that in all likelihood the geochemistry is merely a reflection of specific physico-chemical processes common to all these magmas by virtue of their volatile contents.

The occurrence of "kimberlites" in certain alkaline complexes has been discussed in Chapter 1 and these rocks have been shown in reality to be lamprophyres. They are always minor, late stage intrusions and are of insufficient volume to be the parent of the large masses of ijolite, nepheline syenite and carbonatite found within the same complex. Verwoerd (1966) considers that these minor lamprophyres can be ascribed to reaction between alkaline rest liquid and already crystallised mafic minerals or basalt and to the reaction of liquid basalt with solid alkaline material. Verwoerd (1966) also discounts the possibility that carbonatites are the ultimate differentiation products of kimberlite magmas.

The experimental data of Franz (1965) and Wyllie (1966) is of the utmost importance in understanding the evolution of kimberlites but it does not necessarily demonstrate a connection with carbonatites (senso stricto). The importance lies in the fact that it demonstrates that the calcite found in kimberlite can be of primary origin, and that a carbonate-rich fluid phase might develop from a carbonated ultrabasic magma by fractional crystallisation (at high pressure or under the influence of alkalies) or by liquid immiscibility. Roedder (1965) has demonstrated that fluid inclusions in ultramafic and mafic rocks contain abundant carbon dioxide of possible juvenile origin. Heinrich (1966, p. 316) has interpreted Roedder's (1965) data to imply that "carbonatitic alkaline complexes are not unique merely because of the presence in them of juvenile carbon dioxide and carbonate minerals, but are merely unique because they represent the end product of a special set of environmental circumstances that have combined successfully to produce local extraordinary concentrations of carbon dioxide and its mineral derivatives". It is possible that such concentration processes are not confined to alkaline carbonatitic complexes alone but that they occasionally occur in kimberlites, the calcareous kimberlites being the result of such processes and the ultimate stage being the separation of carbonate dykes and lenses as seen at the Premier pipe. These dykes are not true carbonatites of the type found in the alkaline complexes but represent the complete replacement of pre-existing kimberlite as lens shaped bodies by a carbonate-rich fluid (Wagner 1914, Daly 1925, Verwoerd 1966).

The Tanzanian tuff cones and the Soloman Islands rocks might also be manifestations of such differentiation processes. The occurrence of late stage carbonate dykes and calcite-rich tuffs does not, however, seem to be typical of kimberlites, in contrast to alkaline complexes, and it must be concluded that extensive differentiation is not typical of kimberlites presumably because of the very different conditions of intrusion. If differentiation of kimberlites to carbonate-rich phases can be definitely proved, then there will exist a case for recognising at least two types of carbonatite, those derived by fractionation of kimberlite and those derived by the fractionation of some other magma and found associated with alkaline complexes. That diverse carbonated magmas can differentiate to carbonate-rich phases is supported by the experimental studies of Koster Van Gross and Piwinskii (1968) who have found that a miscibility gap exists between silicate melts, of basaltic, ijolitic and pantelleritic composition, and carbonate-rich melts.

Basalts and kimberlites

A characteristic feature of kimberlite provinces is their constant association with rocks of basaltic composition, e.g. the Karroo dolerites and the Stormberg basalts of southern Africa (Du Toit 1954, Dawson 1962) and the plateau basalts (trap rocks) of Siberia (Lebedev 1964, Odintsov 1959). The constancy of the association on a world-wide scale has been noted by Wilson (1948) and has been further substantiated by examples from Angola (De Sousa Machado 1958), Sudan (Marvier 1956), Bakwanga (Meyer de Stadelhofen 1961), Tanzania (Mannard 1962) and Lesotho (Dawson 1962). In all cases the basalts were extruded prior to the intrusion of the kimberlites. Insufficient radiometric ages are available to ascertain the time lapse between the two periods of activity or to determine whether or not any of the periods overlapped (this is possible in Siberia where several episodes of basalt extrusion have occurred). The constant spatial association and temporal sequence is considered by some geologists to be evidence of a genetic relation between basaltic magma and kimberlites, e.g. Leontiev and Kadensky (1957), Nalivkin (1960), Marvier (1958), Meyer de Stadelhofen (1961), Verwoerd (1966) and Verschure (1966). Other geologists are, however, not convinced of the genetic association, e.g. Pavlov and Chuprynina (1960) and Lebedev (1964).

Whilst arguments for and against the association are somewhat tenuous, being based almost entirely on the spatial and temporal association, it should be noted that a stronger case might exist for the association of kimberlite and basalt, than for kimberlite and carbonatite, principally because basalt is extremely abundant and has the status of a primary magma. Basaltic magma has its source in the mantle and it is possible that kimberlite also originates in the mantle. In such a case some genetic connection may be advanced in the sense that if kimberlite and basalt are abstracted from the same source rocks, they may represent different fractions of that rock, i.e. kimberlite might be the result of a slight degree of partial melting whilst basalt may represent a greater degree.

Potassic rocks

The recent discovery of a diamond-bearing leucite lamproite (fitzroyite) near Seguela, Ivory Coast (Bardet 1966, Dawson 1966) is of great importance and prompts the question as to whether or not kimberlites are the only primary source of terrestrial diamond. In this connection the conclusions of Wade and Prider (1940) concerning the origin of the potassic rocks of West Kimberley, Australia, are of some significance. Wade and Prider (1940) consider that wolgidite (a leumafite lava of similar chemical composition to kimberlite) is derived by the subtraction of olivine from a kimberlitic magma. Further fractionation of wolgidite produces the more siliceous differentiates fitzroyite and cedricite. If this hypothesis is correct, then any diamond contained in the original kimberlite might be carried through the differentiation process and into the late stage differentiates and would not imply the need for a second primary source of diamonds. Such a differentiation sequence is not as yet proven and may be too simple as the production of potassic lavas may involve the incongruent melting of phlogopite to produce leucite-bearing liquids. However, it is significant that potassic micaceous kimberlites appear to be closely associated with the Seguela, a fitzroyite (Bardet 1966). The preservation and occurrence of diamond is discussed in Chapter 4.

The exact relationship of kimberlites in the U.S.A. described by Watson (1967), Hearn (1968) and Miser and Ross (1922) to the extensive series of leucite-bearing rocks of Montana, Arizona and Wyoming, and to such leucite-bearing lavas as madupite (Carmichael 1967) and jumillite (Borley 1967), cannot as yet be elucidated. In general the leucite-bearing lavas, whilst possessing some mineralogical and chemical similarities to kimberlite, tend to be more siliceous and in some cases contain sanidine. A differentiation relation to kimberlite as proposed by Wade and Prider (1940) and Carmichael (1967) may be possible but as yet any conclusions are merely conjectoral.

Verwoerd (1966) has considered that the Premier kimberlite pipe is a part of the alkaline activity (syenite, foyaite, trachyte and trachyandesite) found at the Roodeplaat volcano just to the north-east. The volcano is the same age (Precambrian) as the kimberlite pipe. Further study is required to establish the validity or otherwise of this hypothesis, it may well be that the association is merely geographical and devoid of genetic significance.

CHAPTER FOUR

THE GENESIS OF DIAMOND DEPOSITS-PETROLOGICAL AND EXPERIMENTAL STUDIES OF KIMBERLITE

Before discussing some of the theories of petrogenesis of kimberlite it is necessary to acquire some knowledge of the physico-chemical conditions prevailing at the site of kimberlite genesis and in the kimberlite magma. Experimental work on synthetic minerals provides an insight into such problems and presents some idea of the possible paths of crystallisation of kimberlite magmas. The following discussion concentrates to a large extent on diamond for two reasons. Firstly, diamond plays a key role in delineating supposed temperature and pressure relations at the site of kimberlite genesis in many petrogenetic theories. Secondly, because of its value as a gem and industrial mineral, a large amount of data concerning its formation,structure and properties has accumulated which is of use in geological problems. Diamond is, however, a minor mineral in kimberlite, in fact few pipes contain diamond and the richest contain only one part diamond in twenty million parts silicate (Tolansky 1962).

Trace elements in diamond

Not many elements are capable of substituting for carbon at lattice sites within diamond, however the lattice is a relatively open one and provides ample space for the interstitial incorporation of trace elements. Investigations by emission spectrography and neutron activation analysis have revealed that diamonds can contain the following elements - B, Na, Mg, Al, Si, P, Ca, Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Sr, Ag, In, Sn, Sb, Ba, La, Sm, Hf, W, Ir, Au, Pb, and that all diamonds contain Mg, Al, Si, Ca and Ti (Chesley 1942, Raal 1957, Freedman 1952, Straumanis and Aka 1951, Bunting and Van Valkenburg 1958, Lightowlers 1967). Some of the trace elements are undoubtedly due to the presence of inclusions of silicates but others have been found to be zonally distributed (La, Cu, Mn, Na; Kodochigov et al. 1967) or to be responsible for the colour of diamond (Mn). The trace element assemblage is very heterogeneous, no one geochemically or physically similar group is definitely concentrated or excluded - a feature typical of interstitial trace element assemblages. The apparent discrimination against the rare earths apart from La and Sm is unusual in view of the group's overall geochemical similarity. The presence of boron is interesting with regard to the high concentration of boron reputed to occur in some kimberlites (Cherepanov 1967) and because of the ease with which boron has experimentally been found to diffuse into diamond (Drake-Bell and Leivo 1958).

Gases in diamond

Diamond coat is a concentrically layered structure which occasionally surrounds the clear central core of diamond. Chrenko et al. (1967) using infra-red spectrometry have established the presence of varying amounts of H_20 and $C0_2$ in the coat. The change from clear core to coat indicates abrupt changes in the conditions of growth and Chrenko et al. (1967) consider that $C0_2$ and H_20 are not initially incorporated into the core because of the PTX conditions prevailing and that the concentric rings are due to either changing pressure and temperature, or to changing degrees of supersaturation in the magma. Grantham and Allen (1960) have described coated diamond overgrown by a new layer of clear diamond associated with diamonds which are not coated. The regrowth of clear diamond is not considered to support any theory that the coated stones may have started life at depths as clear stones and then grown their coats during ascent in the pipe where crystallisation conditions were different. Rozhkov and Abrashev (1965) have found carbonate crusts surrounding some Yakutian diamonds. Chrenko et al. (1967) consider that diamond coats grew from a phase rich in carbon rather than from a dilute solution in the magma.

The presence of nitrogen in diamond as discrete "platelets" is a now well established feature of diamonds and even forms the basis for a classification of diamond (Kaiser and Bond 1959, Evans and Phaal

1962). Concentric shells in diamond have been found to have varying nitrogen contents indicating that during growth abrupt changes in the composition of the melt from which they grew occurred (Frank 1967). The nitrogen is assumed to have entered the diamond lattice in solid solution and then at lower temperatures to have aggregated into the platelets by solid state diffusion.

Crystalline inclusions

Diamond contain abundant crystalline inclusions which provide an insight into the mineralogy of the regions of diamond growth. Most of the inclusions are monomineralic (Meyer and Boyd 1969) and are subhedral to euhedral indicating growth in a fluid phase. The inclusions are under high pressure within the diamond as evidenced by the strain birefringence patterns around them and by the tendency of diamonds to fracture around the inclusions (Lonsdale and Milledge 1965). Meyer & Boyd (1969) have shown that the cell size of garnet enclosed within diamond is different to that found for the same mineral when freed from diamond. The preservation of inclusions under high pressure is considered to indicate that diamond originally grew under high pressure and did not subsequently undergo very much expansion during re-equilibration at lower pressures. The silicate inclusions were prevented from expansion by the diamond which acts as a pressure chamber. The relative abundance of the inclusions is similar to that seen in garnet peridotite nodules and the minerals bear a close resemblance in composition to those of garnet peridotite and to the primary minerals of kimberlite. A major difference is that Cr contents of the inclusions are very high, in fact the Cr content of garnet and chromite are the highest ever found for those minerals (Meyer & Boyd 1969, 1968, Meyer 1968). The principal inclusions found in diamond are olivine, pyrope-almandine, enstatite, diopside and chromite. Other minerals rarely found as inclusions are coesite biotite, (?) muscovite (Meyer 1967), rutile (Dawson 1968), pentlandite (Sharp 1966), magnesian ilmenite (Grantham and Allen 1960) and diamond (Williams 1932). Pyrrhotite has been found to be a common inclusion in South African diamond (Sharp 1966) which implies that there existed a high partial pressure of $S0_2$ or S_2 within the fluid from which diamonds form.

The occurrence of coesite enables an upper limit to be placed on the growth conditions of some diamonds. Fig. 12 shows the quartz-coesite univariant curve to intersect the estimated Precambrian shield geotherm in the vicinity of 30 kbs., pressure at $1000^{\circ}C$. The occurrence of this pure $Si0_2$ phase in such an ultrabasic rock is important and difficult to explain in view of the well known incompatability of magnesian olivine and silica at low pressures and the supposed derivation of kimberlite from an undersaturated picritic magma (O'Hara and Yoder 1967).

The chromites described by Meyer & Boyd (1968) show extremes of composition and indicate diamond formation over a very wide range of conditions. In addition, spinel is not considered to be a mantle mineral phase above about 25 kb. pressure (Fig. 12).

Diamond stability and morphology

Fig. 11 shows the phase diagram for carbon and indicates the regions in which diamond synthesis has been achieved. The univariant curve representing the graphite-diamond phase transition has been accurately determined by theoretical and experimental studies (Bundy et al. 1961) and has been used to place limits upon the formation of natural diamond and the depths of generation of kimberlite magma. Fig. 12 shows that the intersection of the phase transformation curve with the estimated Precambrian shield geotherm takes place at about 1200°C and 45 kbs. pressure, implying that diamonds are formed at depths in the mantle of below 150 km.

Giardini and Tydings (1962) have emphasized that caution must be used in the application of the graphite-diamond curve to natural systems for the following reasons:

1. Diamond is a trace component in kimberlite in contrast to the experimental studies, in which graphite is the only major phase.
2. Possible catalysts in nature are not present in the forms used in the synthetic processes.
3. The high shock pressures needed in some syntheses are unlikely to be realised in nature.
4. The time factor is ignored, diamond synthesis in the laboratory being a virtually instantaneous process.

An additional, and to the writer's mind, more pertinent factor is that it is not certain that graphite plays any role in the formation of diamond in kimberlites. Graphite is present in some garnet peridotites, eclogites and kimberlites (Williams 1932) but diamond has never been found to contain inclusions of graphite as it might be expected to do if formed from graphite. Graphite when found in association with diamond is solely as a coat upon the surface of diamond and has been produced by the breakdown of diamond. Diamond only occurs in kimberlite and rarely in eclogite and has never yet been found in garnet peridotite (Davidson 1967b). Facts which indicate that conditions for diamond growth are only found in fluid phases are the presence of H_2O and CO_2 in diamond and the occurrence of CO_2 as an abundant constituent of fluid inclusions in kimberlitic olivines. Porphyroblastic growth of diamond in a solid (garnet peridotite) can be discounted on the evidence of the euhedral inclusions found in diamond. These inclusions are monomineralic and present some analogies with phenocrysts in magmas later enclosed poikiloblastically by other minerals. If porphyroblastic growth had occurred, inclusions of aggregates of anhedral crystals would be common.

The fluid in which diamonds grow is undoubtedly a silicate melt saturated with "gases" (at high pressures a true vapour phase will probably not be present). The composition of the fluid phase ~~in~~ in association with the silicate melt is very important. French (1966) has investigated the system C-H-O at various temperatures up to pressures of 10 kb. and has found that the composition of the fluid phase in equilibrium with graphite or various silicate-oxide buffers varies to a great extent with temperature and pressure. The dominant fluid phases are CO, CO_2, H_2O and H_2. At low pressures methane (CH_4) also becomes an important phase. The results unfortunately cannot be extended to higher pressures as the buffer assemblages are unlike kimberlite and not stable at high pressures in the mantle, and because the increasing non-ideality of gases within the postulated regions of diamond stability prevents accurate delineation of fugacities. The

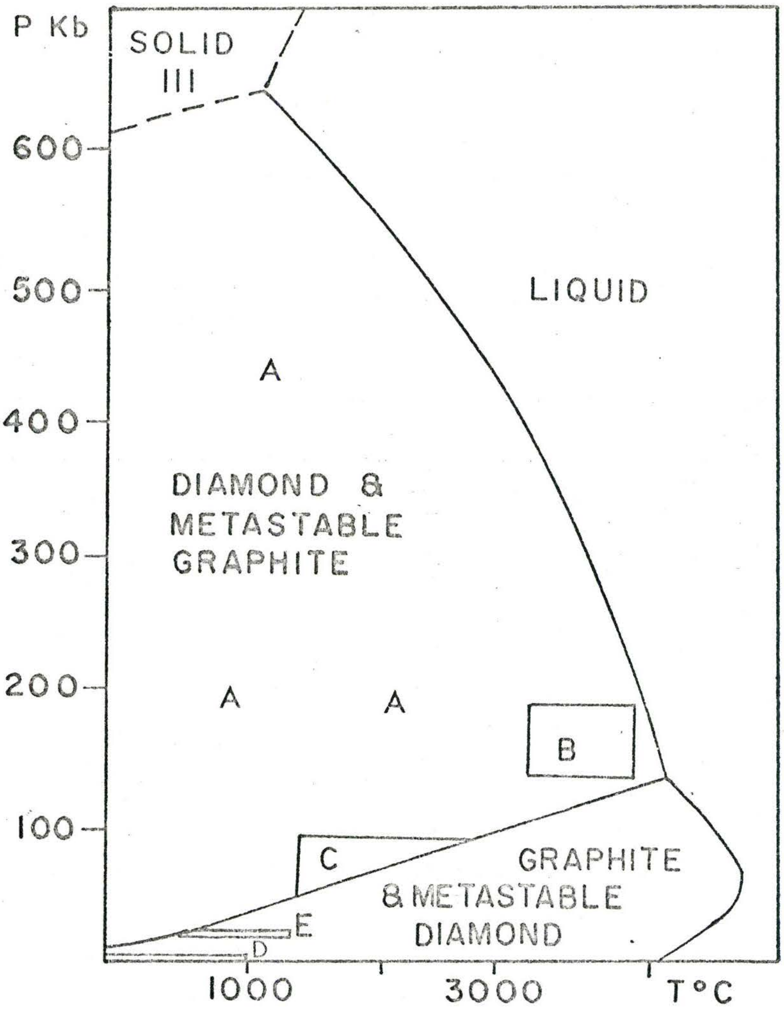


Fig. 11. Phase relations of carbon and areas of diamond synthesis.

Carbon phase relations from Wentorf (1965) and De Carli (1967).

A - Shock wave synthesis region (De Carli, 1967)

B - Direct graphite-diamond static synthesis (Bundy 1963)

C - Static catalysis methods (Wentorf 1965)

D - Eversole and Takasu processes (Wentorf 1965)

E - Bezrukov et al. 1966 (Davidson 1967b)

Fig. 12. Petrogenetic grid for kimberlite formation.

Garnet peridotite solidus and subsolidus phase relations including Al_2O_3 isopleths (---) from Green and Ringwood (1967b) and Macgregor (1967). Precambrian shield geotherm from Clark and Ringwood (1964).

Diamond-graphite equilibrium curve (Bundy et al. 1961).

Quartz-coesite equilbrium curve (Stishov 1963).

Phlogopite+forsterite+gas → forsterite+liquid+gas (Yoder and Kushiro 1968).

(A) - field of equilibration of garnet-peridotite nodules in kimberlite.

(B) - field of diamond genesis postulated on the basis of the equilibrium graphite-diamond transformation.

Abbreviations: Fo, forsterite; En_{ss}, enstatite solid solution; Di_{ss}, diopside solid solution; An, anorthite; Sp, spinel; Py, pyrope garnet; Ph, phlogopite; L, liquid; G, gas.

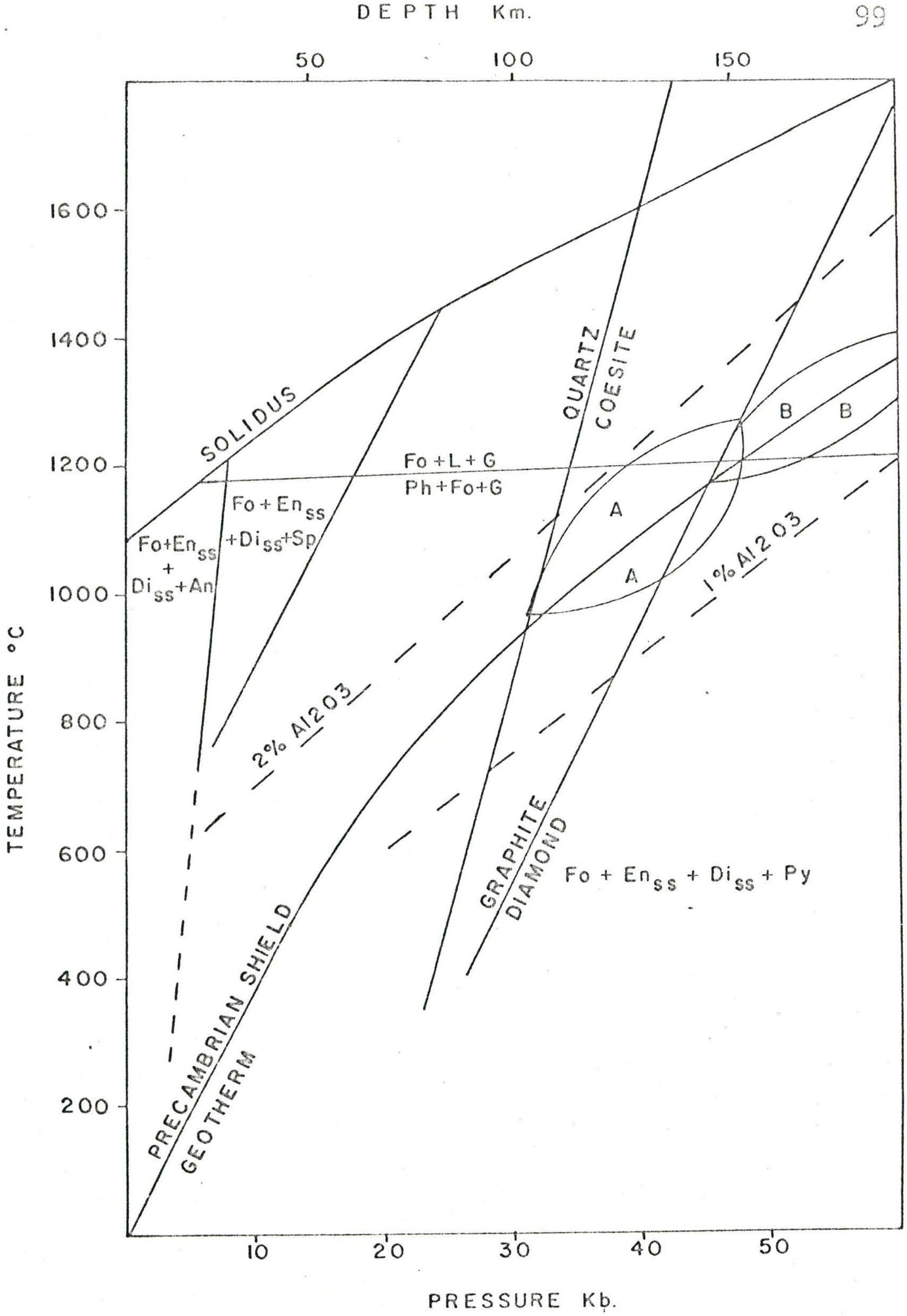


FIG. 12. PETROGENETIC GRID FOR KIMBERLITE FORMATION.

system does, however, serve to illustrate the complex nature of the fluid phase associated with kimberlite and how large changes in its composition can occur with changing temperature and pressure.

As a consequence of the composition of the fluid phase it is possible that reduction processes within the silicate-fluid system can bring about the reduction of certain gases to elemental carbon. Such reductions may not take place until high concentrations of "carbon" have been built up in the fluid phase by release of gases from mantle material by partial melting. Gas reduction mechanisms for producing elemental carbon and diamond have previously been suggested by Sobolev (Lebedev 1964) and O'Hara and Mercy (1963). The reductions may be of the following type:

$$CO_2 + 2H_2 \rightleftharpoons 2H_2O + C_{\text{diamond or graphite}}$$

$$CO + H_2 \rightleftharpoons H_2O + C_{\text{diamond or graphite}}$$

$$CO_2 \rightleftharpoons O_2 + C_{\text{diamond or graphite}}$$

Such reactions are undoubtedly a gross oversimplification but indicate the nature of the reduction. Methane, in addition, is easily reduced to carbon and may play an important role in diamond formation under some conditions (see below). The important feature of such gas reduction mechanisms is that they cannot be represented in terms of the graphite-diamond equilibrium phase transformation (if the product is diamond) as the process is a solid-fluid reaction and not an equilibrium solid-solid transformation. In addition, kinetic factors might be of extreme importance and so cause metastable diamond growth in the regions of graphite stability predicted by the equilibrium transformation curve. In reduction processes, carbon must be reduced to zero valence but the phase formed may not be graphite as two reaction paths are possible:

$$\begin{tikzcd}
 & \text{diamond} \\
\text{carbon bearing fluid} \arrow[ur] \arrow[dr] & \\
 & \text{graphite} \arrow[uu]
\end{tikzcd}$$

Which reduction path is taken is probably determined by kinetic factors. For such reductions to occur it is necessary that the pO_2 of the fluid be very low. The very complex nature of the fluid system may preclude accurate calculation of pO_2 in kimberlites but some evidence is available which indicates that it is low. It has been noted above that pyrrhotite is a very common inclusion in diamond and that magnetite does not occur as inclusions, in fact magnetite appears to be a stable phase only during the later stages of kimberlite crystallisation (i. e. groundmass). The presence of pyrrhotite indicates that a significant pSO_2 or pS_2 existed in the fluid phase. Verhoogen (1962) has noted that S_2 presence is a very important means of lowering pO_2 in magmas, e.g. at 1400°K the pO_2 of pure water is 3.7×10^{-5} atmospheres, but that of a mixture of H_2O and S_2 in the molecular ratio 100/1 is only 1.9×10^{-10} atmospheres. Krauskopf (1957) has also concluded that pO_2 in magmatic rocks is likely to lie between 10^{-21} and 10^{-15} at 600°C. If it were lower than 10^{-21} then no iron oxides would co-exist in equilibrium and pyrrhotite would be the dominant iron sulphide and methane would be the dominant carbon gas.

The above discussion is largely concerned with equilibrium processes of diamond formation but it is by no means certain that such processes are important in natural systems. The very fact that diamond exists today at the surface of the earth proves metastability, graphite is also known to form metastably within the field of diamond stability (Wentorf 1965). Such phenomena indicate that metastable growth and persistence may be very important in all aspects of diamond genesis. Wentorf and Bovenkerk (1961) have pointed out that natural diamonds occur as monocrystals or as small aggregated polycrystals and have suggested that the former grew near equilibrium and the latter, well above equilibrium. Cryptocrystalline masses of impure diamond such as carbonado, boart and framnesite all may represent metastable growth. Kennedy and Nordlie (1968) have discounted dis-equilibrium and metastable processes of diamond growth on the evidence of "the crystal perfection and external morphology of diamond" which to them indicates equilibrium growth. However, as will be shown below, diamonds are rarely ever perfect and provide substantial evidence that equilibrium conditions did not prevail during their growth.

Considerable effort has been devoted to growing diamonds by metastable processes and though some success has been achieved, the metastable nucleation of diamonds has yet to be demonstrated. Three examples of metastable growth have been described:

1. Eversole (Wentorf 1965, Giardini and Tydings 1962) has demonstrated that a variety of simple saturated aliphatic compounds or carbon monoxide are decomposed in the presence of diamond seeds at 1000°C at low pressures (2 kb.). Metastable diamond is added to the seeds by epitaxial growth processes.
2. Takasu (Wentorf 1965) has reported that diamond is formed by decomposition of methyl-chlorosilane over silicon crystals at 800-1000°C at 2-4 atmospheres pressure.
3. Bezrukov et al. (Davidson 1967b) have reported that diamond can be synthesised at 523-1323°C at c. 15 kb. No experimental details are available.

Such processes although being unlike natural systems demonstrate that fluid-solid reactions which produce diamond are possible and that similar processes involving the complex fluid phase may take place in kimberlite.

The metastable growth of diamond in the laboratory and its possible occurrence in natural systems is not in agreement with Kennedy and Nordlie's (1968) theory that diamond only grows by equilibrium processes and produces perfect diamond crystals. Diamonds, however, even large ones, are often far from perfect and only one fifth of the total amount mined is suitable for gems (Tolansky 1962). As noted above, diamonds contain zonally distributed trace elements (generally a sign of non-equilibrium conditions) and included fluids which indicate abrupt changes in the composition of the fluid from which they grew. Such changes are not conducive to retaining equilibrium in the system. Most diamonds have also suffered periods of dissolution (Frank 1967) followed by periods of regrowth (Grantham and Allen 1960). The wide range in composition of the inclusions in diamond also points to growth under a number of different conditions.

Such facts demonstrate that any given diamond has had a very long and varied growth history characterised by abrupt changes in the composition of the growth medium (Frank 1967). It is thus very unlikely that equilibrium between diamond and the fluid was maintained throughout this period.

The distribution of diamonds within pipes and fissures has been cited by some geologists as evidence of metastable growth or as growth within the crust (Davidson 1964, Trofimov 1965). The hypotheses are based upon the fact that each diamond pipe contains a characteristic assemblage of diamonds and that the tenor decreases with depth. An example of the characteristic diamond assemblage is seen at the Swartruggens fissure, here in the Mallin mine most of the diamonds are of the industrial type, butin the Helam mine the jewel type is predominant (Fourie 1958). The diamond assemblage in each of the pipes of the Kimberley district is also so distinct, e.g. colour, that diamond merchants can tell exactly from which pipe any given diamond came. Diamonds are also considered to be more abundant in the brecciated parts of pipes. Formation of diamonds is generally accredited to overpressures generated by explosive eruptions in the magma chamber at the base of each pipe. The overpressure theory can easily be discounted on the grounds that such overpressures do not explain why diamonds are found in fissure kimberlites which show no signs of brecciation, e.g. Swartruggens. The distinct diamond assemblage within each pipe is, however, very difficult to explain by assuming that all diamonds were formed at very great depths and subsequently transported up into the pipes as even closely related pipes such as the Kimberley group exhibit great variations in diamond type. It may be that these assemblages are the result of metastable diamond formation within the pipe either by some process of direct metastable nucleation or by epitaxial growth upon some centre of nucleation. Such centres could be seed diamonds produced at depth or some other mineral, e.g. rutile has been suggested as a centre of nucleation by Furtergendler (Dawson 1968). By either process a distinct diamond assemblage would result as a consequence of differences in the composition of individual kimberlite bodies. In this context the report that diamonds are found in the wall rock limestones and limestone inclusions at the Mir pipe (Lebedev 1964, Davidson 1967b) is very significant.

The question of the tenor of diamonds decreasing with depth is possibly connected with the solubility of diamond. It has been found that carbon is soluble in serpentine-KCl and kimberlite-KCl mixtures (Wentorf 1965). The fact that most diamonds show features of dissolution (Frank 1967) is an indication that natural carbon in the form of graphite or diamond is soluble in the alkaline kimberlite magma. Mining in several South African pipes has demonstrated that the highest production of diamonds comes from the brecciated portions of pipes. As the pipes are traced downwards the amount of brecciation decreases, the amount of massive kimberlite increases and the diamond tenor falls off. If diamond is readily soluble in kimberlite, then contact with the relatively quiet kimberlite magmas which formed the massive kimberlite will promote rapid dissolution of diamond. (N.B. diamond will only dissolve when the magma becomes undersaturated in carbon, the loss of gases during intrusion may promote such conditions. Hence the violent brecciation of kimberlite, as noted by Bardet (1965), will lead to the preservation of diamond. Dissolution of diamond in relatively quiet magmas also explains why the majority of pipes contain few or no diamonds, and why fissure kimberlite is in general not as productive as pipe kimberlite. Thus, the generation of barren kimberlite is probably not due to formation under very different conditions but solely due to the conditions of intrusion.

An interesting consequence of the proposed metastable occurrence of diamonds is that diamonds should form in any magma which attains the requisite conditions of an abundant carbon-bearing fluid with a low $p0_2$. An obvious candidate is carbonatite and the interesting report by Von Eckermann (1967) of partially resorbed diamond in the Alnö carbonatite is important. Whether carbonatites would have low $p0_2$ values is uncertain, it may be that the large $C0_2$ reservoir of carbonatite will buffer the reduction and therefore, be too oxidising for carbon reduction to take place. If $p0_2$ is sufficiently low for diamond formation, then the general lack of diamond could be ascribed to the generally quiet intrusive conditions of carbonatite which would promote rapid dissolution of diamond.

Apart from simple dissolution processes some diamonds may be destroyed by graphitisation. In most kimberlites graphitised diamonds are uncommon but they occur in abundance at the Premier pipe. Here the coat of graphite is easily removed and would not have survived violent intrusion (Lonsdale and Milledge 1965). Tolanksy (1968) has surmised that the diamonds were subject to graphitising temperatures after formation and after some drop in pressure had taken place. In the presence of oxygen graphitisation would indicate temperatures of about 1100°C. For graphitisation to occur at such temperatures it must have taken place at the base of the pipe, as the upper regions seem to have been intruded at very low temperatures, such a conclusion is at variance with Lonsdale and Milledge's (1965) proposal of post-intrusive graphitisation. The lack of graphitised diamonds in many pipes could be due to the solution of graphite from the surface of diamond.

Some geologists have considered that the morphology of diamond can be used to indicate the pressure and temperature conditions of formation as Wentorf and Bovenkerk (1961) have shown that the morphology of synthetic diamonds is very dependent upon the conditions of synthesis. The morphology of any given crystal is strongly dependent upon the concentration of its components in the solution from which it grew, trace elements in particular seem to have considerable effects upon crystal morphology. The changing growth conditions in natural kimberlite are reflected in the growth of several forms on individual diamonds. Grantham and Allen (1960) have also demonstrated that in the Sierre Leone kimberlites "a particular morphological type cannot be attributed to a particular phase of the physico-chemical environment".

Ultramafic nodules

A wide variety of ultramafic nodules are found in kimberlite and of these garnet peridotite (or garnet lherzolite) is considered by most petrologists to be representative of the composition of the upper mantle at the site of kimberlite magma generation (O'Hara 1968). Geochemical and petrological studies of these nodules have been extensive and have been summarised in the book "Ultramafic and Related Rocks" (Wyllie 1967) and need not be repeated here. Certain observations are, however, pertinent to the problems of kimberlite genesis as garnet lherzolite has been invoked by O'hara and Yoder (1967) to be the source rock of kimberlite magma.

The mineralogy of a mantle of garnet peridotite composition has been discussed by Macgregor (1967) and Green and Ringwood (1967b). These studies have shown that three sub-solidus phase assemblages are possible depending upon the prevailing pressure and temperature conditions (Fig. 12). The mineral assemblage found in garnet peridotites xenoliths is typical of much of the upper mantle, e.g. olivine-enstatite-clinopyroxene-garnet.

Experimental studies of the synthetic system enstatite-pyrope and of synthetic peridotites have shown that the $Al_2 0_3$ content of enstatite in equilibrium with pyrope decreases with pressure increase (Boyd and England 1964, Green and Ringwood 1967b). Analyses of enstatite co-existing with garnet in garnet peridotite xenoliths indicate an $Al_2 0_3$ content of about 1%. Those which co-exist with subcalcic $Al_2 0_3$ poor diopside have been estimated to have formed at temperatures of about 1350°C implying a maximum pressure of formation of about 55 kb. (O'Hara and Yoder 1967). The Precambrian Shield geotherm (Fig. 12), however, lies between the 1-2% $Al_2 0_3$ isopleths over a wide range of temperature and pressures (Green and Ringwood 1967b) and lower pressures than 55 kb. may be more typical as indicated by O'Hara (1967).

Davis and Boyd (1966) have shown that the diopside solvus in the system $CaMgSi_2 0_6$-$Mg_2 Si_2 0_6$ at 30 kb. is not significantly different to that at 1 atmosphere and that the composition of diopside in equilibrium with enstatite can be used as a geothermometer which is independent of pressure. Boyd (1967) has analysed naturally co-existing pyroxenes in nodules and found equilibration temperatures to lie within the range 900-1100°C with one sample from Shinyanga giving a maximum temperature of 1300°C. Meyer and Boyd (1968) have found that the composition of diopside included in diamond indicates an equilibration temperature of 950°C (N.B. enstatite was not present in the crystal). These temperatures indicate pressures of formation mainly in the 30-40 kb region and possibly as great as 55 kb.

O'Hara (1967) in a detailed and comprehensive discussion of the composition of co-existing pyroxenes and garnet reached the conclusion that garnet peridotite nodules equilibrated at pressures of 30-45 kb.

Thus it is considered that garnet peridotite nodules indicate depths of formation of from 100-150 km at temperatures between 900 and 1300°C.

At this point it should be noted that the equilibration temperatures and pressures of garnet peridotite (Area A, Fig. 12) are less than those postulated by the diamond-graphite transformation (Area B, Fig. 12). Metastable diamond growth can explain the discrepancy but several other factors regarding the partial melting of garnet peridotite to form kimberlitic magmas (O'Hara and Yoder 1967) must be considered, e.g. composition of included minerals in diamond (see Chapter 5).

The ultrabasic nodule evidence is also limited in interpretation because the validity of the geothermal gradient is unknown, although it appears to be a reasonable approximation (Clark and Ringwood 1964). The pyroxene data also appear to be approximately valid as synthetic and natural samples have been used to obtain the relationships.

Kennedy and Nordlie (1968) in a recent study consider that diamond grows in the fluid phase produced by the partial melting of garnet peridotite but only at points where the geothermal gradient, the diamond-graphite curve and the solidus of garnet peridotite intersect. As a consequence of such limitations, the minimum depth of kimberlite formation and diamond growth is about 200 k~~b~~m (70 kb) and at very high temperatures c. 2000°C). The production of a melt in Kennedy and Nordlie's (1968) hypothesis is a consequence of thermal processes only, no role is given to the possible production of a melt by pressure release at lower temperatures and pressures. Melting consequent upon pressure release is one of the more favoured mechanisms of magma generation (Turner and Verhoogen 1960, Harriss 1967) and should therefore not be neglected. The low equilibration temperatures of garnet peridotites also do not provide evidence in support of Kennedy and Nordlie's (1968) hypothesis.

Synthetic Kimberlites

The major oxide components of kimberlite can be represented by the quinary system CaO-MgO-SiO_2-H_2O-CO_2. This system includes some of the major silicate and carbonate phases found in kimberlite and has been investigated at 1 kb. by Franz (1965), and discussed by Franz and Wyllie (1966) and Wyllie (1966).

Fig. 13 illustrates the quaternary system CaO-MgO-SiO_2-H_2O (Franz and Wyllie 1966, Fig. 7, p. 19). The principal feature of this sytem is the occurrence of a vapour saturated liquidus surface (VSLS). At this surface liquids containing dissolved vapour co-exist with crystalline phases and vapour. The VSLS is divided into two portions by a thermal divide XYB; low temperature crystalline phases lie on the silica-poor side of this thermal divide.

The quaternary system CaO-MgO-SiO_2-CO_2 is very similar to the above system, the VSLS and the thermal divide persist but hydrated phases are replaced by carbonated phases.

In the quinary system CaO-MgO-SiO_2-H_2O-CO_2, the two volatiles can be represented by the same corner of the tetrahedron. The general arrangement of the silicate phase fields on the VSLS above the thermal divide with liquids containing dissolved CO_2 H_2O will be similar to that shown in Fig. 13. The relations below the thermal divide are more complicated as the compositions of the primary phases change in accordance with change in the composition of the vapour phase between CO_2 and H_2O. These phases correspond to synthetic carbonatite magmas (Wyllie 1966).

Bulk compositions lying upon the CO_2-H_2O side of the VSLS in the system at high temperatures will be initially liquid plus vapour. With falling temperature vapour is evolved from the liquid and the liquid moves onto the VSLS where crystallisation of solid phases takes place. When crystalline phases begin to precipitate, the liquid follows a crystallisation path on the VSLS, while the vapour composition follows a corresponding path on a vaporous surface (not shown) until all the liquid is used up. At this point crystalline phases co-exist with a vapour which is a mixture of CO_2 and H_2O. During the crystallisation of the liquid, vapour is continually evolved and the composition of the vapour phase is continually changing. Paths of crystallisation on the VSLS can take either of two directions. Liquids richer in SiO_2 than the thermal divide will only yield silicates and a separate vapour phase. A low temperature residual melt capable of precipitating hydrated and carbonated phases will not result from fractional crystallisation. Any liquid with a composition poorer in silica than the thermal divide will yield a hydrated low temperature residual liquid by fractional crystal-

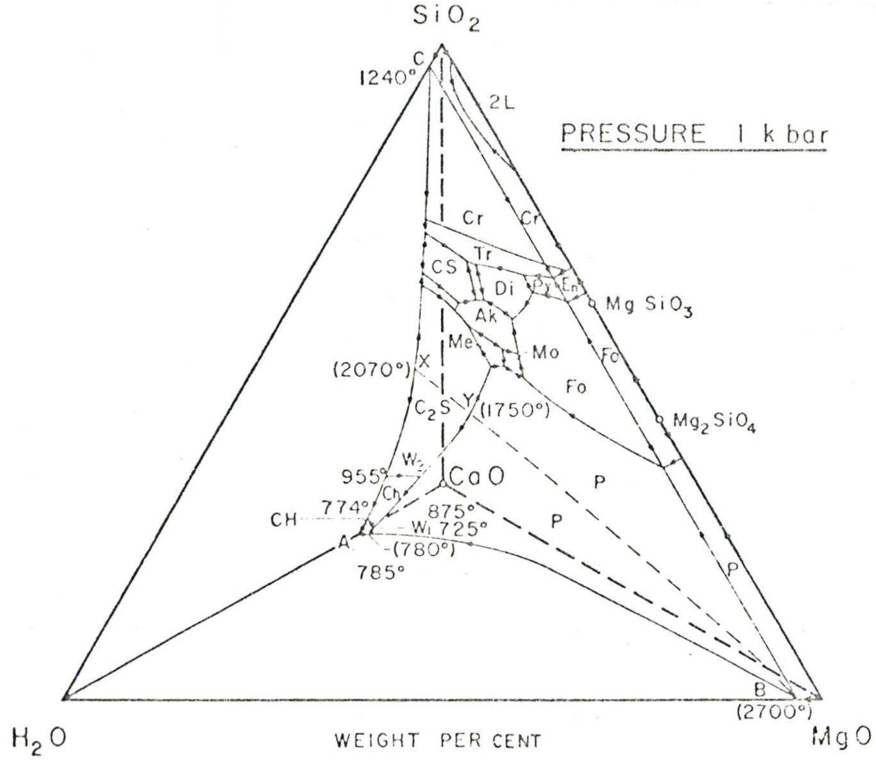


Fig.13.Phase relations in the system $CaO-MgO-SiO_2-H_2O$ at 1 kb. Cr-cristobalite, Tr-trydimite, CS-wollastonite, Di-diopside, En-enstatite, Ak-akermanite, Mo-monticellite, Me-merwinite, Fo-forsterite, P-periclase, CH-portlandite, Ch-calciochondrodite C_2S-dicalcium silicate, L-liquid, XYB-thermal divide, ABC-vapour saturated liquidus surface.(after Franz and Wyllie 1966 Fig.7, p.11).

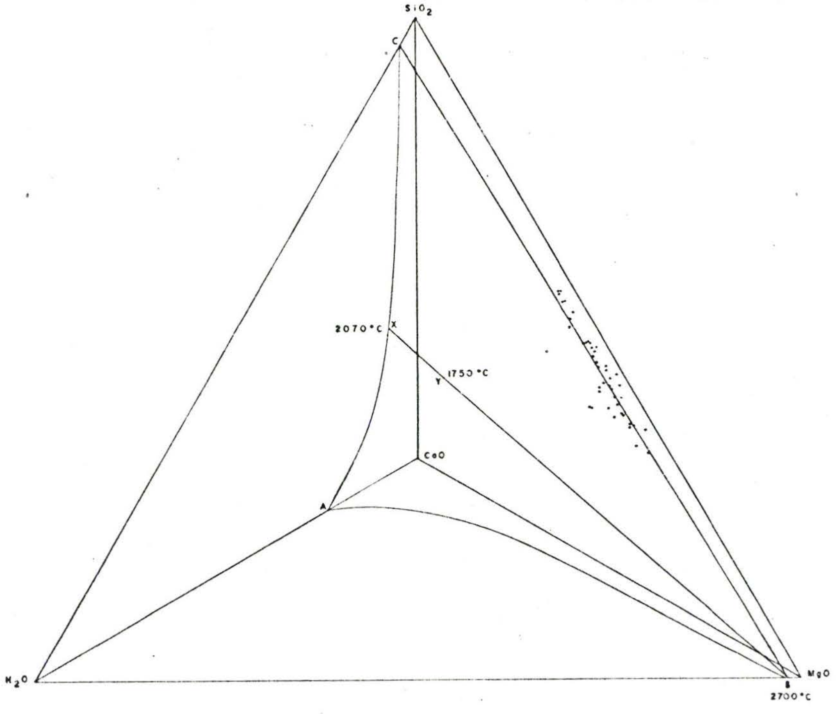


FIG.14. THE SYSTEM CaO - MgO - SiO_2 - H_2O. WHOLE ROCK KIMBERLITES ARE SHOWN PROJECTED FROM H_2O ON TO THE SiO_2 - MgO - CaO FACE OF THE TETRAHEDRON. XYB IS A THERMAL DIVIDE. ABC IS THE VAPOUR SATURATED LIQUIDUS SURFACE.

lisation which will precipitate hydrated and carbonated phases.

The above considerations led Franz and Wyllie (1966) and Wyllie (1966) to conclude that at 1 kb pressure high temperature silicate melts precipitating originally minerals such as olivine, pyroxene, melilite and monticellite are incapable of yielding low temperature residual melts which precipitate carbonated and hydrated phases. Thus, they consider that a carbonated peridotite magma cannot yield a carbonatite magma by fractional crystallisation.

With regard to kimberlites it is known from petrographic observation that olivine is one of the first minerals to crystallise from a kimberlite magma. Moreover, olivine continues to crystallise throughout much of the rocks crystallisation history . The groundmass of kimberlite contains abundant primary carbonate phases thought to represent the crystalline phases produced from a low temperature residual liquid. These observations are in direct contrast to the experimental studies.

The composition of some kimberlites with regard to the system CaO-MgO-SiO_2-H_2O is shown in Fig. 14. The analyses represent whole rock kimberlites and are taken here to represent "derivatives" of some initial liquid. (Data from Wagner 1914, Williams 1932, Dawson 1962.) The plots are not strictly correct as no allowance is made for lost vapour phases or the amounts of phenocrystal material, but serve to illustrate how kimberlites lie in the system with regard to the thermal divide and the low temperature liquidus. As Fig. 14 shows the rocks plot above the thermal divide and would not therefore be expected to be able to produce residual low temperature liquids. To explain the observed mineralogy and petrology of kimberlite it is necessary to postulate that at high pressures the thermal barrier is removed or is bypassed by the introduction of some other component. Removal of the thermal barrier is possible also when different mineral assemblages are introduced at high pressure. Modification of the system by alkali addition would seem to represent a likely possibility and Wyllie (1966) considers that a carbonated alkali peridotite magma may provide alternate crystallisation paths which would bypass the thermal barrier and lead to low temperature liquids.

A third possibility is that liquid immiscibility may play some role in the development of the carbonate-rich portions of kimberlite. It has been established experimentally that liquid immiscibility exists between silicate and carbonate melts (Wyllie 1966). Kooster van Gros and Piwinski have also demonstrated that liquid immiscibility appears in carbonated melts of pantellerite, basalt, ijolite and melteigite compositions at 10 kb. and 600-750°C, thus demonstrating that calcite-rich melts can be generated from a variety of magmas rich in CO_2. Of interest in this context is Wagner's (1914) description of rounded and ellipsoidal amygdales of calcite arranged in rows in a kimberlite dike. Such anygdales may represent crystallised immiscible liquids.

A second consequence of Franz's (1965) work is that in the quinary system decarbonation reactions involving high temperature silicate minerals such as olivine and the carbonated phases (calcite) occur. The presence of H_20 in the vapour phase causes divariant dissociation reactions to become involved with the low temperature liquidus relations giving rise to the appearance of high temperature minerals such as olivine and pyroxene on the low temperature liquidus below the thermal divide. Thus, even though liquids are unable to cross this barrier, high temperature minerals may be precipitated alongside calcite from low temperature synthetic carbonatite magmas. A large number of crystallisation paths are possible in the quinary system involving crystal-liquid equilibria at low temperature (600-800°C) where calcite and olivine co-exist, such paths can account for the reaction of olivines (primary high temperature type) with liquid to give calcite and monticellite pseudomorphs and may also play some role in the development of the two generations of olivine seen in kimberlite.

As a consequence of the experimental work carried out by Wyllie (1966) and others, it has been shown that synthetic carbonatite magmas can exist in a liquid state down to very low temperatures. The relevance of studies to kimberlite is that they show that calcite can be a primary crystalline phase and need not be an alteration product of pre-existing minerals. Only rarely has carbonate in kimberlite been regarded as a primary phase and it is more usual to consider the carbonate as a product of weathering, as a product of hydrothermal fluids from younger intrusions, as a deuteric mineral or to be derived from xenoliths of limestone. Recent petrological thought is, however, turning to the possibility of primary calcite in kimberlite, e.g. Watson (1955) and renders unnecessary the complex petrological theories of Shand (1934) and Taljaard (1936).

Potassium bearing systems

Seifert and Schreyer (1966) have investigated the system $K_2O-MgO-SiO_2-H_2O$ at 1 kb and at temperatures from 500-900°C. Within this system extensive fields of silicate liquid are found to persist to very low temperatures (700°C). Seifert and Schreyer (1966) consider that small amounts of potassium may be able to convert solid ultrabasic rocks into crystalline mushes capable of low temperature intrusion. At 500°C the liquid is replaced by a gas rich in potassium which is considered to be able to leave the solidified rock and induce potassium metasomatism in adjacent country rocks.

Seifert and Schreyer's (1966) study is important that it demonstrates that the two primary phases of kimberlite, olivine and phlogopite can crystallise together over a wide range of temperature. The lower temperatures are well below those of the thermal barrier in the quinary system of Franz (1965) and thus it is possible that addition of K_2O to the system will enable liquids to cross the thermal barrier. The occurrence of potassium metasomatism is not a typical feature of kimberlites, in fact, country rocks adjacent to pipes and fissures are usually either unaltered or subject to slight carbonatisation. Only one example of potassium metasomatism adjacent to kimberlite is known, this being adjacent to a micaceous kimberlite at Seguela, Ivory Coast (Bardet and Vachette 1966), where potash fenites are developed.

Yoder and Kushiro (1968) have studied the system Fo-H_2O-(Lc:Ks) at 10 kb. and 1225°C and have shown that forsterite and phlogopite co-exist as liquidus phases under these conditions. Melting relations of phlogopite are very important in kimberlite petrology as phlogopite may be one of phases which melts in garnet peridotite in the mantle to give kimberlitic fluids. Yoder and Kushiro (1968) have studied the melting relations of phlogopite co-existing with olivine, e. g.

$$\text{phlogopite} + \text{olivine} + \text{gas} \rightleftharpoons \text{olivine} + \text{liquid} + \text{gas}$$

The univariant curve representing this reaction passses through the field of equilibration of garnet peridotites in Fig. 12 and indicates that melting of phlogopite is possible at these temperatures and pressures.

Luth (1967) has investigated the system $KAlSiO_4$-Mg_2SiO_4-SiO_2-H_2O. The results are not strictly applicable to kimberlites but Luth (1967) considers that the distinction between kimberlite and micaceous kimberlite can be possibly due to the reaction:

$$\text{phlogopite} + \text{enstatite} \rightleftharpoons \text{forsterite} + \text{liquid} + \text{vapour}$$

Enstatite does not, however, play a major role in kimberlite petrology but the reaction may be of importance in producing the distinction between pyroxene bearing micaceous kimberlites and pyroxene free micaceous kimberlites as described by Wagner (1914).

From the above discussion several conclusions can be drawn:

1. If kimberlites are derived by partial melting of garnet peridotite then they are formed deep in the mantle, i.e. 100-150 kms.
2. Diamond crystallises over a wide range of pressure and temperature and is of little use in determining the site of kimberlite genesis.
3. Kimberlite magmas contain abundant volatiles (CO_2, CO, H_2O, H_2, N_2, SO_2).
4. Diamond, olivine, garnet, phlogopite and calcite can all crystallise as primary phases from a kimberlitic magma.

5. Low temperature carbonate-rich fluids can be derived by the fractional crystallisation of a high temperature alkali-rich kimberlitic magma.

The subject of the temperature of kimberlite intrusion has been extensive discussed by Davidson (1964), Mikhayenko and Nenashev (1962) and Dawson (1967a) and it would seem that the upper parts of pipes are intruded at very low temperatures. However, high temperature kimberlite magma is known to persist at high crustal levels as evidenced by chilled margins (Mannard 1962) and the presence of partially melted xenoliths (Grantham and Allen 1960). The development of the low temperatures seen in the pipes is related in some manner to the fluidisation developed during their intrusion.

CHAPTER FIVE

PETROGENESIS OF KIMBERLITE

Theories of petrogenesis of kimberlite are few, and have for the most part been based upon little petrological and geological evidence. Most geologists have been concerned with the mechanism of intrusion of kimberlite magmas rather than with its actual genesis.

Three main groups of petrogenic thought exist. These conclude that kimberlites are derived from:

a) olivine-melilitites (Holmes 1936, Taljaard 1936).

b) carbonatites (Franz 1965, Dawson 1966, 1967).

c) peridotite fusion (O'Hara and Yoder 1967, Sobolev 1968b, Artsybasheva et al. 1964).

Olivine Melilitites

Holmes (1936) and Taljaard (1936) considered that there exists a close chemical and spatial relationship between kimberlite and melilitite. Holmes (1936) regarded kimberlite as an original magma of olivine melilitite from which "emanations" of H_20, CO_2,

P_2O_5 had been lost, and to which had been added xenolithic ultrabasic mantle material. Taljaard (1936) regarded kimberlite as hydrothermally altered melilitite.

The relationship has been discussed in Chapter 3 and has been found to be unconvincing; consequently these theories of kimberlite petrogenesis will not be further discussed.

Carbonatites

Two hypotheses have been presented which consider carbonatite to be the parent magma of kimberlite. Carbonatite is, however, a magma of more extreme composition than kimberlite and thus may itself be an advanced differentiate of some other magma of less extreme composition. Moreover the source of carbonatite magma is unknown and thus considering carbonatite to be the parent of kimberlite, is merely begging the question and provides a convenient way out of certain petrological difficulties.

Hypothesis of Franz (1965)

Franz (1965) regards all the ultrabasic inclusions found in kimberlite to be xenolithic and to be mantle material randomly incorporated in a carbonatite moving upwards from depth in the mantle. Reaction of carbonatite with xenoliths to produce phlogopite occurs as the carbonatite moves upward. The stable phases which co-exist with calcite at this time are forsterite, phlogopite, monticellite, perovskite, apatite and magnetite. The reaction with xenoliths is thought to form a "micaceous kimberlite magma" saturated with a vapour phase. Franz (1965, p. 124) further states, "Because of the tendency for micaceous kimberlites to occur as dikes and the basaltic to occur as pipes and because of the chemical differences between them, the basaltic kimberlite may be formed from the micaceous kimberlites by the removal of its groundmass".

Thus, as a micaceous kimberlite nears the surface the dissolved vapour comes out of solution and the gas bubbles expand explosively to cause the eruption of a carbonatite tuff cone: vapour is considered to react with phlogopite and the xenoliths, removing K_2O and Al_2O_3 and leaving behind calcium and magnesium silicates in the form of a basaltic kimberlite.

Franz's (1965) hypothesis is based upon his studies of the system CaO-MgO-SiO_2-CO_2-H_2O and has the merit of showing that low temperature liquids equivalent to kimberlite are possible. Carbonatite is chosen as a parent magma because of the supposed association of kimberlites and carbonates (Dawson 1966) and because of the existence of a thermal divide in the synthetic system which prevents carbonated peridotites differentiating by fractional crystallization to carbonatites. Franz & Wyllie (1966) and Wyllie (1966), however, state that several mechanisms for bypassing this thermal barrier exist.

The most important criticisms of Franz's (1965) hypothesis are:

1. Reactions between carbonate and xenoliths in kimberlite are rare. Any which occur appear to be merely replacement of mafic minerals by a fluid which already contains phlogopite.
2. Reactions between carbonatite and xenoliths would not provide a means of producing the high K_20 content of kimberlite as both reactants are K_20 poor.
3. No evidence is found for phlogopite reacting with vapour to give olivine. Olivine crystallises as a primary mineral of two generations whilst phlogopite is largely confined to the groundmass.
4. Considering kimberlite to be equivalent to micaceous kimberlite minus groundmass is based upon purely arbitrary chemical calculations, and no petrological evidence supports this relationship. Evidence for the assumption that micaceous kimberlites are precursors of kimberlite is doubtful. Franz (1965) cites Dawson's (1962) evidence that a micaceous kimberlite forms a dyke below a kimberlite pipe in Lesotho. However,

Dawson (1962) himself states that the Lesotho area is predominantly kimberlite. Similar adverse volumetric evidence is seen in Tanzania (Mannard 1962), Siberia (Lebedev 1964) and South Africa (Williams 1932). In South Africa, micaceous kimberlites tend to form a separate province of kimberlite magmatism distinct from that of kimberlite. Where differentiation of kimberlite has taken place, e.g. late stage cross cutting dykes, it appears that mica is present in greater quantity than in the parent pipe (Wagner 1914).

5. The hypothesis does not account for the ubiquitous occurrence of phenocrystal olivine, chrome-pyrope, magnesian ilmenite and to a lesser extent diamond in kimberlite as these minerals are not typical of carbonatites.

In summary, Franz's (1965) hypothesis is inadequate in accounting for the observed petrological and geological features of kimberlite.

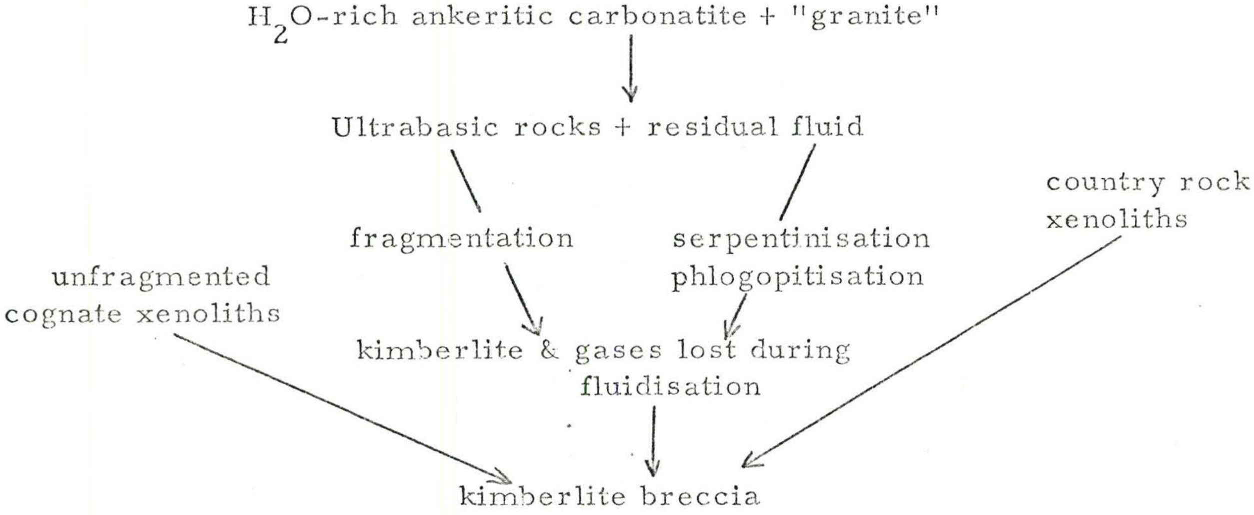
Hypothesis of Dawson (1966, 1967b)

Dawson's (1966, 1967b) hypothesis bears some similarity to that of Franz (1965), but Dawson regards the ultrabasic xenoliths as cognate.

Basically the hypothesis states that "crustal granite" is incorporated into a water-rich ankeritic fraction of a carbonatite magma.

Reactions occur which produce ultrabasic xenoliths, which become disrupted during the intrusive phase. Some of the xenoliths become the large rounded xenoliths found in the pipes whilst crystals from others react with the residual fluid to form kimberlite.

The process has been summarised by Dawson (1966, p. 3, Fig. 2) as follows:



The theory is based upon the supposed association of kimberlites and carbonatites (Chapter 3). It is similar to that of Holmes (1950) and represents a version of the limestone-assimilation hypothesis of Daly (1933) and Shand (1947), a hypothesis which has largely been discredited as a means of producing large volumes of alkaline rock (Turner and Verhoogen 1960, Heinrich 1966). The major points against Dawson's (1966) theory are:

1. There is no experimental or geological evidence available which indicates that "granite" reacts with carbonatite to give kimberlite.
2. Addition of "granite" to carbonatite would increase its Na_2O, K_2O, Al_2O_3 and SiO_2 content, but the final Al_2O_3 and SiO_2 contents would be too high and the Na_2O/K_2O ratio would be the reverse of that generally found in kimberlites. The production of calcium-poor kimberlites is particularly hard to account for.
3. Dawson (1966) does not discuss the source of his "granite", but it presumably can represent incorporation of an anatectic melt or fused xenoliths. In either case it is very unlikely that carbonatite would possess sufficient superheat to cause much partial melting or fusion.
4. Known contact effects between granite and limestones never develop rocks of kimberlitic aspect nor do eclogite and garnet peridotite form. Reaction zones are small in extent and the hybrid rocks generated are syenitic or are grossular-idocrase-diopside skarns (Muir 1953, Tilley 1949).
5. In order to account for the MgO content of kimberlite, Dawson (1966) postulated that only ankeritic carbonatite reacts with granite. This is a rather strained assumption as reactions at granite dolomite contacts are very similar to those at

granite-limestone contacts (Tilley 1949). Moreover, dolomitic and ankeritic carbonatite are relatively rare compared to the amounts of calcite carbonatite. Appealing to the fact that kimberlite is itself a rare rock (Dawson 1966) proves nothing concerning their supposed relation. Dawson (1966) also considers that dolomite reacts preferentially because it has a lower dissociation temperature than calcite at 1 atmosphere, however Wyllie (1966) has found that dolomite is stable on the liquidus phase only at high pressures in the system CaO-MgO-FeO-CO_2-H_2O.

6. Garnet peridotite xenoliths in all South African kimberlites have been shown to possess a uniform garnet composition (Rickwood et al. 1968), if these xenoliths were reaction products in a crustal environment no such constancy of composition could be expected.
7. The hypothesis cannot explain the high Cr, Ni, Co content, i.e. the ultrabasic geochemical assemblage of kimberlite as neither carbonatite nor granite possesses high concentrations of these elements.
8. The hypothesis does not explain the high Th/U ratios, the possible rare earth Eu anomaly nor the high Hg and B contents of kimberlite.

9. Other processes can account for the abundances of Sr, Nb, Zr, etc., rather than assuming that carbonatite is the only source of these elements (see Chapter 2).

In conclusion the theory does not account for the observed mineralogy and geochemistry of kimberlite and moreover, provides no means of generating the various types of kimberlite.

Peridotite Fusion

O'Hara and Yoder (1967) have developed a theory of kimberlite genesis based upon the following observations:

1. Garnet lherzolite nodules in kimberlite yield an acceptable estimate of the composition of the upper mantle.
2. Partial melting of such garnet lherzolites at 80-100 km., in depth will produce a liquid with the composition of hypersthene normative picrite basalt.
3. Garnet lherzolite begins to melt at high pressures at temperatures below that at which bimineralic eclogite begins to melt. Where both rock types are available to be melted under natural circumstances liquid should be produced preferentially from the garnet lherzolite.

4. The reaction relationship:

olivine+hypersthene normative picritic liquid → garnet+diopside

has been inferred from natural assemblages in kimberlite (O'Hara and Yoder 1963) and has been confirmed to occur at 20kb., in experiments on natural picrite (O'Hara 1968).

5. The reaction relationship:

orthopyroxene+hypersthene normative picritic liquid →

diopside+garnet (±olivine)

has been found in the system $CaO-MgO-Al_2O_3-SiO_2$ and from natural garnet peridotite systems at 30 kb. (O'Hara 1968).

These reaction relationships are considered essential for the development of a kimberlitic fluid by the separation of an eclogitic accumulate by the high pressure fractionation of hypersthene normative picritic basalt.

If partial melting of a four phase garnet lherzolite occurs, then all four phases will melt together and if the degree of melting is insufficient to cause the disappearance of any phase, then the same minerals will remain as solids. The solids will have compositions differing from the original phases which crystallised at the initial solidification point and the minerals left will be enriched in magnesium relative to the original composition, thus:

garnet lherzolite-I $\rightarrow$ garnet lherzolite-II + liquid

The liquid will have a higher Fe/Mg ratio than the melt which would have been formed by the complete melting of garnet lherzolite-I and will have the composition of a hypersthene normative picritic basalt (O'Hara and Yoder 1967, Rickwood et al. 1968). If this liquid migrates away from the source rocks, an opportunity may occur for crystallisation to take place. At 30 kb. orthopyroxene and olivine have a reaction relation to the liquid and are not precipitated, fractionation takes place by the separation of the minerals characteristic of bi-mineralic eclogite. The type of eclogite which crystallises during the fractionation process will depend upon the pressure and temperature conditions prevailing and at low temperatures more calcic and aluminous eclogites will separate. The composition of the liquid remaining after eclogite fractionation is believed to have a composition similar to potassic lavas or to the groundmass of kimberlite. Thus, O'Hara and Yoder (1967) consider that kimberlite may be a serpentinised mixture of xenocrysts peridotite and de-gassed fluid which is itself a residual liquid developed after the fractionation of eclogite from a liquid which is the partial melting product of four phase garnet lherzolite. The geochemical effects of eclogite fractionation are considered by O'Hara and Yoder (1967) to account for the high Cr, Ni, Co, V, Mg and high Sr, Ba, Rb, K, Ti, P content of kimberlites as the separation of clinopyroxene and garnet is considered to fractionate these elements into the liquid phase.

To examine the plausibility of O'Hara and Yoder's hypothesis it is necessary to consider the distribution and occurrence of eclogite and garnet peridotite in kimberlite. In many pipes such ultrabasic xenoliths are absent, in others they occur sparingly and in exceptional cases comprise as much as 2% of the rock (Davidson 1967b). As a general rule the most abundant xenoliths are garnet peridotite; eclogites are relatively rare. Occasionally considerable concentrations of eclogite occur, in these occurrences garnet peridotite is either absent, e.g. Zagodochnaya (Sobolev et al. 1968) or rare, e.g. Roberts Victor (Williams 1932).

Unfortunately little work has been undertaken which relates the xenolith content of kimberlite to the type of kimberlite but in a general manner it appears that the olivine-rich mica poor kimberlites are poor in eclogite but contain abundant garnet peridotite. The highly micaceous and calcareous kimberlites such as Zagodochnaya, Roberts Victor and Bellsbank, contain abundant eclogite and it is in these kimberlites that the rare kyanite-eclogites and grosspydites are found.

The most important question raised by the xenolith distribution is whether the small of eclogite found can account for the production of kimberlite magmas and in particular the olivine-rich mica-poor varieties.

Some facts which appear to be against eclogite fractionation are:

1. In many pipes kimberlite grades into micaceous kimberlite and appears to represent differentiation within the pipe. Eclogite is not involved in this differentiation process.
2. If eclogite fractionation has occurred why are eclogites so poorly represented in the xenolith suite? If the eruption possessed sufficient power to bring up mantle garnet peridotite xenoliths, why are eclogite xenoliths excluded?
3. Examination of the heavy mineral fraction of kimberlite generally reveals the presence of two types of garnet; pyrope (and chrome pyrope) and almandine-grossular (eclogitic garnet). O'Hara and Mercy (1963) and O'Hara and Yoder (1967) consider that pyropes are xenocrysts. Other geologists consider them to be phenocrysts and the eclogitic garnets to be fragmented eclogite xenoliths. The interpretation is facile as no reason exists why eclogite should disaggregate in preference to garnet peridotite. The interpretation of pyrope purely as a xenocryst is also doubtful as aggregates of pyrope and other minerals are not found and because euhedral pyropes are found as inclusions in diamond. (N.B. The rounded ilmenites found in kimberlite are very similar in habit to the pyropes, yet they are never considered to be xenocrysts, primarily because ilmenite does

not occur in the garnet peridotite nodules. It is entirely possible that phenocrystal pyrope achieved its rounded form in the same manner as did the ilmenite). This would indicate a phenocrystal origin. As crystallisation of kimberlite is undoubtedly a polybaric-polythermal process various types of garnet can be expected to crystallise at different times during its crystallisation history. Thus all the garnets may be phenocrystal.

4. Whilst eclogite garnets are common in the heavy mineral fraction of kimberlite it would seem that eclogitic pyroxenes are scarce (Nixon et al. 1963).

5. Kimberlites range in K_2O/Na_2O ratio from about 0.2 (Mannard 1962) to about 4 (Dawson 1967b) most lying in the range 2-4 (Williams 1932, Lebedev 1964, Dawson 1967b). The mineralogy of all such kimberlites is much the same and increasing K_2O contents are reflected in an increasing modal mica content. Increase in K_2O is not accompanied by an increase in the amount of eclogite.

6. Not all geologists are convinced that eclogite is a cognate xenolith. The evidence that eclogite is a crustal xenolith not connected with kimberlite genesis has been summarised by

Davidson (1964, 1967b) and is supported by the Rb-Sr and Pb age studies of Manton and Tatsumoto (1969).

Some evidence in favour of eclogite fractionation is that:

1. Eclogites are often banded, as are other cognate xenoliths (e.g. ilmenite nodules) and such banding can be attributed to crystal accumulation in a magma chamber prior to eruption.
2. Eclogites are more abundant in kimberlites which are richest in CaO and K_2O in accordance with O'Hara and Yoder's hypothesis. These kimberlites have high (c. 7) K_2O/Na_2O ratios and the wide variety of eclogite types is interpreted as being due to the effects of extensive fractional crystallisation (Rickwood et al. 1968).

One problem raised by O'Hara and Yoder's theory is associated with diamond genesis. Diamond does not contain inclusions of the minerals of bimineralic eclogite. The included minerals are typically those of kimberlite itself and garnet peridotite. The only diamond bearing eclogites known are of unusually calcic compositions (Sobolev 1968a). If diamond is assumed to form only within the stability field defined by the diamond-graphite curve then the presence of olivine, pyrope and orthopyroxene as liquidus phases is difficult to account for if diamond grew in a liquid with the composition of picritic basalt. The restriction of diamond in eclogites to the later stages of eclogite fractionation is also difficult to account for. The paradox can be resolved by any of the following assumptions:

1. All inclusions in diamond are xenocrysts.
2. Diamond did not grow from a melt of picritic basalt composition and hence the inclusions represent liquidus phases.
3. Diamond grew in regions where eclogite fractionation did not occur, e.g. metastable growth at low temperatures and pressures outside the fields of eclogite stability.

Which of these assumptions is correct is unknown at the present time.

In conclusion it appears that O'Hara and Yoder's (1967) hypothesis is capable of accounting for the genesis of micaceous kimberlite by eclogite fractionation. It is uncertain though whether the parent liquid of micaceous kimberlite is itself the result of eclogite fractionation. Kimberlite can possibly be accounted for by eclogite fractionation but in view of the paucity of eclogite accumulates, appears unlikely. Other methods of producing a liquid of kimberlite composition are not considered by O'Hara and Yoder (1967) although they are equally likely, e.g. partial melting of alkali-rich mantle phases or zone refining of peridotite (Harriss 1967). In this context it should be noted that O'Hara and Yoder (1967) have to invoke eclogite fractionation to increase the K_20 content of partial melts of garnet peridotite as they only consider the partial melting of four phase garnet lherzolite. The possible occurrence of phlogopite or amphibole as a minor mantle mineral is neglected, melting of such phases may be important in the generation of alkali-rich magmas of small volume.

In summary, all theories of kimberlite petrogenesis have numerous points against them either of a geological or geochemical nature. Of the theories, O'Hara and Yoder's (1967) hypothesis of eclogite fractionation is the most likely method of generating micaceous kimberlites, whilst none of the theories can adequately account for the production of olivine-rich mica-poor kimberlite.

CHAPTER SIX

EXPERIMENTAL PROCEDURES, ANALYTICAL RESULTS AND THE Rb-Sr SYSTEM

Sample Preparation

Large (c. 500 g.) samples were prepared for whole rock analysis. Each sample was initially broken up in a pre-contaminated steel jaw crusher. The crushed material was then ground to less than 200 mesh in a "Shatterbox" (Spex Industries Ltd., New Jersey) tungsten carbide crusher. All samples were stored in polyethylene bottles.

Reagents and Equipment

Significant concentrations of Rb and Sr can be found in commercially prepared reagents and it has been demonstrated (Shields 1964) that a significant increase in the precision of analyses can be obtained by purification of these reagents. Kimberlites and alkaline rocks analysed in this work possess such high concentrations of Rb and Sr that for most samples blank corrections were insignificant. However, purified reagents were used in their analysis in order to keep the general level of contamination at a minimum.

The principal reagents employed were H_2O, HCl, HNO_3, $HClO_4$ and HF.

De-ionised water was prepared by passing tap distilled water slowly through a mixed bed ion exchange resin (Barnstead Bantam Demineraliser Still).

Reagent grade HCl and HNO_3 were purified by mixing 500 ml of acid with 500 ml of de-ionised water and distilling in a vycor (silica) glass still. Approximately 750 ml of the distillate were collected per distillation and the residue discarded. The still was washed out with de-ionised water between each distillation. All acid was collected and stored in polyethylene bottles. HCl normalities were monitored continuously by density determinations.

Perchloric acid ($HClO_4$) was purchased as doubly vacuum vycor distilled acid from the G. Frederick Smith Chemical Company, Columbus, Ohio.

Two grades of hydrofluoric acid were used and for samples of low Rb and Sr content, was prepared by dissolving anhydrous hydrogen fluoride gas in de-ionised water until the water was saturated. For samples of high Sr and Rb content, reagent grade HF was used.

Wasserburg et al. (1964) have demonstrated that significant amounts of contamination were introduced by utilisation of pyrex glassware in the analytical procedure. This source of contamination is especially serious for warm solutions containing fluoride ions. Consequently, in the present work all dissolutions and evaporations were carried out in teflon, polyethylene or vycor ware.

Ion Exchange Columns

Rb and Sr were separated from each other and other elements by ion exchange techniques. The resin used for this purpose was Dowex 50-X-12 cation ion exchange resin. Sized resin was cleaned of gross contaminants (iron filings) by alternate treatments with reagent grade 6N HCl and distilled water, and then loaded into vycor glass columns of 1.5 cm diameter. The vycor columns were equipped with pinch cocks and the resin was supported by a plug of quartz wool. The length of the resin beds was about 20 cm, which was sufficient to separate Rb from Sr. A quartz wool plug was placed on top of the resin bed to prevent disturbance of the resin when loading samples onto the column. A 600 ml polyethylene acid reservoir was connected to the top of the vycor column. With the reservoir full and the pinch cocks fully open flow rates of about 1 ml/min. were obtained. Columns were further cleaned by eluting cations with 1000 ml of 6N vycor distilled HCl followed by 1000 ml of 2N vycor distilled HCl. When not in use, columns were stored in 2N HCl.

The columns were operated in batches of six, after each elution the resin was requilibrated and cleaned by passing through the column 500 ml of 6N HCl and 500 ml 2N HCl.

Chemical Procedure for Strontium Isotopic Analysis

About 100 mg of sample were weighed into a teflon evaporating basin. To this sample were then added 25 ml HF and 1 ml $HClO_4$. The basin was covered with a teflon lid and placed upon a waterbath and left overnight at a temperature of about 70°C. After overnight digestion the sample was left to digest over a boiling water bath for about three hours. The teflon lid was then removed and the solution evaporated down to fumes of $HClO_4$. The evaporated sample was then taken up in 25 ml 2N HCl and further evaporated down to about 1 ml of solution. To this solution was then added about 50 ml of de-ionised water. Heating on the water bath was continued until the solution became clear. At this point the evaporating basin was removed from the water bath and the solution allowed to cool. Cooling is necessary in order to determine whether or not dissolved salts will precipitate out at room temperatures, as such precipitates cannot be allowed to contaminate the ion exchange resin. No precipitates were observed in the present work. To the cooled solution was then added 1 ml of Sr^{89} in 2N HCl

($T_{1/2}$ = 51 days). The Sr^{89} served as a radiotracer to determine the location of Sr ions on the ion-exchange column at any time during elution. The Sr^{89} beta-activity was monitored with a geiger counter. The cooled sample was then loaded onto the ion-exchange column and absorbed onto the resin. Absorption was carried out using a slow flow rate (0.5 ml/min.). This slow absorption rate together with the fact that the sample solution was a weaker acid (c. 0.25 N HCl) than that with which the column had been equilibrated (2N HCl) ensured that absorption was limited to a very thin band at the top of the resin bed.

When all the sample had been absorbed onto the resin, the acid reservoir was filled with 2N HCl and the elution commenced at a rate of about 1 ml/min. Cations are eluted from the column in the following order - Fe, Mg, Al, K, Rb, Ca, Sr.

About 400 ml of 2N HCl were required to elute the Sr^{89} activity down to the base of the resin bed. At this point the elutate was collected in 30 ml fractions in disposable polyethylene beakers. The 30 ml fractions were collected until the Sr^{89} activity fell to background level at the base of the resin bed. The fractions were then evaporated on a low temperature sand bath (250°C) beneath infra-red lamps to ~1 ml. The activity in each beaker was then monitored with a geiger counter and the three or four beakers containing the maximum activity combined. This solution was then further evaporated to ~1 ml, transferred to a small (5 ml) vycor glass beaker and evaporated to dryness. In order to destroy any resin washed out of the column about 0.5 ml $HC1O_4$ was added to the residue in the vycor beaker and evaporated to dryness at 550°C on a hot plate. The residue was then ignited at red heat in a Meeker burner flame to destroy perchlorates. The ignited residue was then taken up in a few drops of 1:1 HCO_3 and evaporated to dryness. The vycor beaker was then sealed with "Parafilm", labelled and stored for mass spectrometric analysis.

Sr and Rb analyses

Sr and Rb were determined by the method of isotope dilution, which involves addition of a known amount of spike to a known weight of sample and subsequent measurement of the resulting isotopic ratio on a mass spectrometer. The spike is a solution of the element to be determined whose isotopic composition has been greatly altered by the enrichment of the isotopes of this element. For maximum precision, it is necessary that the spiking results in a final isotopic ratio as near to unity as possible so that the isotopic ratio can be measured on the same scale of the recording equipment of the mass spectrometer. The principles of isotope dilution have been discussed by Webster (1960).

To achieve an isotopic ratio of unity upon spike addition it is necessary to measure the approximate concentration of the element to be determined in the sample by some other method. Once this is known, the correct amount of spike is easily determined.

In this work approximate Sr and Rb contents of samples were determined by X-ray fluorescence spectrometry using pressed powder pellets.

The spikes employed in this work were enriched in Sr^{86}, Sr^{84} and Rb^{87}. Spike solutions were made up by dissolving accurately known weights of spike in accurately known weights of 2N HCl. Dilute spike solutions were made from concentrated spike solutions by diluting with known weights of 2N HCl. All spike concentrations were calculated on a weight basis, e.g. µg/grm of 2N HCl and the concentrations were cross-checked using shelf solutions of known concentration. The compositions and concentrations of spike solutions are shown in Table 9.

Sr analyses

To a known weight of sample (c. 100 mg) was added sufficient spike to produce an isotopic ratio in the mixture of near unity. Spikes were added on a weight basis using a weighing bottles as follows. The approximate weight of spike was carefully added to a weighing bottle by means of a pipette and the bottle stopper emplaced. The weighing

Table 9. Composition (atom %) and concentration of spikes

Sr^{84} spike ORNL 163101 - Sr $(NO3)_2$

Sr^{84} = 82.24%

Sr^{86} = 3.71

Sr^{87} = 1.56

Sr^{88} = 12.49

Atomic weight of the Sr^{84} spike is 84.5328 (physical). Concentration of Sr^{84} spike No. 1 = 9.031 μgSr/gram of 2N HCl.

Sr^{86} spike ORNL LH1368(A) - $Sr(NO3)_2$

Sr^{84} = 0.05%

Sr^{86} = 97.60

Sr^{87} = 0.68

Sr^{88} = 1.73

Atomic weight of the Sr^{86} spike is 86.0012 (physical). Concentrations of Sr^{86} spike are: No. 1 = 5.260 μgSr/gram 2N HCl

No. 3 =41.292 μgSr/gram 2N HCl

Rb^{87} spike ORNL LY1448(A) - RbCl

Rb^{85} = 0.84%

Rb^{87} = 99.16

Atomic weight of the Rb^{87} spike is 86.8924 (physical).

Concentrations of the Rb^{87} spike are:
No. 1 = 2.815 μgRb/gram 2N HCl
No. 1A = 15.095 μgRb/gram 2N HCl
No. 2 = 2.089 μgRb/gram 2N HCl
No. 4 = 1.131 μgRb/gram 2N HCl

bottle and spike were then accurately weighed on a five place Mettler balance. When using volumes of spike greater than 1 ml evaporation does not take place during the weighing process unless splashes occur on the walls of the weighing bottle. After weighing,the bottle is emptied into the teflon basin containing the sample and then quickly returned to the balance for reweighing to determine the weight of spike added. Care was taken in the final weighing to read the balance immediately after it stabilized (30 secs.) as loss of weight by the evaporation of the few drops of spike remaining in the bottle can be quite rapid.

The sample and spike were then processed in a manner analogous to that employed for samples used to determine strontium isotopic ratios and stored for mass spectrometric analysis.

Rb analyses

Rb spikes were added to samples in the manner described above for Sr. The sample plus spike was then digested overnight in 30 ml HF plus 1 ml $HClO_4$ on a boiling water bath. The solution was then evaporated to fumes of $HClO_4$ and then taken up in 20 ml of 2N HCl. Care was taken to ensure that all the sample went into solution. The solution was then evaporated down to about 1 ml and transferred to a small vycor beaker (5 ml) and stored for mass spectrometric analysis No attempt was made to separate Rb from any other element.

Mass Spectrometry

All mass spectrometric analyses were made with a 10" radius, 90° sector solid source mass spectrometer. A single filament source utilising tantalum ribbon (thickness 0.001", width 0.030") was employed with an accelerating voltage of 5Kv. The source is of the type described by Inghram and Chupka (1952), but multiple filament surface ionization techniques were not employed because under these conditions the source became so hot that during Sr analysis Rb began to emit from the bead resin (AEI style 297157) and the source case plates. Mass spectra were scanned by varying the magnetic field strength. The ion beam was measured with a Faraday coupled to either a Cary 31 or Cary 401 vibrating reed electrometer (VRE). A 10^{11} ohm resistor was employed in the pre-amplifier of the VRE's.

The mass spectra were displayed on a Brush Mark 10 Recorder fitted with engineered chart paper so that direct measurements of peak heights could be made during the analysis. Peak heights were generally of the order of 75% full scale deflection of the recorder.

Vacuum in the mass spectrometer was maintained by two 50 liter/sec. Ultek ion pumps. For all Sr analyses a source vacuum of at least 4×10^{-7} torr was maintained in order to resolve the Sr^{87} peak from the much larger Sr^{88} peak. Vacuum conditions are given in Table 10.

Table 10. Vacuum Conditions. Pressure in torr

	Source	Collector
Sr^{87}/Sr^{86} ratio determinations	9×10^{-8}-4×10^{-7}	4×10^{-8}-2×10^{-7}
Rb-Sr isotope dilutions	2×10^{-7}-8×10^{-7}	9×10^{-8}-4×10^{-7}

Determination of Sr^{87}/Sr^{86} Ratios

Chemically processed Sr samples were dissolved in one drop of vycor distilled 1:1 HNO_3 and loaded onto a tantalum filament which had been pre-baked at high temperature in vacuum to remove any possible Rb and Sr contamination in the tantalum. Loading of the filament was achieved by adding the sample to the centre of the filament by means of a drawn glass capillary pipette. Evaporation of the sample was hastened by passing a slight current through the filament. Every effort was made to ensure that all samples were loaded in the centre of the filament and covered as small an area as possible.

The loaded filament was placed in the mass spectrometer and the system evacuated. The filament current was then slowly turned up (increments of about 0.1 amp.), so that degassing of the sample during nitrate decomposition did not physically blow the sample off the filament, until Sr emission just commenced as indicated by the appearance of the Sr^{88} peak on the 30 mv scale of the VRE. The sample was then left at this temperature for about one hour to burn off any Rb present and to condition the sample. A conditioned sample has a faster response to filament current changes than one that is not and possesses better emission characteristics. The conditioning effect appears to be due to diffusion of the sample into the tantalum filament during its re-crystallisation, the closer contact between tantalum and strontium atoms promoting increased ionisation of Sr. After conditioning, the filament current was gradually increased until steady emission of Sr was achieved. All the determinations of the Sr^{87}/Sr^{86} ratio were made on the same VRE scales (and all on the Cary 31), namely Sr^{88} on 3v, Sr^{87} and Sr^{86} on 300mv. Determination of the Sr^{87}/Sr^{86} ratio was only made when very steady emission had been achieved, e.g. a variation in peak height of less than 25 chart units per 10 minutes of emission (f.s.d. 1000 chart units). A beam intensity which grows or dies outside these limits is unacceptable as the peak height variation introduces large errors into the isotopic ratios. In all the analyses the presence of isobaric contamination at mass 87 by Rb^{87} was checked by scanning the spectrum at mass 85 for the presence of Rb^{85}. No Rb contamination was present in any of the samples reported in this work.

Filament currents employed for determining Sr^{87}/Sr^{86} ratios ranged from 2.4 to 3.0 amps, the majority being 2.6-2.7 amps. The variation in filament currents is considered to be due to variations in the matrix of the sample, position on the filament and length of the filament.

An average analysis for the Sr^{87}/Sr^{86} ratio consisted of recording from 40 to 50 repeated scans of the mass spectrum (masses 86, 87, 88).

Sr Isotope Dilution

The mass spectrometric procedure for Sr isotope dilution was identical to that described for the determination of Sr^{87}/Sr^{86} ratios. Major differences are that there is no isobaric interference from Rb, and that a slightly greater degree of beam intensity variation can be tolerated, e.g. 50 chart units per 10 minutes (f. s. d. 1000 chart units). Analyses were made using the 100 mv and 300 mv scales of both VRE's and consisted of about 25 repeated scans of the appropriate mass numbers, e.g. Sr^{86} and Sr^{88} or Sr^{84} and Sr^{86} depending upon the spike employed. Filament currents ranged 2.3 to 2.8 amps.

Rb Isotope Dilution

A few drops of the sample solution were evaporated to dryness on a baked tantalum filament, enough current was passed through the filament to completely degass it. The sample was then loaded into the mass spectrometer and the system evacuated. The filament current was increased slowly (by 0.1 amp. increments) to about 1 amp., thereafter the current was increased very slowly (1 division increments of the turns counting dial of the power supply) until the first traces of Rb emission appeared on the 30 mv scale of the VRE. The Rb beam was then left for a few minutes to "grow in" (e.g. increase in Rb emission for no current increase) until a steady beam was obtained. The current was then slightly increased and the "growing in" procedure repeated until the Rb peaks registered on the 100 mv scale of the VRE. If this slow current increase procedure is not followed Rb emission is rapid and unstable, and the Rb is quickly burnt off the filament. Beam intensity variation during runs was similar to that obtained for Sr isotope dilutions. About 25 scans of the mass spectrum (masses 85 and 87) were taken. Filament currents ranged from 1.3 to 1.6 amps.

Data Reduction

Sr^{87}/Sr^{86} Ratios

Sr^{86}/Sr^{88} ratios and Sr^{87}/Sr^{86} ratios were calculated from the mass spectra as averages of sets of four scans. Significant mass fractionation occurs during Sr isotopic analyses due to fractionation from the filament during emission. The Sr^{86}/Sr^{88} can be used as a measure of the degree of fractionation if it is assumed that normal unfractionated Sr has a constant Sr^{86}/Sr^{88} ratio of 0.1194 (Nier 1938, Faure and Hurley 1963). Consequently, all the measured Sr^{86}/Sr^{88} ratios have been adjusted to this value. The deviation of the measured Sr^{86}/Sr^{88} ratio from the assumed value is also used to correct the measured Sr^{87}/Sr^{86} ratio for fractionation. Only one half of the correction to the Sr^{86}/Sr^{88} ratio is applied to the measured Sr^{87}/Sr^{86} ratio as the mass difference between Sr^{87} and Sr^{86} is only one half of that between Sr^{86} and Sr^{88}. This method of correction results in a marked improvement in the reproducibility of the Sr^{87}/Sr^{86} ratios. The calculation of a corrected Sr^{87}/Sr^{86} ratio is outlined below:

If the measured $(Sr^{87}/Sr^{86})_M$ ratio = 0.7072 and the measured $(Sr^{86}/Sr^{88})_M$ ratio = 0.1199, then the corrected $(Sr^{87}/Sr^{86})_C$ ratio is defined as follows:

$$(Sr^{87}/Sr^{86})_C = (Sr^{87}/Sr^{86})_M \left[\frac{(Sr^{86}/Sr^{88})_M + 0.1194}{0.2388} \right]$$

$$(Sr^{87}/Sr^{86})_C = 0.7072 \times 1.00209$$

$$(Sr^{87}/Sr^{86})_C = 0.7087.$$

The final average corrected Sr^{87}/Sr^{86} ratio of the sample is obtained by averaging the ratios of the sets. An instrumental precision error designated $\overline{E}$ was calculated for each run from the ratios obtained from the sets. This is the per cent standard deviation of the mean of the sets, e.g.

$$\bar{\sigma} = \sqrt{\sum \frac{d^2}{n(n-1)}}$$ where $\bar{\sigma}$ is the standard deviation of the sets

$$\bar{E}\% = \frac{\bar{\sigma}}{\bar{X}} \times 100$$ n is the number of sets

$d^2 = (\bar{X} - X)^2$ where $\bar{X}$ = mean

X = average of 4 sets

This error is a measure of the internal scatter of the Sr^{87}/Sr^{86} ratios within a single run and is a useful criterion for judging the quality of an analysis. Faure and Hurley (1963) consider that an analysis is satisfactory when $E < 0.1\%$. This criterion was satisfied for all the determinations of the Sr^{87}/Sr^{86} ratio in this work.

Isotope Dilutions

For isotope dilutions no correction can be made for internal fractionation, concentrations of elements are calculated directly from the measured isotopic ratios according to the general isotope dilution equation:

$$(R)_m = \frac{A(N) + C(S)}{B(N) + D(S)}$$

where A and B are the natural isotopic abundances of two isotopes of any element and C and D are the isotopic abundances of the same two isotopes in a spike which is preferentially enriched in one of these isotopes compared to the natural abundances. (N) and (S) are the total numbers of atoms of normal and spike respectively, and $(R)_m$ is the resulting isotopic ratio of a mixture of normal and spike atoms.

The equation is solved for the atomic ratio N/S which can be transformed to a weight ratio by multiplication by a weight factor (k) = (atomic weight normal element)/(atomic weight spike). Therefore,

$$(N/S)_{wt} = (N/S)_{atom} \times \frac{\text{(Atomic weight normal element)}}{\text{(Atomic weight of spike)}}$$

The (N/S) weight ratio is then solved for N, the weight of the normal element in the sample

$$N = \left(\frac{N}{S}\right)_{atom} \times (k) \times \frac{\text{(weight of spike added)}}{\text{(weight of sample taken)}} \ \mu\text{gm/gram of sample i.e. ppm.}$$

Precision and Accuracy of Results

Isotopic analyses by mass spectrometry are subject to several errors most of which are difficult to predict or even evaluate with any certainty. For example, errors due to sample inhomogeneity, contamination during chemical processing, variable effects of mass fractionation in the mass spectrometer, electronic noise, instrumental drift, instability of accelerating voltage or magnetic field strength, VRE scale errors, non-linearity of VRE's and recorders, and the reading of the chart must be considered in an evaluation of the data. Most of these sources of error are random and thus affect the precision and accuracy of single analyses. Some errors, such as contamination,may be systematic for a single analysis but random for a series of analyses. Other errors are constant for all analyses, e.g. non-linearity of instruments.

Attempts to eliminate some of these errors can be made. All the Sr^{87}/Sr^{86} ratios were determined on the same scales of the Cary 31 VRE with approximately the same peak heights so that any error introduced here remains constant. The effects of isotopic fractionation were corrected for by normalisation of the isotopic ratios to an assumed arbitrary constant value of Sr^{86}/Sr^{88}.

Contamination does not present a serious problem in the present series of analyses because of the generally high levels of concentration of Sr and Rb in kimberlites, hence blank corrections are insignificant in most cases. Blank corrections have been applied to all the analyses. Table 11 gives the levels of contamination of Rb and Sr incurred during the processing of 100 mg samples. The levels compare favourably with those found by other workers.

The precision of the Sr^{87}/Sr^{86} ratios was determined by replicate analyses of the M.I.T. $SrCO_3$ standard (Eimer and Amend Lot No. 492327) and a triplicate sample analysis (Tables 12, 13) and was calculated as the standard deviation of a single analysis (σ)

$$\sigma = \sqrt{\frac{\sum d^2}{n-1}}$$ where d^2 is the square of the deviation from the mean ($\bar{X}$) of n replicate analyses.

and $$R\% = \sigma/\bar{X} \times 100$$

A precision error of ±0.001 implies a 68% probability that an additional measurement will fall within a band 0.001 above or below the value of the mean. The precision error (σ) as defined above is generally greater than the instrument precision error ($\bar{\sigma}$) because it includes errors resulting from sample inhomogeneity and contamination as well as all the variable and constant errors of the mass spectrometry. Tables 12, 13 show that the precision σ obtained in this work is well within the acceptable limits of ±0.001 (Faure and Hurley 1963).

The absolute accuracy of a Sr^{87}/Sr^{86} ratio cannot be determined because the true value of the measured quantity is usually not known. Analysis of the M.I.T. $SrCO_3$ standard provides an inter-laboratory standard which enables comparision of results obtained by other workers. The Sr^{87}/Sr^{86} ratio of this standard given in Table 12 compares favourably with the values obtained in other laboratories.

Isotope dilution analyses are subject to certain errors in addition to those which apply to Sr isotopic analysis. The most important errors being those incurred during the spiking procedure and those incurred due to lack of fractionation corrections.

Triplicate isotope dilution analyses for Rb and Sr are given in Tables 14 and 15. The errors are within the range of from ±1 to 5% expected for the technique (Webster 1960).

Analytical results for the determination of the Sr^{87}/Sr^{86} ratio of kimberlites are given in Table 16 or for rocks of the Fen complex in Table 17. Rb and Sr concentrations of kimberlites and Fen rocks are given in Tables 18 and 19 respectively.

Sr concentrations for the Fen rocks were obtained by atomic absorption analysis. Also given in Table 19 is the Rb content as determined by atomic absorption. For silicate rocks this value is within 10% of the isotope dilution value. For carbonatitic rocks the value bears little correspondence to the isotope dilution value, this deviation probably being due to an interference effect.

Table 11. Rb and Sr blank determinations. Concentrations are in µgm/100 mg of sample processed.

Rb		Sr	
1.	0.021	1.	0.032
2.	0.003	2.	0.020
3.	0.003	Average Sr blank	0.026 µgms Sr/ 100 mg sample
4.	0.006		
Average Rb blank	0.008 µgms Rb/ 100 mg sample		

Table 12. Isotopic Composition of the M. I. T. Standard $SrCO_3$.

(Aimer and Emend Lot 492327)

No.	$(Sr^{87}/Sr^{86})_M$	$(Sr^{86}/Sr^{88})_M$	$(Sr^{87}/Sr^{86})_C$	$\bar{\sigma}$	$\bar{E}$%
1.	0.7062	0.1201	0.7082	±0.0002	0.03
2.	0.7028	0.1212	0.7083	±0.0002	0.03
3.	0.7044	0.1207	0.7082	±0.0001	0.01
4.	0.7060	0.1204	0.7088	±0.0003	0.04
5.	0.7086	0.1193	0.7083	±0.0004	0.06
6.	0.7080	0.1194	0.7080	±0.0001	0.01
7.	0.7038	0.1210	0.7086	±0.0005	0.07

Mean $\bar{X}$ = 0.7083

σ = ±0.0003

R% = ±0.04

$Sr^{87}/Sr^{86} = 0.7083 \pm 0.0003$

Table 13. Isotopic Composition of Doornkloof Kimberlite

No.	$(Sr^{87}/Sr^{86})_M$	$(Sr^{86}/Sr^{88})_M$	$(Sr^{87}/Sr^{86})_C$	$\bar{\sigma}$	$\bar{E}\%$
1.	0.7106	0.1211	0.7156	±0.0002	0.03
2.	0.7144	0.1197	0.7152	±0.0003	0.04
3.	0.7155	0.1194	0.7155	±0.0004	0.05
		Mean $(\bar{X})$	= 0.7154		

σ = ±0.0002

R% = ±0.03

Sr^{87}/Sr^{86} = 0.7154±0.0002

Table 14. Precision of Sr Analyses

1. Swartruggens		Sr p.p.m.
a.		1138.3
b.		1146.8
c.		1126.4
	Mean ($\bar{X}$)	= 1137.2
	σ	= 10.25
	R%	= ±0.9%
Therefore	Mean	= 1137±10

Table 15. Precision of Rb Analyses

Granite-Gneiss		Rb p.p.m.
a.		156.6
b.		153.6
c.		156.2
	Mean ($\bar{X}$)	= 155.5
	σ	= ±1.6
	R%	= 1.0%
Therefore	Mean	= 156±2

Table 16. Isotopic Composition of Strontium in Kimberlites.

No.	Location	$(Sr^{87}/Sr^{86})_M$	$(Sr^{86}/Sr^{88})_M$	$(Sr^{87}/Sr^{86})_C$	$\bar{\sigma}$	$\bar{E}$%
1.	Swartruggens	0.7084	0.1205	0.7117	±0.0004	0.06
2.	Swartruggens	0.7032	0.1212	0.7087	±0.0003	0.04
3.	Swartruggens	0.7076	0.1198	0.7088	±0.0002	0.03
4.	Swartruggens	0.7025	0.1217	0.7094	±0.0002	0.03
5.	Swartruggens	0.7060	0.1207	0.7099	±0.0004	0.06
6.	Swartruggens	0.7046	0.1212	0.7098	±0.0004	0.06
7.	Swartruggens	0.7116	0.1198	0.7128	±0.0002	0.03
8.	Swartruggens	0.7152	0.1198	0.7163	±0.0002	0.03
9.	Swartruggens	0.7119	0.1206	0.7139	±0.0004	0.06
10.	Wesselton(P)	0.7095	0.1204	0.7123	±0.0002	0.03
11.	Wesselton(P)	0.7042	0.1209	0.7088	±0.0003	0.04
12.	Wesselton(P)	0.7053	0.1202	0.7078	±0.0006	0.08
13.	Wesselton(P)	0.7060	0.1209	0.7103	±0.0002	0.03
14.	Wesselton(P)	0.7061	0.1200	0.7080	±0.0003	0.04
15.	Wesselton(P)	0.7096	0.1202	0.7120	±0.0007	0.09
16.	Wesselton(D)	0.7151	0.1195	0.7154	±0.0006	0.08
17.	Wesselton(D)	0.7118	0.1194	0.7118	±0.0005	0.07
18.	Wesselton GMP	0.6971	0.1224	0.7058	±0.0006	0.08
19.	Wesselton ECL	0.7053	0.1218	0.7123	±0.0004	0.06

Table 16. (continued)

No.	Location	$(Sr^{87}/Sr^{86})_M$	$(Sr^{86}/Sr^{88})_M$	$(Sr^{87}/Sr^{86})_C$	$\bar{\sigma}$	$\bar{E}$%
20.	Premier	0.7138	0.1200	0.7156	±0.0002	0.03
21.	Premier	0.7170	0.1197	0.7180	±0.0005	0.07
22.	Premier	0.7176	0.1207	0.7214	±0.0007	0.09
23.	Monastry	0.7065	0.1195	0.7067	±0.0006	0.08
24.	Dutoitspan	0.7067	0.1193	0.7063	±0.0004	0.06
25.	Bultfontein	0.7020	0.1207	0.7058	±0.0003	0.04
26.	Doornkloof	0.7119	0.1205	0.7152	±0.0005	0.07
27.	Kirkland Lake	0.7095	0.1198	0.7082(1)	±0.0004	0.06

Notes. (1) Initial ratio is 0.7072. Age correction for 151 m.y. (Lee & Lawrence 1968).

(P) pipe rock; (D) late stage dyke; GMP garnet mica peridotite; ECL eclogite.

Sample locations and petrography given in Appendix I.

Table 17. Isotopic Composition of Sr in Fen Rocks

No.	Rock	$(Sr^{87}/Sr^{86})_M$	$(Sr^{86}/Sr^{87})_M$	$(Sr^{87}/Sr^{86})_C$	$\bar{\sigma}$	$\bar{E}\%$
1.	Melteigite	0.7084	0.1182	0.7049	±0.0003	0.04
2.	Vipetoite	0.7067	0.1200	0.7086	±0.0003	0.02
3.	Søvitic Melteigite	0.7037	0.1207	0.7074	±0.0001	0.01
4.	Søvitic Melteigite	0.7023	0.1206	0.7058	±0.0002	0.03
5.	Søvitic Melteigite	0.7061	0.1203	0.7086	±0.0002	0.03
6.	Søvite	0.7062	0.1183	0.7028	±0.0003	0.04
7.	Søvite	0.7062	0.1195	0.7064	±0.0003	0.04
8.	Rauhaugite	0.7070	0.1205	0.7104	±0.0002	0.03
9.	Rødberg	0.7048	0.1206	0.7083	±0.0003	0.04
10.	Damtjernite	0.7062	0.1202	0.7085	±0.0003	0.04
11.	Malignite	0.7099	0.1193	0.7096	±0.0004	0.06
12.	Fenite	0.7186	0.1196	0.7193	±0.0003	0.04
13.	Fenite	0.7128	0.1194	0.7128	±0.0003	0.04
14.	Granite-Gneiss	0.7272	0.1199	0.7287	±0.0003	0.04

Notes: Sample locations are given in Appendix I.

Table 18. Rb and Sr contents of Kimberlites (p.p.m.)

No.	Location	Rb	Sr	Rb/Sr
1.	Swartruggens	208	1138	0.183
2.	Swartruggens	93	817	0.113
3.	Swartruggens	136	835	0.163
4.	Swartruggens	265	1462	0.181
5.	Swartruggens	20	274	0.075
6.	Swartruggens	63	377	0.167
7.	Swartruggens	195	1498	0.130
8.	Swartruggens	147	622	0.237
9.	Swartruggens	254	1099	0.231
10.	Wesselton(P)	121	1118	0.108
11.	Wesselton(P)	94	1472	0.064
12.	Wesselton(P)	88	1201	0.073
13.	Wesselton(P)	122	1136	0.107
14.	Wesselton(P)	80	751	0.107
15.	Wesselton(P)	113	1004	0.112
16.	Wesselton(D)	95	1232	0.077
17.	Wesselton(D)	94	1282	0.073
18.	Wesselton GMP	20	83	0.242
19.	Wesselton ECL	7	68	0.108
20.	Premier	15	284	0.053
21.	Premier	18	101	0.182
22.	Premier	5.6	48	0.095
23.	Monastry	5.3	592	0.009
24.	Dutoitspan	4.5	994	0.005
25.	Bultfontein	64	569	0.113
26.	Doornkloof	109	1883	0.058
27.	Kirkland Lake	205	1302	0.157

Table 19. Rb and Sr content of Fen Rocks (in p. p. m.)

No.	Rock	Sr(AA)	Rb(ID)	Rb(AA)	(Rb/Sr)	% Erro Rb(AA
1.	Melteigite	2089	41	31	0.020	- 24
2.	Vipetoite	1033	56	45	0.054	- 20
3.	Søvitic Melteigite	1466	99	146	0.068	+ 47
4.	Søvitic Melteigite	4181	8.7	0	0.002	-
5.	Søvitic Melteigite	2144	329	564	0.153	+ 71
6.	Søvite	7027	3.8	0	0.0005	-
7.	Søvite	5749	2.5	10	0.0004	+233
8.	Rauhaugite	4606	2.9	0	0.0006	-
9.	Rødberg	1572	0.6	3	0.0004	+200
10.	Damtjernite	1022	68	55	0.067	- 24
11.	Malignite	1593	137	147	0.086	+ 7
12.	Fenite	297	128	130	0.430	+ 2
13.	Fenite	293	44	38	0.151	- 9
14.	Granite-Gneiss	294	155	170	0.533	+ 10

Notes:

Sr(AA) - Sr determined by atomic absorption. Analyst Mr. J. Muysson

Rb(AA) - Rb " " " " "

Rb(ID) - Rb determined by isotope dilution.

Rb/Sr ratios are calculated from Rb(ID) and Sr(AA) values

% Error Rb(AA) indicates the deviation of Rb(AA) from Rb(ID) in terms of a percent error from the Rb(ID) value.

The Rubidium-Strontium System

Sr has four naturally occurring stable isotopes Sr^{84}, Sr^{86}, Sr^{87} and Sr^{88}. One of these Sr^{87} is in part produced by the radioactive decay of Rb^{87} and therefore its abundance is variable with time. The abundance of Sr^{87} is normalised to the abundance of Sr^{86} which has remained constant throughout time and is commonly expressed as the Sr^{87}/Sr^{86} ratio. For any closed Rb-Sr system the rate of growth of the Sr^{87}/Sr^{86} ratio is proportional to the Rb/Sr ratio. Thus, the Sr^{87}/Sr^{86} ratio which is measured in any system today is dependent upon the time the system has remained closed to Rb and Sr migration, the initial Sr^{87}/Sr^{86} ratio of the system, the Rb/Sr ratio of the system and the decay constant of Rb^{87}. The value of the decay constant (λ) used in the present work is 1.47×10^{-11} years^{-1} (Flynn and Glendenin 1959, McMullen et al. 1966). The decay of Rb^{87} to its daughter product Sr^{87} can be represented by the radioactive decay equation

$$Rb_p^{87} = Rb_o^{87} e^{-\lambda t} \qquad (1)$$

where Rb_p^{87} = present number of Rb^{87} atoms

Rb_o^{87} = initial number of Rb^{87} atoms

t = time during which radioactive decay has occurred.

The amount of the radiogenic daughter $^{*}Sr^{87}$ is

$$^{*}Sr^{87} = Rb_o^{87} - Rb_p^{87} = Rb_p^{87}\,(e^{\lambda t}-1) \qquad (2)$$

The total number of atoms of the isotope Sr^{87} in a given system is:

$$Sr^{87} = Sr_o^{87} + {}^{*}Sr^{87} \qquad (3)$$

where Sr_o^{87} is the number of Sr^{87} atoms at time t=0. Therefore the total number of atoms of Sr^{87} in a given system at any time t is

$$Sr_t^{87} = Sr_o^{87} + Rb_p^{87}(e^{\lambda t}-1) \qquad (4)$$

Each term in equation (4) can be normalised to the number of Sr^{86} atoms which remains constant thus:

$$(Sr^{87}/Sr^{86})_t = (Sr^{87}/Sr^{86})_o + \frac{Rb_p^{87}}{Sr^{86}}\,(e^{\lambda t}-1) \qquad (5)$$

When $t \gg (\lambda t)^2/2!$ the term $(e^{\lambda t}-1)$ can be approximated to λt. For young systems the error introduced is negligible. For samples of age commensurate with the age of the earth an error of about 3% is introduced. This equation (5) reduces to

$$\left(\frac{Sr^{87}}{Sr^{86}}\right)_t = \left(\frac{Sr^{87}}{Sr^{86}}\right)_o + \frac{Rb_p^{87}}{Sr^{86}}\,\lambda t \qquad (6)$$

N.B. All the terms in equation (6) are atom ratios. Equation (6) defines a straight line of the type $y = mx+c$ and provides two models for interpreting Rb-Sr data.

A. Isochron Model - Nicolaysen diagrams

In this model $y = (Sr^{87}/Sr^{86})_t$

$m = \lambda t$ (slope)

$x = Rb^{87}_p/Sr^{86}$

$c = (Sr^{87}/Sr^{86})_o$ i.e. intercept on y axis when $x=0$.

An isochron is illustrated in Fig. 15. Whole rocks of differing Rb/Sr ratio lie on a straight line representing constant time and called an isochron, the model is useful in determining whether or not a given suite of samples are cogenetic. Full discussions of the theory of Rb-Sr isochrons are given by Hamilton (1964), Nicolaysen (1961) and Lamphere et al. (1963).

B. Development Diagrams

In this model $y = (Sr^{87}/Sr^{86})_o$

$m = \lambda Rb^{87}/Sr^{86}$

$x = -t$

$c = (Sr^{87}/Sr^{86})_p$ (intercept on y at time t=0

i.e. present).

A development diagram is shown in Fig. 16. When using this type of diagram it is convenient to express the $^{87}Rb/Sr^{86}$ atom ratio as a weight ratio. Thus,

$$(Rb_p^{87}/Sr^{86})_{atom} = (Rb/Sr)wt \times \frac{\text{Atomic weight of Sr} \times \text{Abundance of } Rb^{87}}{\text{Atomic weight of Rb} \times \text{Abundance of } Sr^{86}}$$

(N.B. Since the atomic weight of Sr and the abundance of Sr^{86} varies slightly depending upon the abundance of radiogenic Sr^{87}, the value of the conversion factor should strictly be evaluated for each sample. The value of the conversion factor increases by 1.35% when the isotopic composition of Sr varies between the limits Sr^{87}/Sr^{86} 0.712-0.850. For the samples studied in the present work, a constant conversion factor equivalent to Sr^{87}/Sr^{86} 0.712 has been used.)

Thus,

$$(Rb_p^{87}/Sr^{86})_{atom} = (Rb/Sr)wt \times \frac{(87.6165 \times 0.2785)}{(85.557 \times 0.0986)}$$

$$= (Rb/Sr)wt \times 2.893$$

Therefore, the slope m of a development line is (Rb/Sr)wt x 2.893 x λ.

Development diagrams are of use in interpreting crust-mantle isotopic relationships. The initial Sr^{87}/Sr^{86} ratio of the earth as a system is based upon analyses of meteorites which 4.5 b.y. ago possessed an initial Sr^{87}/Sr^{86} ratio of 0.698 (Shields 1964, Pinson et al. 1963, Hedge and Wallhall 1963). The isotopic composition of Sr in recent oceanic volcanic rocks is thought to be representative of the isotopic composition of the upper mantle at the present time, the Sr^{87}/Sr^{86} ratios of these rocks are low 0.702-0.704 as are the Rb/Sr ratios 0.04-0.06. This present day mantle ratio is thought to have grown from an initial value of 0.698 during the last 4.5 b.y. (Faure and Hurley 1963, Hurley 1967). The primary growth lines of the Sr^{87}/Sr^{86} ratio in the source regions of basalt (upper mantle) are shown in Fig. 16.

Chemical differentiation processes operating since early in geologic time have resulted in an enrichment of Rb in the upper regions of the continental crust. Therefore it is expected that the abundance of Sr^{87} has increased at a greater rate in the crust than in the upper mantle. This crustal material exhibits higher Sr^{87}/Sr^{86}

ratios (e.g. greater than 0.720) and high Rb/Sr ratios (e.g. 0.25). Fig. 16 illustrates the separation of material possessing a high Rb/Sr ratio from the source regions of basalt 1.5 b.y. ago (line AB).

Faure and Hurley (1963) have advanced the hypothesis that there is sufficient enrichment of Sr^{87} in crustal materials so that the value of the Sr^{87}/Sr^{86} ratio (initial ratio) of igneous rocks at the time of crystallisation can be used as a criterion for the origin of the material. The initial ratio of an igneous rock formed by assimilation, remelting or granitisation of old crustal material enriched in Rb is thus expected to be measurably higher than that of rocks derived from the upper mantle regions.

Faure and Hurley's 1963 hypothesis has gained general acceptance but it should be realised that the following assumptions are made:

1. The earth originally had an isotopic composition of Sr akin to that of meteorites.
2. The present distribution of Rb and Sr in the upper mantle is relatively uniform, e.g. it possesses a constant Rb/Sr ratio. This assumption also requires that the lower mantle also is well mixed and is of the similar composition.
3. All igneous rocks of low Sr^{87}/Sr^{86} ratio are derived from the source regions of (oceanic) basalts.

4. All igneous rocks of high Sr^{87}/Sr^{86} ratio are somehow related to crustal process or have been in contact with crustal material.

Whether or not those assumptions are justified is uncertain. Of particular importance is the fact that geochemical studies are beginning to reveal that the upper mantle is heterogeneous, e.g. basalts have distinct Sr contents in different regions of the earth (Turekian 1963). Variations in the Sr^{87}/Sr^{86} ratios of oceanic basalts between islands can only reflect slight variations in the Rb/Sr ratio of the underlying mantle (Gast et al. 1964, Bence 1966). The concept of a mantle which is chemically zoned due to varying degrees of partial melting is considered valid by several petrologists (Gast 1966, Clark and Ringwood (1964), Oxburg and Turcotte 1968). There is also considerable evidence that degassing of the earth is still taking place (Ruby 1951, Nicholls 1968) which casts some doubt on the postulate that the mantle is well mixed.

No allowance is made for the fact that crustal rocks may possess low Rb/Sr ratios (Heier 1964) or for the occurrence of potassium-rich (and hence Rb-rich) low melting phases in the mantle. That all igneous rocks originate in the source regions of (oceanic basalts) is definitely a questionable assumption.

Several groups of rocks, e.g. alpine ultramafic rocks (Steuber and Murthy 1966) and alkaline oceanic basalts (Bence 1966) do not fit into the simple development scheme as their development

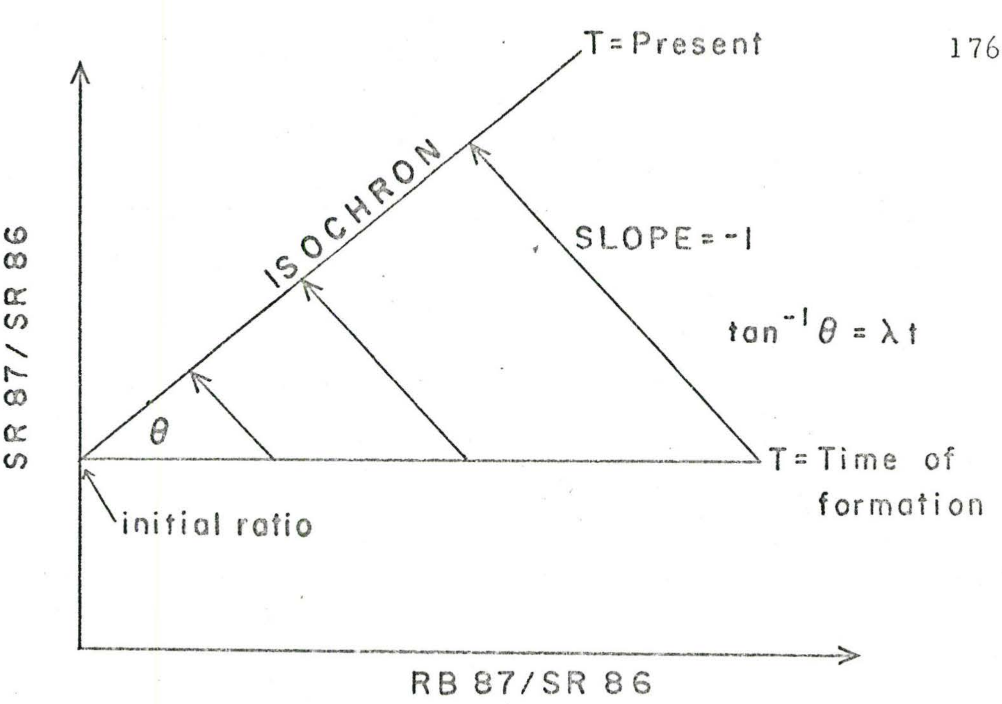


FIG.15. RB-SR ISOCHRON MODEL, A NICOLAYSON DIAGRAM.

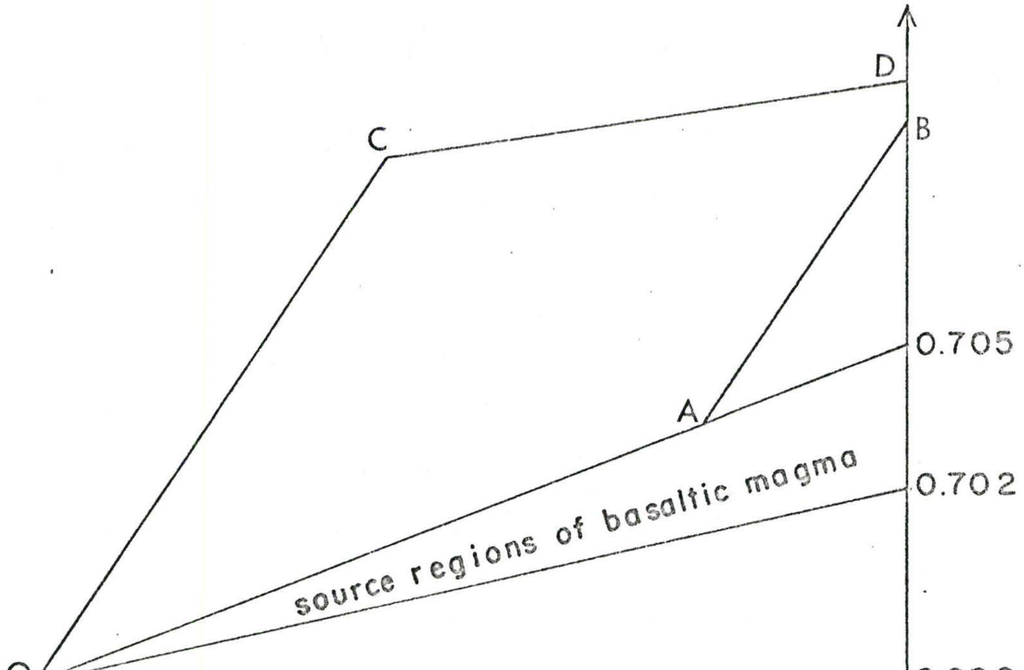


FIG.16. RB-SR DEVELOPMENT DIAGRAM.

lines do not intersect the development lines for the source regions of basalt. Such deviations are commonly explained by assuming that the rocks underwent two stages of development and that they represent melts of residues from a system which previously possessed a high Rb/Sr ratio (e.g. line OCD, Fig. 16).

CHAPTER SEVEN

STRONTIUM ISOTOPES AND KIMBERLITE PETROGENESIS

Previous Studies

Very little is known of the isotopic composition of Sr in kimberlites. Table 20 summarises the available data.

Powell (1962, 1966) has concluded that his data are consistent with Dawson's (1966) hypothesis that kimberlite forms by reaction between granite and carbonatite. Powell (1962) also noted that the high Sr^{87}/Sr^{86} ratios could be due to the presence of small inclusions of country rock, although he discounts the possibility as being likely (see below). Powell's (1962, 1966) data are incomplete in that no reference is made as to the condition of the specimens studied, i.e. whether they were yellow ground, blue ground, brecciated or massive kimberlite, moreover Powell (1966) fails to note that the Premier pipe is of Precambrian age (Jones and McElhinny 1966) and thus the Sr^{87}/Sr^{86} ratios given are not initial ratios.

Bardet and Vachette (1966) have considered that the Sr^{87}/Sr^{86} ratios of kimberlites appear to be related to those of crustal rocks and that "kimberlite is already a differentiated rock".

Brookins (1967) has analysed carbonates extracted from the upper levels of the Riley Co. kimberlite pipes of Kansas and has concluded that the isotopic composition of Sr is due to contamination of carbonatite Sr with Sr derived from country rock limestones and shales.

Table 20. Isotopic composition of Sr in kimberlites found by previous investigators

Powell (1962, 1966)	Sr^{87}/Sr^{86}	Bardet and Vachette (1966)	Sr^{87}/Sr^{86}
Premier R4831	0.721	Seguela	0.706
Premier R40	0.711	Sekonomata	0.712
Premier R41	0.711	Koidu	0.713
Premier R42	0.717		
Kimberley R5015	0.706	Brookins (1967) - Interstitial	
Kimberley R4829	0.707	and Replacement Carbonates	
Monastry R4830	0.718	Bala	0.7075
Murfreesboro R4832	0.708	Randolph No. 1	0.7051-7057
Marakabei	0.705	Randolph No. 2	0.7055-7066
Koidu	0.707		
Koidu	0.706		

Results of the present work

Fig. 17 illustrates data for the Swartruggens kimberlite in the form of a development diagram. The Swartruggens kimberlite is situated about 5 miles NNW of the town of Swartruggens, N. Transvaal. The kimberlite consists of a series of vertical dykes ranging in thickness from one inch to seven feet. The dykes meander and split in many directions and become thicker in depth. Not all of the dykes encountered in the mines outcrop and it is postulated that a large kimberlite body exists at depth. The dykes are emplaced in the middle Precambrian Ongeluk basic lavas of the Pretoria series and intersect an earlier series of quartz veins. A zone of carbonitisation extends beyond the dykes into the lavas (Fourie 1958, DeKun 1965). All the samples analysed in the present work were of massive unweathered kimberlite, except for two samples of yellow ground (numbers 2 and 5). No country rock xenoliths were present in any of the samples. The Swartruggens kimberlite is a typical fissure kimberlite and is a micaceous calcareous type. Deuteric alteration of the kimberlite has been extensive and all pre-existing olivine has been converted to serpentine and calcite, much of the phenocrystal phlogopite has been altered to chlorite and been replaced by carbonates.

The Sr^{87}/Sr^{86} ratios range from 0.709-0.716 and average 0.711. The regression lines illustrated in Fig. 17 cut the mantle-basalt development lines at very old Precambrian ages in contradiction to the estimated Cretaceous geological age. /N.B. The Pretoria kimberlite group is of Precambrian age (Jones & McElhinney 1966, Allsopp et al. 1967) and forms a distinctly separate group of kimberlites from the Cretaceous-Tertiary groups of Lesotho and Central S. Africa. The Swartruggens kimberlite and a number of other kimberlites lying to the N.W. of Pretoria may also belong to the Pretoria group and also be of Precambrian age. Fig. 17 shows that development lines for the majority of the Swartruggens samples cut the uppermost mantle-development line at 750-1250 m.y. in the past indicating initial ratios of from 0.703-0.704/.

Fig. 18 presents data for the Wesselton kimberlite pipe. This is a typical pipe and is one of the important Kimberley group of pipes. It is emplaced in a thick series of metamorphic, volcanic and sedimentary rocks. From oldest to youngest these being gneisses of the basement Swaziland system, the Ventersdorp lavas and quartzites and the Dwyka series. Inclusions of the Stormberg basalts, now completely eroded away in the area, can be found in the pipe along with inclusions of all the other country rocks. The kimberlite is an olivine-rich mica poor type. All the samples analysed in this study were of very fresh unweathered massive kimberlite, in fact much of the olivine was unserpentinised. Samples containing inclusions of country rock were avoided. Included in the data are examples of some of the late stage, fine grained cross-cutting dykes which appear to be contemporary with the major parts of the pipe but which represent a later stage of the intrusion. The rocks are xenolith free and have been described by Williams (1932, p. 125). Similar late stage dykes have been found in other pipes (Wagner 1914).

The Wesselton Sr^{87}/Sr^{86} ratios range from 0.708-0.715, the highest ratios being found in the late stage dykes. Once again regression lines cut the mantle-basalt development line at impossibly old ages in contrast to the known geological age, i.e. post-Karroo, possibly late Cretaceous to early Tertiary.

Fig. 19 presents data for the Monastry, Dutoitspan and Bultfontein kimberlites and the Doornkloof and Kirkland Lake (Ontario) micaceous kimberlites. Regression lines are similar to those found for the Swartruggens and Wesselton kimberlites in that they cut the mantle-basalt development lines at impossibly old ages.

Fig. 20 illustrates development lines for garnet-peridotite and eclogite xenoliths found in kimberlites. Data are from this work, Faure (1961), Steuber and Murthy (1966) and Allsopp et al. (1969). The development lines are very similar to those found for kimberlites. It should be noted that the whole rock Sr^{87}/Sr^{86} ratios of garnet peridotites from Wesselton (18 and Af-7) are lower than those found in the whole rock kimberlite at Wesselton.

Fig. 21 illustrates the relation between whole rock Sr^{87}/Sr^{86} ratios and the abundance of Sr in all the samples except the Swartruggens yellow ground and the Premier pipe samples. Within an individual kimberlite body no relation exists between the isotopic composition of Sr and the total Sr content. However, for the total number of samples there appears to be an increase in this ratio with increase in Sr content, but the trend is not well defined.

Fig. 22 illustrates the relation between the Sr^{87}/Sr^{86} ratio and the abundance of Rb in all the kimberlites except the Swartruggens yellow ground and the Premier pipe samples. It can be seen that the Sr^{87}/Sr^{86} ratio bears no relation to the Rb content. Other conclusions which can be drawn from the data given in Tables 16 and 18 are:

1. There is no significant difference between whole rock Sr^{87}/Sr^{86} ratios of micaceous kimberlite and olivine-rich kimberlite, i.e. in this case between fissure and pipe kimberlite.
2. Sr contents of kimberlite range from 569-1472 ppm and average 1032 ppm. Sr contents of micaceous kimberlite range from 377-1883 ppm and average 1135 ppm.

3. Rb contents of kimberlite range from 4.5-122 ppm and average 80 ppm. Rb contents of micaceous kimberlites range from 63-265 ppm and average 176 ppm.

4. Rb/Sr ratios of kimberlites (0.005-0.11; average 0.077) are, as expected, lower than those of micaceous kimberlites (0.06-0.24, average 0.155).

Serpentinisation

As kimberlites are in general extensively serpentinised, it is important to enquire as to how such processes might have affected the isotopic composition of Sr and trace element abundances.

The few previous studies of the effects of serpentinisation have been summarised by Steuber (1965) who concluded that serpentinisation had no effect upon the concentration of Na, Mn, Cr, Sc, Co, K, Rb and Sr in ultramafic rocks. Steuber (1965) and Roe (1964) have also concluded, on the basis that fresh dunite and serpentinised dunite

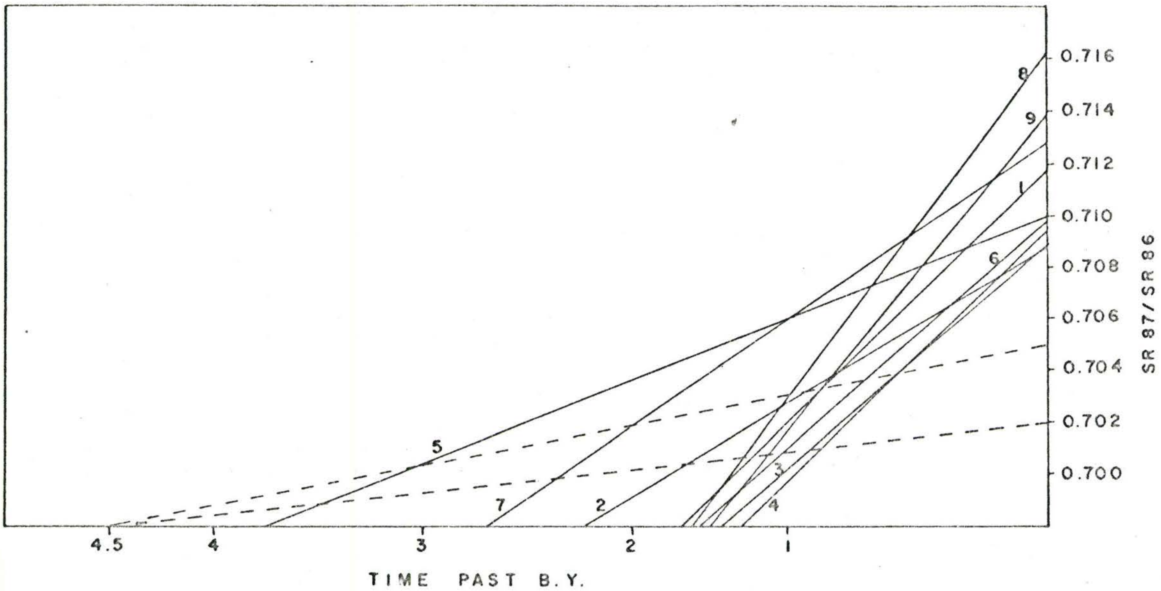


FIG. 17. DEVELOPMENT DIAGRAM FOR SWARTRUGGENS KIMBERLITES.

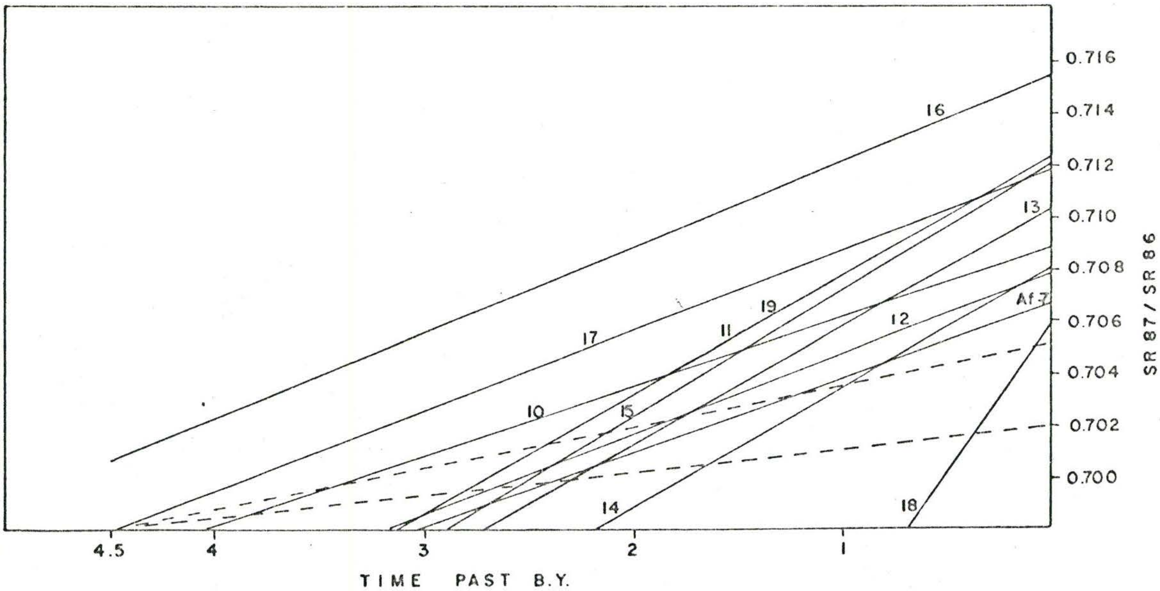


FIG. 18. DEVELOPMENT DIAGRAM FOR WESSELTON KIMBERLITES, GARNET PERIDOTITES (18 AND Af-7) AND ECLOGITE (19). DATA FOR Af-7 FROM STEUBER AND MURTH (1966).

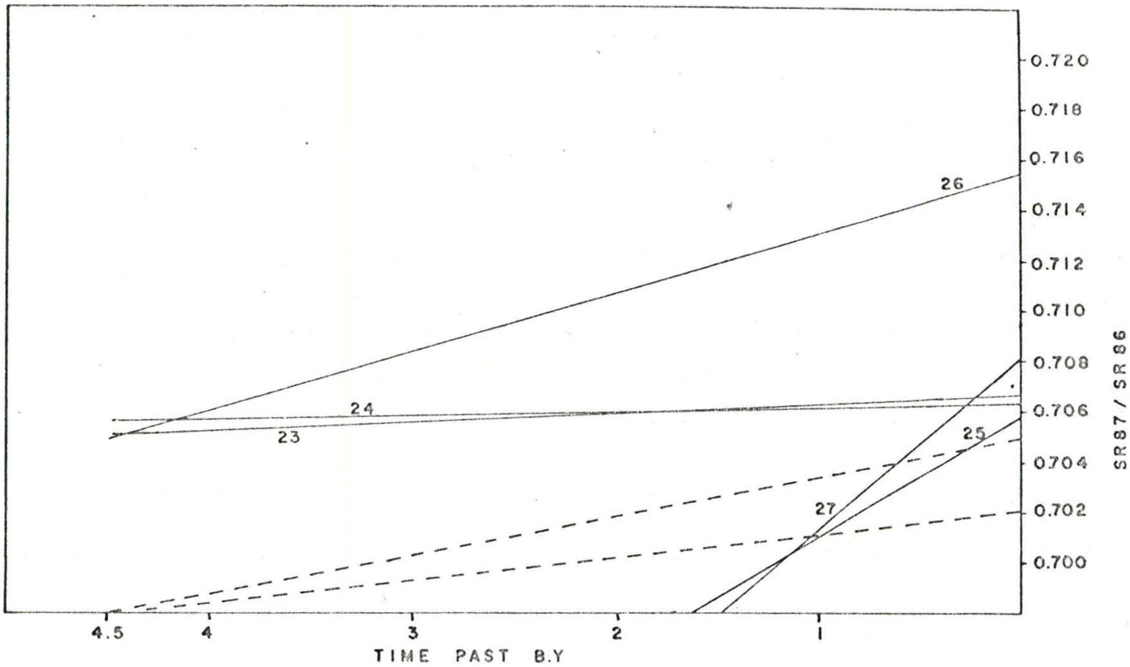


FIG.19. DEVELOPMENT DIAGRAM FOR THE MONESTRY(23), DUTOITSPAN(24), BULTFONTEIN(25), DOORNKLOOF (26) AND KIRKLAND LAKE(27) KIMBERLITES.

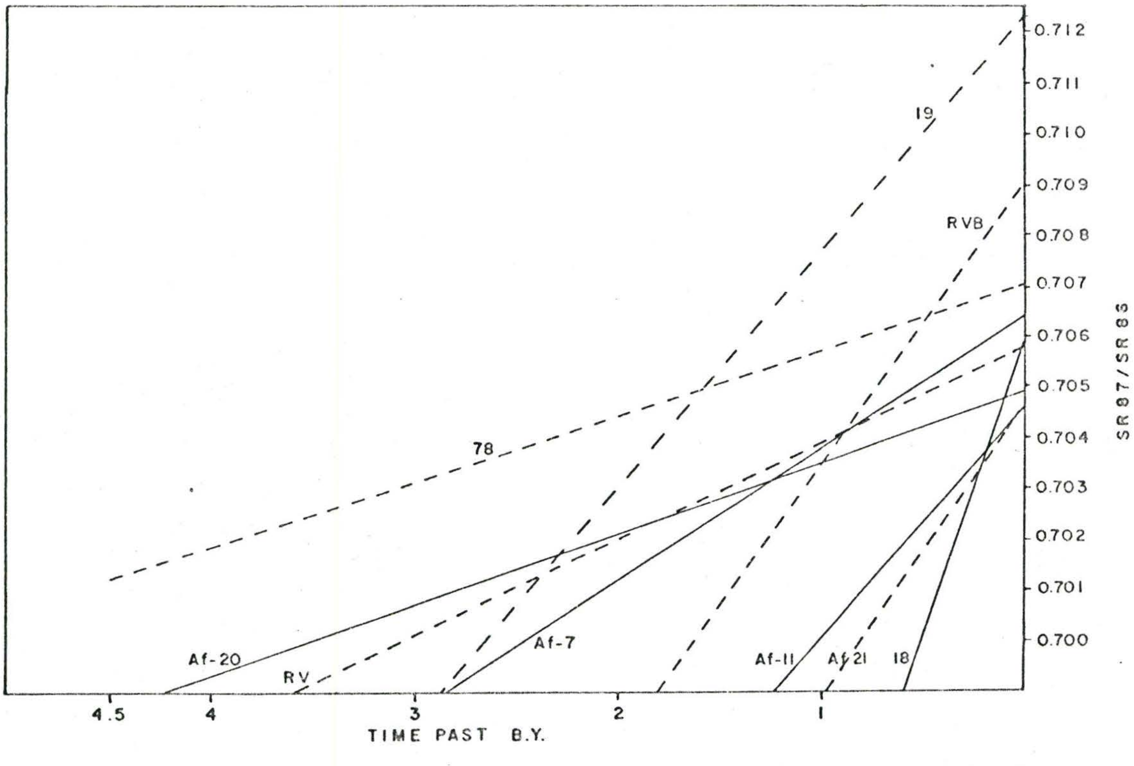


FIG.20. DEVELOPMENT DIAGRAM FOR ECLOGITES (– – –) AND GARNET PERIDOTITES(——) DATA FOR Af-7, Af-11, Af-20, Af-21 FROM STEUBER AND MURTHY(1966), 78 AND RVB FROM ALLSOPP ET AL.(1969), RV FROM FAURE(1961), 18 AND 19 (THIS WORK).

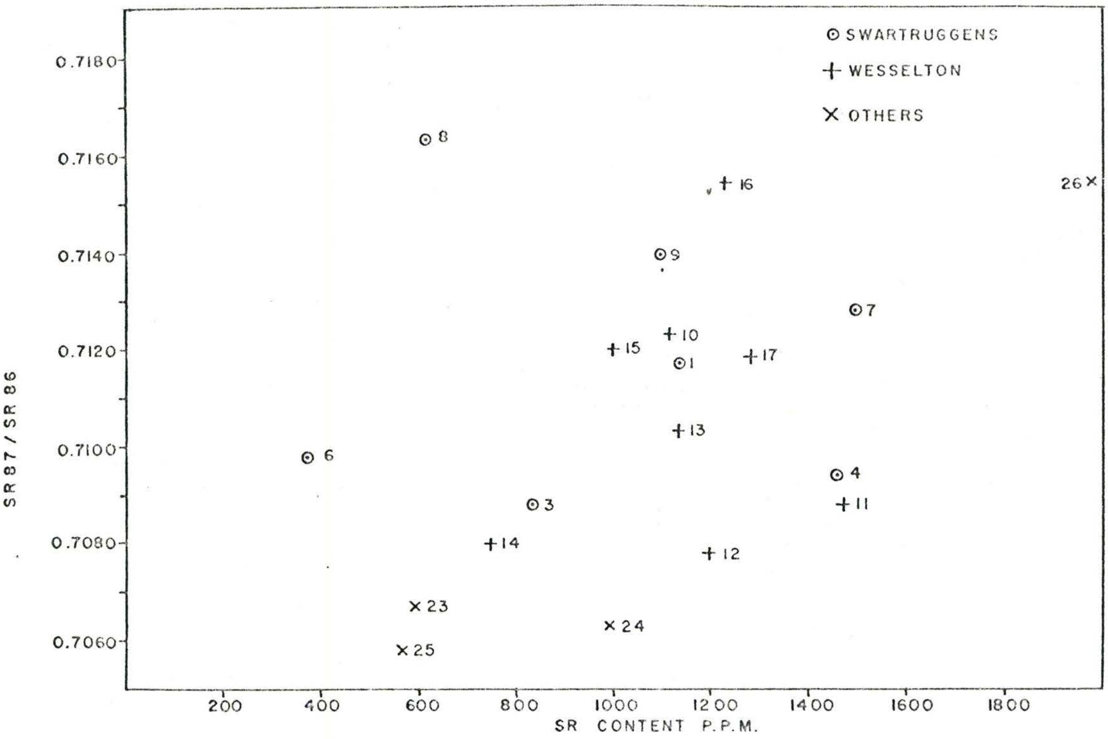


FIG. 21. SR 87/SR 86 RATIO VERSUS THE SR CONTENT OF KIMBERLITES

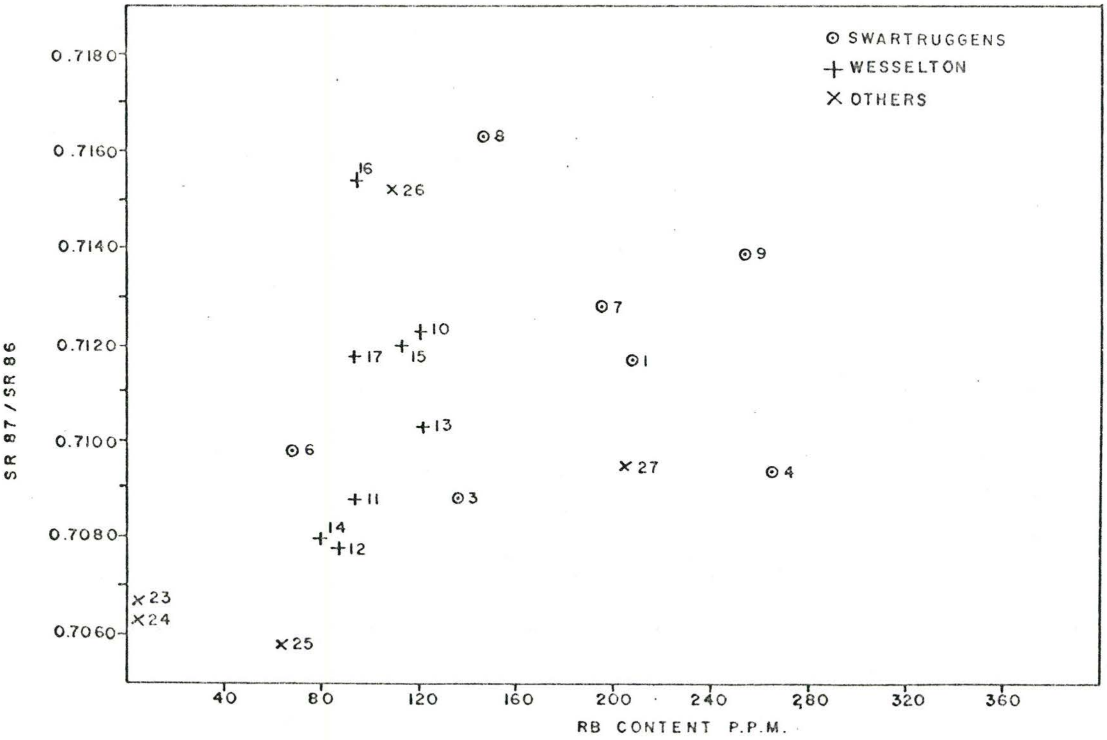


FIG. 22. SR 87/SR 86 RATIO VERSUS THE RB CONTENT OF KIMBERLITES.

have similar isotopic compositions, that serpentinisation has no effect upon the isotopic composition of Sr.

Some estimate of the effects of serpentinisation can be made from a study of yellow ground kimberlite. This material is produced by the extensive weathering and alteration of massive kimberlite. It should be noted that the serpentinisation process in this environment is not directly comparable with the production of deuteric serpentine in massive kimberlite as meteoric water plays a dominant role in the production of yellow ground. Analysis of yellow ground from Swartruggens (samples 2 and 5) has shown that its Sr isotopic composition is essentially similar to that of the massive samples. Analysis of highly weathered samples from the Premier pipe (samples 20-22) shows high Sr^{87}/Sr^{86} ratios, in keeping with the Precambrian age of the kimberlite, which are unrelated to the Rb content. The sample (22) with the highest ratio has the lowest Rb content. This sample also contains abundant altered mica and loss of Rb evidently took place after growth of the Sr^{87}/Sr^{86} ratios. General conclusions which can be drawn are that the weathering and serpentinisation of kimberlite does not alter the isotopic composition of Sr. If serpentinisation and alteration takes place in an open system, Rb loss is very likely to occur. Serpentinisation of kimberlites is considered by most petrologists to be a deuteric phenomenon and exchange of material with meteoric water is not envisaged. The lack of correspondence between Sr^{87}/Sr^{86} ratios and Rb content is thus thought to reflect the very young age of the rocks and to indicate that kimberlite at the time of intrusion was not an isotopically homogeneous body. Likewise the wide variation in Rb and Sr content indicates considerable initial heterogeneity. Deuteric processes have evidently failed to homogenise kimberlites and the reactions involved undoubtedly caused some local Rb and Sr redistribution. The intrusion thus appears to consist of several isolated closed systems and is as a whole not in equilibrium. Such an interpretation is in keeping with the fact that kimberlite is essentially a random mixture of "phenocrysts" and groundmass (fluid), the crystallisation of which was apparently rapid enough to prevent homogenisation. This compositional heterogeneity accounts for the array of development lines found for a single kimberlite body.

Gross Contamination

As noted by Powell (1962, 1966) it is possible that gross contamination by small inclusions of country rock may be responsible for the high Sr^{87}/Sr^{86} ratios. Every care was taken in the present work to avoid analysing samples containing such inclusions and in most of the samples studied no such inclusions were present. It is significant that the highest Sr^{87}/Sr^{86} ratios were obtained from the late stage

Wesselton dykes which are very fine grained xenolith free rocks and the lowest ratios from the Bultfontein kimberlite which did contain a few inclusions. Similar evidence has been cited by Powell (1962) and it is considered that inclusions of country rock are not the cause of the high Sr^{87}/Sr^{86} ratios observed in kimberlites.

Bulk Crustal Assimilation

Before attempting to interpret the Sr isotopic composition of kimberlites in terms of the various petrogenetic theories proposed in Chapter 5, it is necessary to consider whether or not kimberlites have acquired their high Sr^{87}/Sr^{86} ratios by assimilation of material of high Sr^{87}/Sr^{86} ratio.

Faure and Hurley (1963) in the first application of Sr isotopic studies to problems of igneous petrogenesis proposed that the high Sr^{87}/Sr^{86} ratios seen in continental basalts relative to those of oceanic basalts were due to assimilation of crustal material of high Sr^{87}/Sr^{86} ratio. This process of bulk assimilation of crustal material has since been advocated by most petrologists as a means of explaining the high Sr^{87}/Sr^{86} ratios seen in continental igneous rocks. An important aspect of this process, which is seldom noted, is that it is restricted to the upper levels of the continental crust as the values of the Sr^{87}/Sr^{86} ratio in deep crustal material can be expected to approach those of the mantle (Heier 1964).

Recently several petrologists have doubted the validity of Faure and Hurley's (1963) hypothesis as a means of explaining the high Sr^{87}/Sr^{86} ratios seen in Tasmanian and Antarctic dolerites (Heier et al. 1965, Compston et al. 1968). The magmas from which these rocks crystallised cannot have been derived from the crust and contamination of basaltic magma by crustal material has been ruled out by Compston et al. (1968) on general geochemical grounds and on the fact that the bulk contamination processes are unlikely to produce magmas of very uniform composition. Compston et al. (1968) conclude that if contamination has played a role in the development of these magmas then selective contamination by certain components by diffusion processes must have been operative. Compston et al. (1968) also consider that the high Sr^{87}/Sr^{86} ratios may have been acquired in the mantle and involve no crustal contamination.

Green and Ringwood (1967a) are attempted to explain the high Sr^{87}/Sr^{86}. ratios of the Tasmanian dolerites by a process of trace element extraction, akin to zone refining, termed "wall rock reaction". It is proposed that "incompatible elements" i.e. those which are present in the rocks surrounding a magma but which do not enter major mineral phases crystallising in that magma, may be preferentially concentrated in the magma by selective melting processes. The principal elements concerned in a crustal environment would be K, Rb, Ba, U and Th but not Sr. It is thought that a small amount of Sr highly enriched in radiogenic Sr^{87} might be expected to accompany the Rb in the low melting fraction and so raise the magma's Sr^{87}/Sr^{86} ratio. This process will not operate at high pressures where Sr would also be an incompatible element.

Other evidence which is of relevance to assimilation processes has been presented by Moorbath and Bell (1965) who found that basic igneous rocks at Skye have a low initial Sr ratio whereas associated acid igneous rocks have high values. Moorbath and Bell (1965) suggest that basic magmas derived from a source with a low Rb/Sr ratio, have caused partial melting of crustal material to produce the acid magmas. There appears, however, to have been little or no assimilation of acid material by the basic magmas during or after the melting process.

When considering processes of assimilation as applied to kimberlites, it is important to realise that conditions of intrusion of kimberlite and basalt are very different. Kimberlites are intruded into the upper crust at high velocity (Frank 1967, McGetchin 1969), as a fluidised gas-rich system. The high velocity is in direct contrast to the known modes of ascent of basaltic magma which rises slowly and which frequently forms magma pools. Kimberlite thus does not satisfy Green and Ringwood's (1967a) prerequisite that for wall reaction to occur, magma ascent must be slow. The speed of ascent of kimberlite through the mantle and lower crust is relatively unimportant as material of high Sr^{87}/Sr^{86} will not be encountered.

Kimberlites are also of small volume, compared to the amounts of basalt present at Skye for example, they are totally insignificant. Small volumes of magma will not possess much, if any, superheat and thus will not be capable of causing extensive partial melting or assimilating much extraneous material. The lack of alteration of xenoliths and wall rocks in and adjacent to kimberlite intrusions is convincing evidence in support of such conclusions. Addition of molten material, derived from some other source, e.g. anatectic granite, to a kimberlite magma, even if miscible, would cause rapid precipitation of olivine and total crystallisation of the magma would result before much material could be assimilated.

Evidence that small volumes of rapidly intruded gas-rich magmas do not assimilate crustal material is seen in the carbonatite lavas of Oldoinyo Lengai ($Sr^{87}/Sr^{86} = 0.7033$, Powell 1966). Failure of kimberlite to equilibrate with the xenoliths it carries is seen in the Wesselton pipe where garnet peridotite xenoliths possess lower Sr isotopic ratios than the surrounding kimberlite. Similar lack of isotopic equilibration of solid xenoliths with enclosing magmas has been demonstrated by Powell (1962), Leggo and Hutchinson (1968), Ewart and Stipp (1968).

Some of the possibilities of crustal contamination can be examined if it is assumed that mantle derived kimberlite, termed here a protokimberlite, possess a low Sr^{87}/Sr^{86} ratio (0.7040) and is contaminated by assimilation of crustal material. It is possible to calculate the amount of crustal material required to raise the Sr^{87}/Sr^{86} ratio of protokimberlite by contamination, to values observed in kimberlite by use of the following equation:

$$\left(\frac{Sr_k}{Sr_k + xSr_c}\right)\left(\frac{Sr^{87}}{Sr^{86}}\right)_k + \left(\frac{xSr_c}{Sr_k + xSr_c}\right)\left(\frac{Sr^{87}}{Sr^{86}}\right)_c = \left(\frac{Sr^{87}}{Sr^{86}}\right)_{hk} \qquad (7\text{-}1)$$

where Sr_k and Sr_c are the Sr concentrations of protokimberlites and contaminant respectively $(Sr^{87}/Sr^{86})_{k,\ c,\ hk,}$ refer to the isotopic composition of Sr of protokimberlite, contaminant and final hybrid kimberlite respectively. x is the weight proportion of contaminant assimilated by one part of protokimberlite.

Fig. 23 shows the Sr^{87}/Sr^{86} ratios and Sr contents of hypothetical contaminants required to raise the Sr^{87}/Sr^{86} ratios of protokimberlite (Sr^{87}/Sr^{86} = 0.7040) to the average value seen in kimberlites (0.7110) for differing degrees (x) of assimilation. The concentration of Sr in the protokimberlites has been taken to be 1000 or 500 ppm. Equation (7-1) takes no account of the Sr content of the final contaminated magma thus allowance is made for differentiation processes which may modify the Sr content of the contaminated magma but not the Sr isotopic composition (Ewart and Stipp 1968, Pushkar 1967). Such differentiation processes are not important for kimberlites.

Kimberlites are intruded into old cratonic areas and thus the most likely contaminants are the Precambrian granites and gneisses which underlie the younger sediments and lavas and because as noted above, at high levels in the crust kimberlites have little opportunity for assimilation due to their high velocities and small heat content. Consequently, also plotted on Fig. 13 are the Sr^{87}/Sr^{86} and Sr contents of a variety of old granites and gneisses which could act as contaminants. The data are from Allsopp 1961, Allsopp and Kolbe 1965, Allsopp et al. 1962, Hurley et al. 1962, Zwartmann and Stern 1967. From the position of these rocks on Fig. 13 it is evident that they have Sr isotopic compositions and Sr contents which would give the required hybrid kimberlite ratio if a protokimberlite containing 1000 ppm Sr assimilated one half to equal its weight of these materials. If the protokimberlite contained 500 ppm Sr one quarter to one half of its weight of contaminant would be required.

On particular importance with regard to South African kimberlite is the possible assimilation of granites and gneisses of the Swaziland system which are the oldest rocks in that region and which comprise a major part of the basement rocks through which kimberlites are intruded. The Sr^{87}/Sr^{86} ratios of gneisses and sediments of the

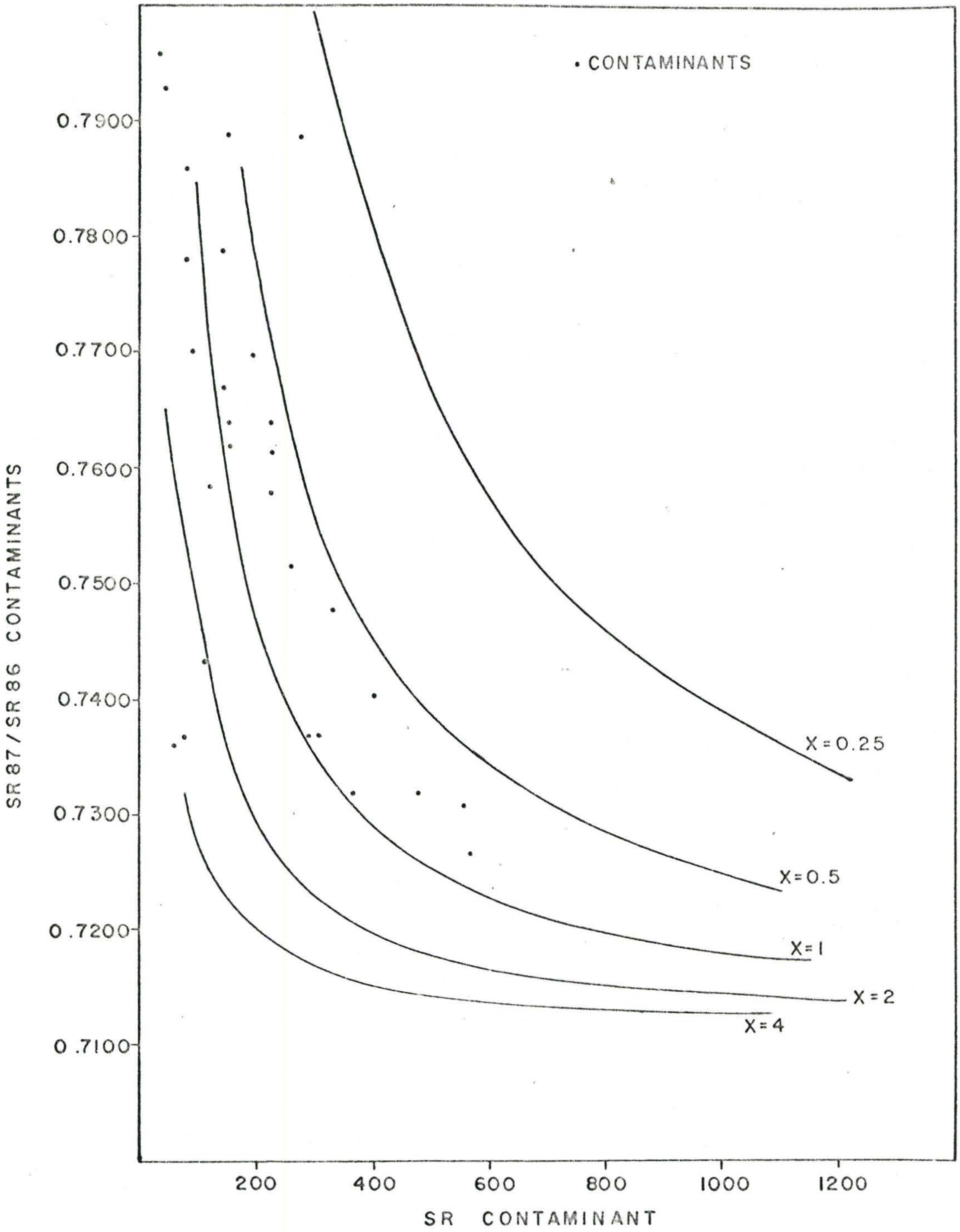


FIG. 23. SR87/SR86 RATIOS AND SR CONTENTS OF POSSIBLE CONTAMINANTS REQUIRED TO RAISE THE PROTOKIMBERLITE SR 87/SR 86 (0.704) RATIO TO THAT OF AVERAGE KIMBERLITE (0.710), FOR VARYING DEGREES OF ASSIMILATION(X). CURVES ARE FOR PROTOKIMBERLITE 1000 P.P.M., FOR 500 P.P.M. READ NEXT LOWEST CURVE AND DIVIDE X BY TWO.

Swaziland system vary from as low as 0.727 to as high as 8.0 in some pegmatites (Allsopp et al. 1962, 1968), and fall on the general trend outlined in Fig. 23. Even for the rocks with very high Sr^{87}/Sr^{86} ratios the amounts of contaminants noted above remain unchanged as these rocks possess very low Sr contents. It should be noted that the Karroo dolerites have passed through these rocks with no discernible assimilation effects ($Sr^{87}/Sr^{86} = 0.7057$; Compston et al. 1968).

There is considerable doubt as to whether a protokimberlite would be able to assimilate the volumes of contaminants suggested above on the basis of the heat content of the small volumes of kimberlite involved. Even if such amounts of assimilation are possible, then it would be necessary to postulate that the bulk composition of the protokimberlite be very different from that of the final hybrid kimberlite in order to account for the observed major and trace element composition.

From the above discussion it is evident that bulk assimilation of crustal material in a kimberlite magma is unlikely to be the means by which the observed isotopic composition of Sr in kimberlite is generated. The fact that similar isotopic ratios are developed in two different types of kimberlites which are geographically widely separated would also seem to preclude random contamination by crustal material.

Sr isotopes as applied to petrogenetic theories

The Franz (1965) and Dawson (1966) hypotheses of kimberlite genesis can be tested by use of equation (7-1), by determining the amounts of granite which must be added to carbonatites to raise their Sr^{87}/Sr^{86} ratios to the values observed in kimberlites.

Fig. 24 shows the Sr^{87}/Sr^{86} ratios and Sr contents of contaminants required to raise the Sr^{87}/Sr^{86} ratio of carbonatite (0.7030; average carbonatite Powell 1966) containing 6000 ppm Sr to the average kimberlite value of 0.7110 for differing degrees of assimilation (x). The data for Precambrian granite is again used as an estimate of the isotopic composition and Sr content of possible contaminants. Fig. 24 thus demonstrates that a carbonatite would need to assimilate from 4 to 6 times its own weight of those contaminants to acquire the typical kimberlite isotopic composition. Such large amounts of contaminants are necessary because of the very high Sr content of carbonatite. Simple calculations show that such mixtures of carbonatite and granite would not give a hybrid rock of kimberlite composition in terms of major and trace elements. Carbonatites are of small volume and assimilation of such large amounts of material is clearly impossible.

Other objections to Franz's (1965) and Dawson's (1965) hypothesis have been noted above (Chapter 5) and it was concluded that carbonate was unlikely to be involved in the generation of kimberlite.

The Sr isotopic evidence provides further grounds for considering the hypothesis to be invalid.

O'Hara and Yoder's (1967) hypothesis predicts that garnet-peridotite partially melts to give a liquid which is fractionated by precipitation of bimineralic eclogite. The hypothesis in its original form is restricted to the melting of a four phase garnet lherzolite, but if the garnet peridotites xenoliths found in kimberlite pipes are considered to be representative of the source rocks, then it is necessary to assume that minor phlogopite is present and plays a role in the generation of the melt. The discussion is, however, quite general and is equally valid for a four phase garnet lherzolite.

Analyses of garnet peridotite from Wesselton in the present work and by Steuber and Murthy (1966) gave whole rock Sr^{87}/Sr^{86} ratios which are lower than those of the whole rock kimberlite. This conclusion is substantiated by analysis of Rb poor minerals from garnet peridotites by Allsopp et al. (1969) who found that chrome diopside from a Wesselton xenolith had a Sr^{87}/Sr^{86} ratio of 0.707. Similar low ratios relative to the host kimberlite are found at Dutoitspan, here chrome diopside has a Sr^{87}/Sr^{86} ratio of 0.705 the host kimberlite being 0.7063. Allsopp et al. (1969) have also demonstrated that the total rock Rb-Sr chemistry of garnet-peridotites is dominated by two phases only, i.e. mica and chrome diopside. Production of a

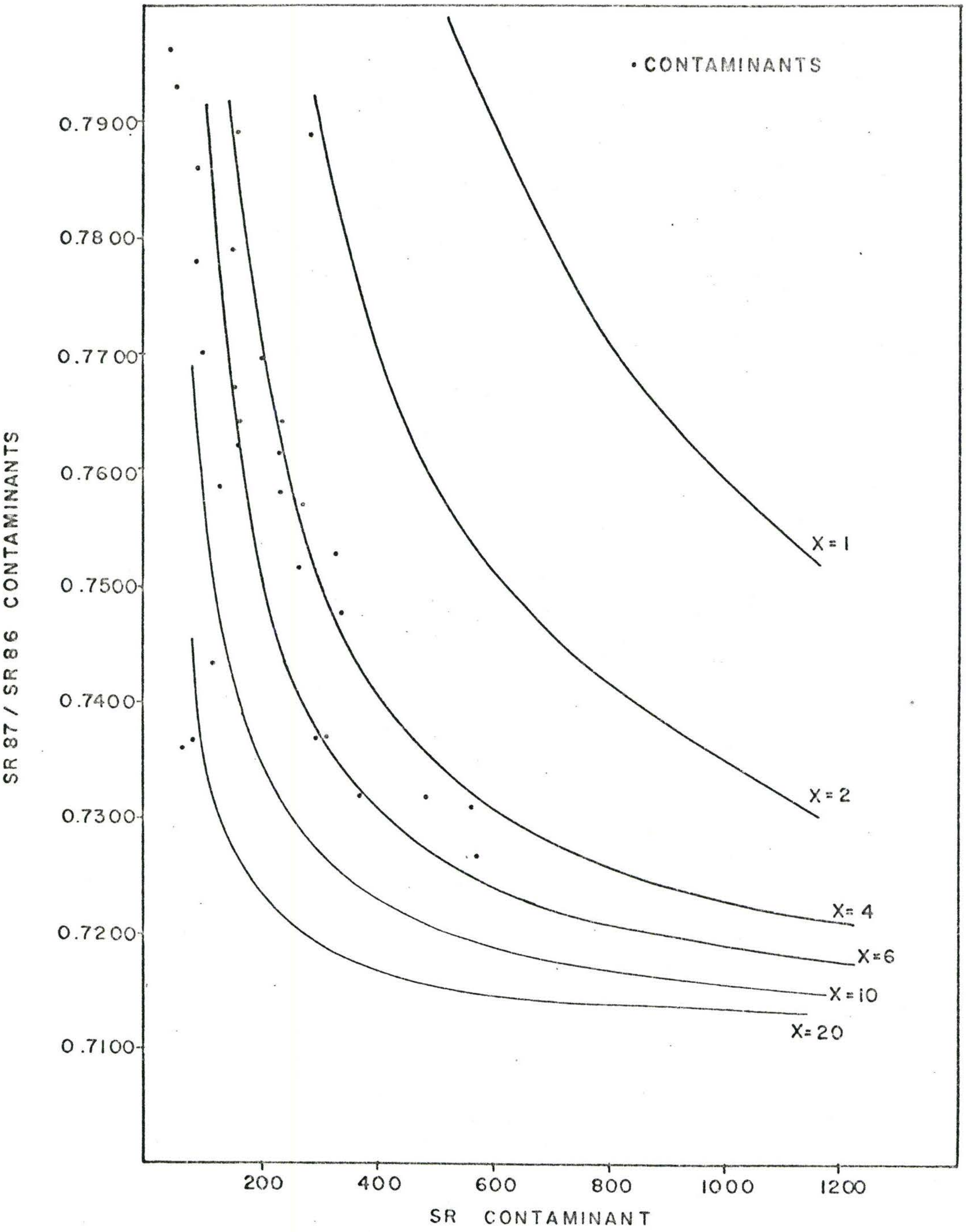


FIG. 24. SR 87/SR 86 RATIOS AND SR CONTENTS OF POSSIBLE CONTAMINANTS REQUIRED TO RAISE CARBONATITE SR 87/SR 86 (0.703) RATIO (6000 P.P.M. SR) TO THAT OF AVERAGE KIMBERLITE (0.710) FOR VARYING DEGREES OF ASSIMILATION (X).

liquid by partial melting of such a rock would involve all phases but it is likely that during the very first stages of melting that the mica and chrome diopside are the dominant contributors to the liquid.

Over very long periods of time as a consequence of their differing Rb/Sr ratios these two minerals would develop extremely varied isotopic compositions. Two boundary conditions are however possible: either the radiogenic Sr^{87} generated in the mica equilibrates with Sr in the chrome-diopside which acts as a Sr sink and so renders the system isotopically homogeneous or isotopic heterogeneities are preserved.

At the supposed depths and temperatures where partial melting is thought to occur (see Chapter 4) it is doubtful that isotopic heterogeneity would persist if the system were open to Rb and Sr diffusion. Heterogeneity may however be preserved if the mica and chrome diopside are sufficiently separated from each other spatially by olivines and orthopyroxenes so that diffusion paths are long and very restricted. This, in effect, means that each mineral is a closed system. In support of such an assumption, analyses of the garnet-peridotite xenoliths now found in kimberlite pipes show that the individual minerals have isotopic compositions which cannot be accounted for simply by the addition of radiogenic Sr^{87} since the time of cooling of the intrusion (Allsopp et al. 1969). The isotopic heterogeneities were evidently present prior to the enclosure of the xenolith in the kimberlite matrix and were preserved even during intrusion.

Melts formed by partial melting of garnet peridotite will be isotopically homogeneous. The isotopic composition of the melt will, if the source rock is heterogeneous, depend upon the amounts of diopside and mica melted. If the source is homogeneous, then the liquid will have an isotopic composition like that of the diopside (this is equivalent to melting four phase garnet-lherzolite). Any eclogite which crystallises from this liquid must have the isotopic composition of the liquid.

Whole rock analysis of the Wesselton eclogite indicates a high Sr^{87}/Sr^{86} ratio (0.7123) which is consistent with crystallisation from a kimberlite melt. However, interpretation of this ratio is difficult in terms of the whole rock data as it has been discovered that the K, Rb and Sr abundances of minerals separated from eclogite cannot account for the total rock abundances of these elements. The eclogites contain an intergranular medium which is rich in Rb and Sr and which possesses a high Sr^{87}/Sr^{86} ratio (Allsopp et al. 1969, Griffin and Murthy 1968, Ehrlank 1969).

Allsopp et al. (1969) considers that this intergranular medium was introduced into the eclogite during intrusion of kimberlite. Whether such an interpretation is true or not is uncertain. If it is, then one must consider whether or not garnet-peridotite xenoliths might have been similarly affected. However, the low Sr^{87}/Sr^{86} ratios of garnet-peridotites appear to indicate no such contamination as these xenoliths should be very susceptible to contamination because they contain very little Sr relative to the host kimberlite. (N. B. intergranular medium in eclogites might also represent in situ breakdown of garnet in response to pressure and temperature changes during transport from the mantle and involve no contamination). Sr isotopic analysis of the minerals of eclogite (Allsopp et al. 1969) has revealed that the Rb poor phase omphacite possesses a very low Sr^{87}/Sr^{86} ratio (0. 701-0. 703). This ratio is lower than that of the Rb poor phases of garnet-peridotite and thus renders unlikely O'Hara's and Yoder's (1967) suggestion that eclogite is a precipitate from a liquid derived by partial melting of garnet peridotite.

Allsopp et al. (1969) have attempted to show how eclogite can still be a crystallisation product of the liquid produced by melting of garnet-peridotite by assuming that eclogite separated out from the liquid at least 2 b. y. ago and preserved its distinct low isotopic ratio until at least Cretaceous times when it was altered by the incursion of crustal Sr^{87} rich fluids during kimberlite intrusion. The higher isotopic ratios of garnet peridotites chrome diopsides are explained by constant equilibration of Sr^{87} between mica and chrome diopside over 2 b. y. Eclogite in such an hypothesis can play no role in developing a fluid of kimberlitic composition by its fractionation. The restrictions imposed by the 2 b.y. old eclogite separation, its removal from the Rb rich garnet peridotite and subsequent re-incorporation with selective contamination, render the hypothesis unlikely. A simpler explanation is to consider the eclogite as representing recrystallised basaltic liquid which never left the mantle and which was accidently incorporated into kimberlite during its ascent. Rb-Sr and U-Pb age studies of eclogite from the Roberts Victor kimberlite by Manton and Tatsumoto (1969) have indicated that eclogite is unrelated to kimberlite and is an older xenolith.

Thus, eclogite fractionation appears to be unlikely as a means of producing kimberlite liquids.

Kimberlites and Potassium in the Mantle

Most discussions of the nature of the upper mantle (e.g. Harris 1967, O'Hara 1968) consider that it has a composition equivalent to that of garnet-peridotite. How then are kimberlites to be accounted for in terms of partial melting of such a mantle? O'Hara and Yoder (1967) consider partial melting of a four phase garnet lherzolite and, noting the K_20 poor nature of this rock, appeal to eclogite fractionation as a means of increasing potassium contents of derivative liquids. O'Hara and Yoder (1967) however, do not consider the possible occurrence of minor potassium-rich phases which might be of importance in the petrogenesis of rare small volume alkaline potassic rocks.

The disparity between the relatively high K_2O contents of basalts, presumably derived from mantle ultramafic rocks and the very low levels of K_2O incorporated in anhydrous mantle material such as olivine has lead Oxburgh (1964) to postulate the presence of a potassium-rich minor phase making up 2 to 20 wt. % of the parent upper mantle. This phase was considered by Oxburgh (1964) to be amphibole. Unfortunately, little is known of the stability of amphibole at high pressures. Ernst (1968) has discussed the problem of amphibole in the mantle and has shown that sodic amphiboles are stable up to at least 30-40 kb. Ernst (1968) also predicts that at high pressures amphiboles might transform into hydrous single chain structures. Gilbert (1968) has shown that calcic amphiboles are not likely to be stable at depths greater than 70-100 kb and that they are not water containers at greater depths.

The stability of phlogopite at high pressures has been investigated by Kushiro et al. (1967) and Yoder and Kushiro (1968) and it has been concluded that phlogopite is most likely to be a minor phase at great depth in the mantle as it is stable up to 40 kb at 1300°C. Of particular importance is the phlogopite breakdown curve in the presence of olivine as determined by Yoder and Kushiro (1968) which indicates that melting of phlogopite could occur in the source regions of kimberlite as deduced by studies of co-existing pyroxenes in ultramafic nodules.

Melting of such a hydrous assemblage would, when free water is present or is produced by the breakdown of the hydrous mineral, produce extremely water-rich magmas. The existence of phlogopite in garnet-peridotite xenoliths in kimberlite which are generally regarded to be representative of the upper mantle (O'Hara and Mercy 1963) supports the assumption that minor phlogopite is of importance in the mantle. Partial melting of phlogopite bearing garnet peridotite has been postulated by Kushiro et al. (1967) as a source of kimberlite magma.

The present writer thus assumes that mantle material which has not been affected by any partial melting processes is a five phase garnet mica peridotite (phlogopite-pyrope-olivine-orthopyroxene-chrome diopside).

Partial melting of garnet peridotite mantle can produce a variety of liquids depending upon the extent of partial melting and the degree of fractionation. The processes of partial melting of the mantle have been discussed in detail by Harriss (1967) and O'Hara (1968). Initial melting of a garnet-mica peridotite mantle would produce a liquid enriched in K, Rb, Ba, U, Th, Nb, Sr, H_20 and possibly, $C0_2$ (Harriss 1967) if the degree of melting was very small ($<1\%$) and involved principally phlogopite and chrome-diopside. More extensive partial melting involving significant amounts of olivine and orthopyroxene would produce melts of the type described by O'Hara (1968), e.g.

hypersthene normative picrite liquid ($<15\%$ liquid). It is important to realise that kimberlites are rocks of small volume which appear infrequently in the geological record whilst basaltic rocks are exceedingly common. Evidently partial melting of the mantle generally exceeds the amounts suggested above for the production of alkali-rich potassic liquids and results in the generation of basalt. In South Africa the intrusion of kimberlite was preceded by enormous volumes of basaltic magma, e.g. Karroo dolerites and Stormberg volcanics. The production of such magmas would have depleted the underlying mantle source regions in alkali elements leaving behind a barren residue. As kimberlites are thought to come from greater depths than basalt, it is likely that underlying this barren zone of mantle is a zone of fresh undepleted garnet peridotite. It is partial melting of this material which gives rise to kimberlite. The melting is probably induced by the same process which gave rise to the generation of the basaltic magmas.

Can the observed Sr isotopic composition of kimberlite be interpreted in terms of this hypothesis? Partial melting of garnet-mica-peridotite has been discussed above and it has been noted that the isotopic composition of the melt produced will depend upon whether the source rocks are isotopically heterogeneous or homogeneous.

If they are isotopically heterogeneous then the isotopic composition of the melt will vary between two extremes, i.e. the isotopic composition of chrome diopside and phlogopite, if these are the only two important phases involved in the partial melting process. Thus isotopically homogeneous melts of high Sr^{87}/Sr^{86} ratio could be produced from rocks which were of lower whole rock Sr^{87}/Sr^{86}. The melt would be rich in alkali elements and in Ca, Mg and Cr but would probably be poor in Co and Ni. Olivine is the most important mineral which crystallises from kimberlite and it would be necessary to add to this liquid sufficient olivine to produce a high normative olivine content and high Co and Ni content in the liquid. This olivine would be of low Sr^{87}/Sr^{86} ratio if it were derived from the residue of partial melting or from barren mantle material encountered by kimberlitic fluids during ascent to the crust. In Chapter 4 it was considered that the fluid from which diamond grew rapidly changed its composition and that the system was unlikely to be in chemical equilibrium. This rise of a random mixture of olivine xenocrysts, low Sr^{87}/Sr^{86}, and fluid , high Sr^{87}/Sr^{86}, to the surface would result in a final consolidated kimberlite of heterogeneous chemical composition. The isotopic composition of Sr in a sample of this rock would depend upon the relative proportions of olivine and fluid in that sample. Samples containing abundant "phenocrystal" olivine would have lower Sr^{87}/Sr^{86} ratios than samples which contained few of these phenocrysts. This condition appears to be met at Wesselton where the late stage dykes which contain little 'phenocrystal' olivine have higher Sr^{87}/Sr^{86} ratios than the pipe rocks which contain abundant phenocrysts. This interpretation thusrequires that the rounded first generation olivine is a xenocryst, and that the second generation olivine is a true primary mineral. Rapid transit from source rocks to final site of consolidation is also required.

The alternative explanation involving an isotopically homogeneous source requires that the melt produced be of similar isotopic composition to that observed in garnet peridotites, e.g. 0.704-706. To raise the ratio to the values observed in kimberlites requires addition of material of high Sr^{87}/Sr^{86} ratio. It was considered above that bulk assimilation of granitic material is unable to account for the observed isotopic composition of kimberlite. Thus, addition of material enriched in radiogenic Sr^{87} must be selective and not involve bulk compositional changes of kimberlite magmas. Pankhurst (1969) in trying to account for the high Sr^{87}/Sr^{86} ratios observed in gabbros in Scotland which show no signs of bulk assimilation of crustal material has invoked a process of Sr isotopic equilibration of magma and country rocks which involves no addition of other elements. The process is similar to Heier's (1964) theory that radiogenic Sr^{87} occupying lattice sites in Rb-rich minerals might diffuse more readily than common Sr in Rb poor minerals. Pankhurst's (1969) theory, like Green and Ringwood's (1967a) hypothesis of wall rock reactions appears inapplicable in accounting for kimberlite isotopic ratios because both theories imply slow intrusion rates and sufficient time being available for equilibration or selective melting to occur. Kimberlites do not appear to meet any of these criteria. The selective assimilation hypothesis is also subject to limitations imposed by the lack of isotopic equilibration between xenoliths and magma even when these are extensively partially melted (Ewart-Stipp 1968).

Selective diffusion processes of the type discussed in the following Chapter to account for isotopic variations in the Fen complex, may have occurred in kimberlites. These would have to occur after the kimberlite had been emplaced in the upper crust and might have involved selective extraction of Sr from granites and gneisses of the Swaziland system by processes akin to diffusion or solvent extraction involving CO_2-rich late stage fluids emanating from the crystallizing kimberlite. The process would be of variable efficiency and would cause development of a final kimberlite which would be isotopically heterogeneous.

The Mantle and Kimberlite Genesis

The initial Sr ratio of the earth based upon meteorite studies is taken to be 0.698 (Hurley 1967). Using this initial ratio, it is possible to calculate the average Rb/Sr of the source regions of oceanic basalt magmas, where present day Sr^{87}/Sr^{86} ratio is 0.702-0.705. Thus, the Rb-Sr ratio of the upper mantle is assumed to be 0.02.

The Sr isotopic data obtained for kimberlites and garnet peridotites can be interpreted in terms of the above model. This requires that some 2-4 b.y. ago differentiation of a mantle with a Rb/Sr of 0.02 occurred. The product of this differentiation was a garnet peridotite with a Rb/Sr ratio greater than 0.02 and a residue of lower Rb/Sr ratio than 0.02. This is in accordance with the observed Rb/Sr ratios of garnet peridotites (0.035-0.242; this work, Steuber and Murthy 1966). It is important to note that this differentiation episode does not result in separation of garnet peridotite out of the mantle into crustal regions. The garnet peridotite would remain isolated and unaffected by partial melting processes until late Cretaceous times when partial melting produced kimberlite magma with a new enrichment of Rb and concomitant increase in Rb/Sr ratio of the liquid to values greater than that of garnet peridotite (0.06-0.24). This model is also in accord with an increased degree of partial melting of similar garnet peridotite at higher levels in the mantle than those of kimberlite genesis to give basalt magmas prior to the eruption of kimberlite. Thus, the Karroo dolerites have Rb/Sr ratios of from 0.10-0.16 (Nockolds & Allen 1956) and Sr^{87}/Sr^{86} ratios of 0.7057 (Compston et al. 1968) which are concomitant with extraction of most of the alkalies from a garnet-peridotite (Sr^{87}/Sr^{86} 0.704-706) by advanced partial melting.

The initial differentiation of the primordal mantle material could account for the low initial Sr isotopic composition of eclogite, if eclogite represents the residua remaining after garnet-peridotite segregation. Similar interpretations of the eclogite data have been given by Allsopp et al. 1969 and are in agreement with Manton and Tatsumoto's (1969) ages of 2 b.y. for eclogite from Roberts Victor.

The model thus explains the similar development lines found for garnet-peridotite eclogite and kimberlite all which indicate very old differentiation ages for separation from a mantle of Rb/Sr ratio of 0.02.

The validity of this hypothesis and its consequences for the interpretation of the development diagrams (Figs. 17-20) is, however, uncertain because of the following observations:

1. The actual Rb/Sr ratios (0.06) of oceanic basaltic magma is much higher than the calculated value. Partial melting of mantle to give basalt will probably involve removal of most of the Rb and Sr into the liquid and leave a barren residue. Thus, the

Rb/Sr ratio of basalts might not be far removed from that of the source rocks. Garnet-peridotites are generally considered to be representative of mantle material and to be the source rocks of basalt magma. Few Rb/Sr ratios have been determined but they are higher than 0.02 and their Sr^{87}/Sr^{86} ratios are higher than those of modern oceanic volcanics. All the garnet-peridotites so far analysed are from kimberlite pipes and this may be taken as representative of the continental mantle. They cannot be regarded as the source of oceanic volcanics because of their high Sr^{87}/Sr^{86} ratios. Thus, applying Hurley's (1967) model implies that the continental mantle and oceanic mantle have had a different geochemical evolution.

2. Pb isotope data is incompatible with Sr isotope data for the evolution of the crust-mantle system (Armstrong 1968). If the results derived from the Pb isotopes are applied to the Sr isotope variations, one must interpret the Rb/Sr ratio of mantle source rocks as the average of two or more ratios. Gast (1967) has concluded that there is no evidence that the Rb/Sr ratio of a given rock is closely related to that inferred from the Sr^{87}/Sr^{86} ratio.

3. Hurley's (1967) interpretation assumes a unidirectional transport of Rb and Sr from the mantle to the crust. The growing recognition of the importance of lateral transport of crustal mantle by sea floor spreading and its return to the mantle make such unidirectional systems invalid (Armstrong 1968).

Conclusion

The above discussion has demonstrated that the high Sr^{87}/Sr^{86} ratios found in kimberlites are not due to bulk assimilation of granitic material in a kimberlitic magma. The theory of Dawson (1966, 1967b) that kimberlites are generated by assimilation of granite in carbonatite magma has also been discredited. O'Hara and Yoder's (1967) hypothesis of eclogite fractionation has been found inadequate to explain the observed Sr isotopic data from kimberlites, garnet peridotites and eclogites. A theory of kimberlite petrogenesis involving partial melting of a five phase garnet-mica peridotite to give a kimberlite of high or low Sr^{87}/Sr^{86} ratio and various processes which might modify this ratio, have been considered.

The study has served to reject some theories of kimberlite petrogenesis and outlined new areas for study. Further work should involve a study of the constituent minerals of kimberlites and the response of the value of the Sr^{87}/Sr^{86} to change in the proportions of modal first generation olivine. Study of individual minerals in kimberlite is rendered difficult by the frequent alteration and carbonitisation but should be possible for the fresh Wesselton kimberlite. To study possible selective Sr contamination a detailed study of kimberlite and adjoining country rock is necessary.

The relation of garnet peridotite and eclogite to kimberlite needs much further study, certainly with regard to the relation of eclogite to micaceous kimberlites. Such studies should involve not only Sr isotopes, but also Pb isotopes and rare earth element distribution patterns so that more definite constraints can be placed upon the interpretations.

CHAPTER EIGHT

Sr ISOTOPIC STUDIES OF THE FEN ALKALINE COMPLEX, NORWAY

Geology and theories of petrogenesis

The Fen complex is situated east of Ulefoss in Telemark, 119 km. southwest of Oslo and 12 km. outside of the Oslo Permian Plutonic province (Fig. 25). At Fen the Precambrian granite-gneiss bedrock has been penetrated by a roughly circular body of silicate rocks and carbonatites, the distribution of which is shown in Fig. 26. The complex has been described by Brøgger (1921), Saether (1957) and Barth and Ramberg (1967). The following rock types are the most important ones found at Fen:

Silicate Rocks

1. Fenite, a syenite consisting of microperthitic alkali feldspar and aegerine.
2. The urtite-ijolite-melteigite series, ijolite is a melanocratic rock which ideally consists of equal proportions of nepheline and sodic pyroxene. Normally the percentages of these minerals found are highly variable and melteigite is the name given to

pyroxene rich types whilst urtite refers to nepheline rich types.

3. Vipetoite is composed of titanaugite, amphibole, biotite and calcite and is a type of lamprophyre.

4. Damtjernite is a lamprophyre containing phenocrysts of biotite and olivine set in a groundmass of titanaugite, amphibole, nepheline perthite and calcite. Some authors, e.g. Barth-Ramberg (1967) consider damtjernite to be a kimberlite, but as noted in Chapter 1 this conclusion is thought to be erroneous.

5. Malignite, a melanocratic variety of nepheline syenite composed of nepheline, aegerine and orthoclase.

Carbonatites

6. Sǿvite, a calcite carbonatite containing minor biotite, magnetite, apatite and koppite.

7. Rauhaugite, an ankeritic carbonatite containing minor calcite apatite and rare microcline and albite. The carbonate contains 10-15 mol. % $CaFe(CO_3)_2$ and 90-85% $CaMg(CO_3)_2$, therefore strictly speaking rauhaugite is a dolomitic carbonatite.

8. Rǿdberg (Redrock), a hematite carbonatite consisting of finely disseminated hematite in a calcitic carbonatite containing minor ankerite chlorite and pyrite.

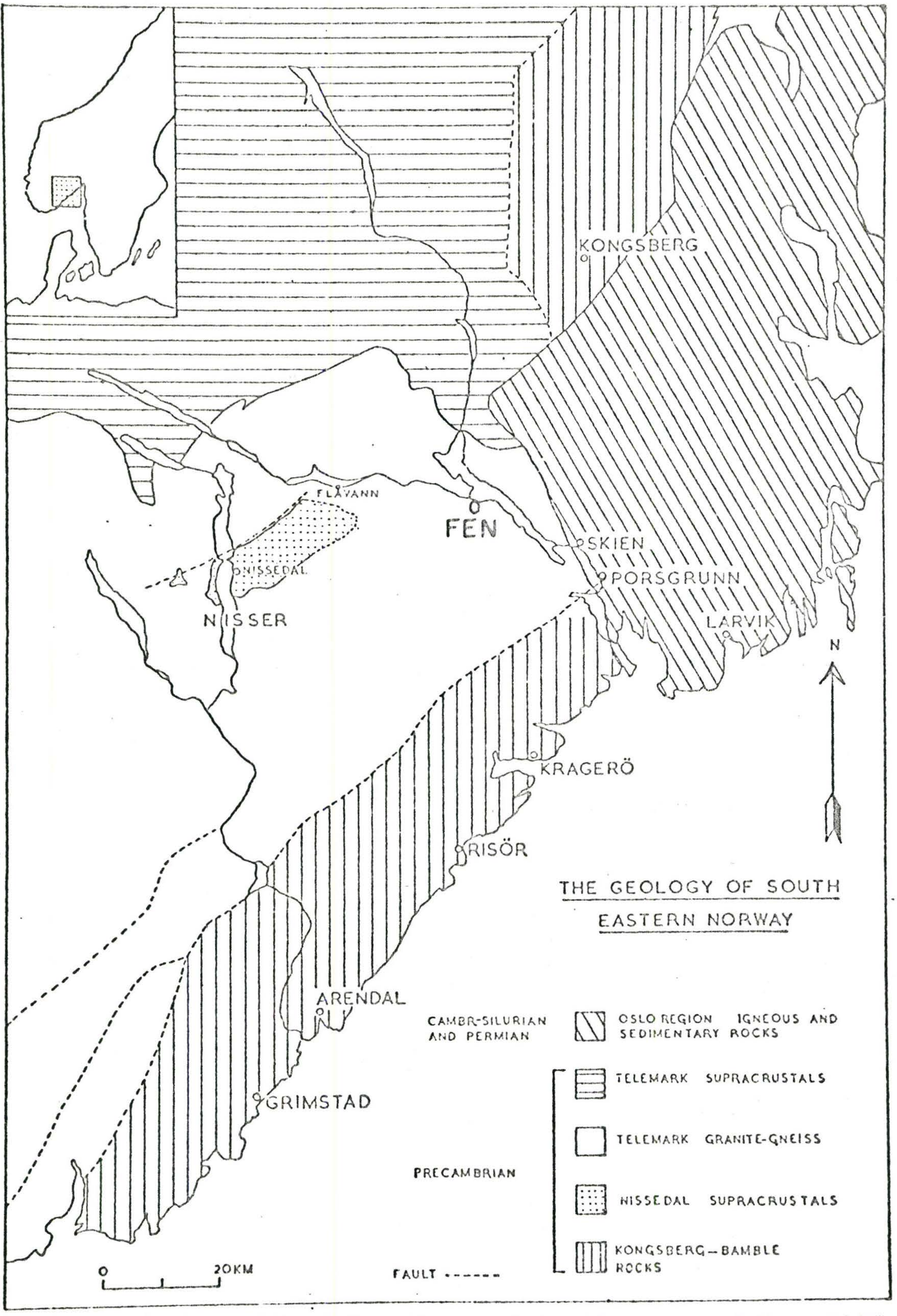


Fig. 25. The Geology of South East Norway. (After HOLTEDAHL & DONS 1960).

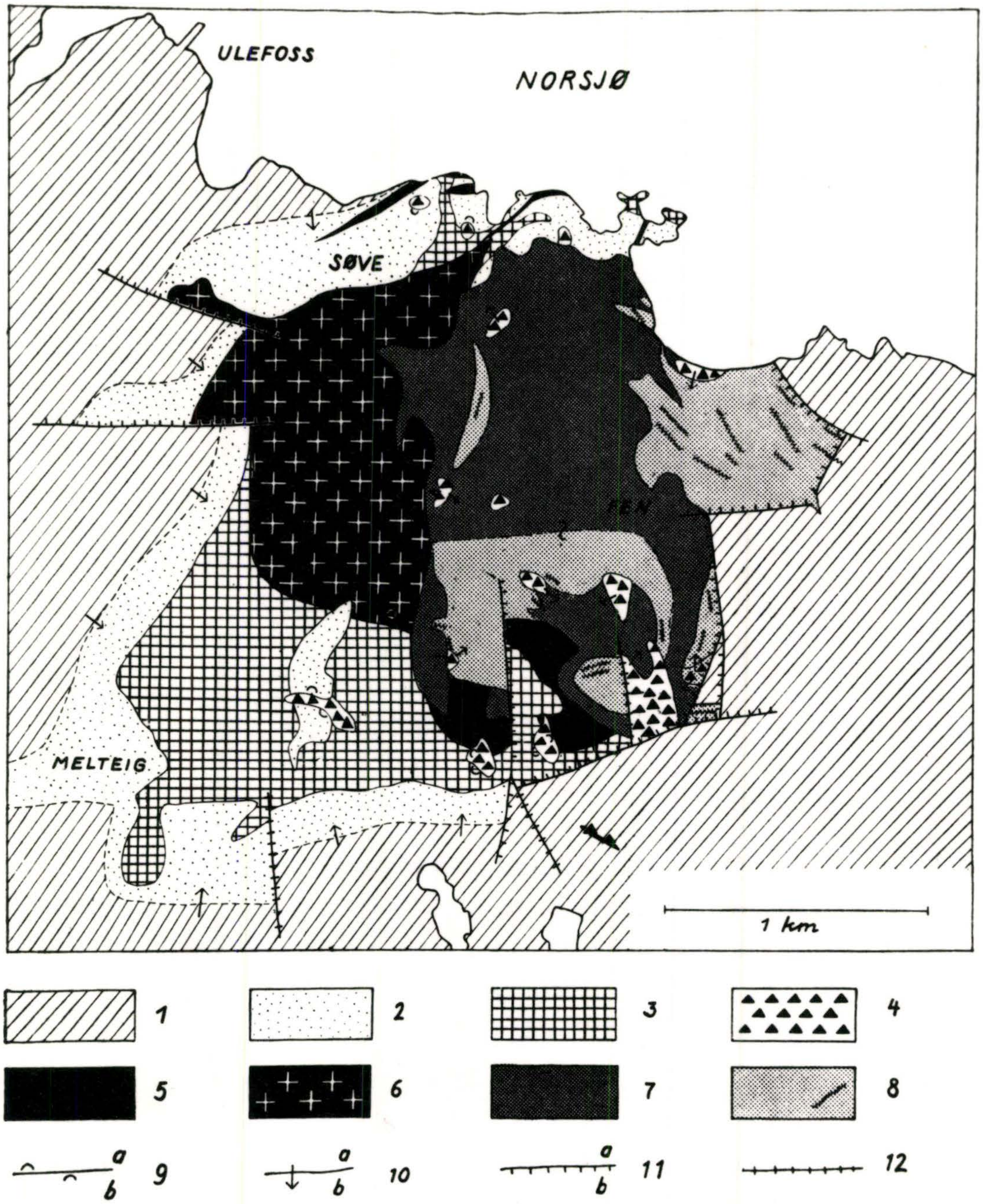


Fig.26. . Simplified map of the rock complex of the Fen area. 1. Precambrian gneiss. 2. Fenite. 3. Different basic rocks (vipetoite, melteigite, ijolite etc.) 4. Kimberlite (Damtjernite). 5. Søvite. 6. Hollaite. 7. Rauhaugite. 8. "Rødberg" (with hematite ore). 9. Intrusive contact (a older rock, b younger rock). 10. Metasomatic contact (rock b is a metasomatic product of a). 11 Fault. 12. Fault (displacement unknown). (After E. Sæther 1947.)

Silicocarbonatites

These rocks are transitional in their mineralogical composition between carbonatites and rocks of the ijolite series. To these rocks Brøgger (1921) gave a wide variety of petrographical names of the type locality variety. Saether (1957) proposed that they should be considered to be varieties of carbonatite and that Brøgger's (1921) names be discarded. The most important types of silicocarbonatites found are:

a) pyroxene søvite, a pyroxene-calcite rock (Brøgger's kåserite).

b) søvitic melteigite, a pyroxene-nepheline-calcite rock (Brøgger's Hollaite).

Petrogenesis

Brøgger (1921) demonstrated that fenite is a metasomatic rock formed from the country rock gneisses by alkali metasomatism. The silicate rocks were regarded as true igneous rocks and it was considered that the søvites were formed by consolidation of a carbonate magma. For the rauhaugite and rødbergite a metasomatic formation from søvite was assumed. Brøgger (1921) proposed that the alkaline rock assemblage was derived from a moderately alkaline magma (essexitic) which had partly assimilated and partly fused a Precambrian limestone at great depth in the crust. The magma had then desilicated in accordance with the Daly-Shand assimilation hypothesis (Shand 1947). The fused limestone was considered to have erupted as a carbonate magma together with the silicate magma.

Bowen (1924, 1926) also considered that the ijolitic rocks were of a magmatic origin but rejected the idea of a carbonate magma and maintained that søvite had been formed from the silicate rocks (fenite and ijolite) by a metasomatic process which lead to more or less complete replacement of the silicates by calcite.

Saether (1957) recognised two sequences of igneous activity separated from each other by a time interval. Each began with the intrusion of a very mafic magma and closed with intense hydrothermal activity. Both magmas were alkaline and rich in CO_2 and were doubtless the offsprings of the same parent magma. Their differences are ascribable to different conditions of differentiation and/or assimilation. The first intrusion produced fenites from the granite-gneiss by alkali metasomatism. Upon crystallisation the magma formed vipetoite, the ijolite series, pyroxene søvites and søvitic melteigites. During the consolidation of the magma residual solutions of lime and magnesian carbonate were expelled and formed the søvites by replacement of both wall rocks and already consolidated alkalic rocks. From the second magma damtjernite crystallised no fenites were formed but carbonate solutions rich in Ca, Mg and Fe were expelled which transformed the damtjernite into rauhaugite and rødberg.

Considerable debate concerning the origins of alkaline rocks and carbonatites occurring together in alkaline complex has taken place since the first description of the association by Brøgger (1921). The numerous hypotheses presented for the origins and relationships of these rocks have been ably summarised by Heinrich (1966) and need not be re-iterated here. The central problems in the genesis of these rocks are:

1. What is the nature of the parent magma, is it an ultrabasic magma or a carbonatite magma?

2. Are the rocks of the ijolite series magmatic and derived by differentiation of an ultrabasic magma, or are they the rheomorphic products of fenitised granite gneiss?

Magmatic ijolites

Many petrologists consider that the parent magma of an alkaline complex is of mafic or ultramafic composition, e.g. alkaline peridotite, kimberlite, pyroxenite, ijolite or nephelinite and that carbonatite is a late differentiate of this magma (Saether 1957, King 1965, Tomkieff 1961, Garson 1962). After extensive studies of the alkaline rocks of Uganda, King (1965) concluded that carbonatites were derivatives of ijolite-nephelinite magmas because:

1. Their volume is insignificant compared to that of ijolite and nephelinite.
2. Their mineralogy and wall rock effects indicate that carbonatites were emplaced at low temperatures: therefore, they must be later than the silicate rocks.
3. Calcite is a common late primary mineral in ijolites and the silicates found in carbonatites are those characteristic of the late silicate rocks. Thus, there is a continuity in mineralogy between carbonatites and ijolitic rocks.

The actual genesis of the alkali parent magma is generally not discussed by proponents of the above differentiation hypothesis, but King (1965) and Verwoerd (1966) envisage some kind of differentiation relationship to basaltic magma. If this is true then low Sr^{87}/Sr^{86} ratios might be expected in ijolites and nephelinites.

Fenitisation and Ijolitic Fenites

Nearly all carbonatites are surrounded by a halo of varying breadth and petrological complexity and consisting of metasomatically altered or completely metasomatic rocks, for which the name fenite has come to be generally employed. The name fenite was introduced by Brøgger (1921) for the metasomatic syenites found at Fen which contained 70-90% alkali feldspar and 25-15% aegerine. In most complexes the fenite can be traced from a very slight alteration of country rock through syenitic fenites to the nepheline bearing pulaskitic and foyaitic fenites. Some of these undersaturated highly fenitised rocks appear to have become mobilised during the fenitisation process and now appear as dykes of an igneous aspect. The process of fenitisation in a number of carbonatite complexes has been envisaged as not ceasing with the production of the nepheline bearing syenites but as having continued still further yielding ultra-alkalic highly undersaturated rock types such as ijolite and malignite. The process has been described from the Alnö complex by Von Eckermann (1948) who found that the granodioritic country rock had been transformed successively into fenite, nepheline syenite and ijolite and that macrostructures in the country rocks can be traced from unaltered gneisses through the fenites and into the ijolites. Similar examples of the production of ijolitic fenite have been described from Nemegosenda Lake (Parsons 1961) and Spitskop (Strauss and Truter 1950).

Von Eckermann (1948) has considered that the process of fenitisation has continued still further until the ijolitic fenites become mobilised and form a fluid magma which on crystallisation has the appearance of an ordinary igneous rock and which exhibits intrusive and cross-cutting relations with the fenites. Such mobilised ijolitic fenites are termed rheomorphic ijolites.

The production of fenite is considered to involve the addition of material to the country rock from the intruding magma. Elements added are Na, Ca, Mg, Fe, Ti, P, K and the only loss from the country rock appears to be Si (Saether 1957, Swift 1952, Garson and Smith 1958, Fockema 1952, Von Eckermann 1948, Strauss and Truter 1950, McKie 1967). The details of the fenitising process have been summarised by Heinrich 1966 and McKie 1967 and need not be repeated here. Little is known of the movement of minor elements during fenitisation. Elements introduced into the country rock include Nb (Parsons 1961), rare earths, Be, Ba, Ti, Nb (Zhabin and Makhitdinov (1959), Sr, Ba, Zr, La, Nb and V (Erickson and Blade 1963). If minor elements follow geochemically similar major elements during fenitisation, then it can be expected that Rb and Sr will be added to the country rock. The only evidence available at the present time shows that Sr has been introduced as predicted (Erickson and Blade 1963). Whilst K appears to have been added to the country rock it should be noted that carbonatites, which are often considered to be the source of fenitising solutions contain very little K and neglible Rb. The apparent increase in K in the country rock may thus merely reflect selective concentration processes and not addition of K to the rock.

Bailey and Schairer's (1966) study of the system Na_20-Al_20_3-Fe_20_3-$Si0_2$ has provided a new insight into the ijolite problem. In this system a liquid at the quaternary reaction point, acmite + hematite + nepheline + albite + liquid is close to the nepheline-acmite join and is therefore essentially identical with a magma of ijolitic composition. The results prove the possibility of the existence of ijolitic liquid and that it might be of a residual nature. Bailey and Schairer (1966) point out that if ijolite is a residual liquid, then it can form by the partial melting of solid materials having a wide range in bulk composition. Being volatile rich it would also tend to metasomatize its wall rocks to a similar composition. Thus, generation of ijolite by partial melting of nepheline and acmite-bearing fenite could be predicted from the existence of the "ijolitic" invariant point in the experimental system. The point is a residuum, however, and other sources of ijolite can be expected. Thus ijolites can be either magmatic and represent derivative liquids of some other magma or be rheomorphic and be formed by partial melting of acmite fenites.

Some aspects of the formation of ijolites can be considered by means of Sr isotopic studies. Ijolites which have formed by rheomorphism of fenites produced from Precambrian gneisses can be expected to have a markedly different Sr isotopic composition to that of ijolites formed by the differentiation of some ultrabasic or basic magma. Three models which apply Rb-Sr data to the problem are discussed below.

Model 1 - Derivation of all rocks from a single magma

If all the rocks of the complex are derived from a single magma, e.g. an ultrabasic magma, by a variety of differentiation processes and carbonatites are considered to represent the residual fractions of this magma, then all rocks will have the same Sr^{87}/Sr^{86} ratio at the time of differentiation. At any later time they will lie on a whole rock isochron which will indicate the time of intrusion of the complex and the initial Sr isotopic composition of the magma. The time of intrusion in effect dates the time at which the system became closed to Rb and Sr migration.

Model 2 - Assimilation and Rheomorphism

The production of rheomorphic hybrid rocks from a single parent magma by metasomatism and mobilisation of country rocks can be described in terms of a Nicolaysen diagram if it is assumed that the process approximates to ideal assimilative processes involving complete mixing.

In Fig. 27 the points A-B represent the whole rock Rb-Sr parameters of the parent magma and the country rock respectively.

A series of hybrid rocks formed by mixing of A and B will lie on the line joining A and B at positions dependent upon the proportions of A and B in the hybrid. If after generation of the hybrids the system becomes closed to Rb-Sr migration, then at any later time T the hybrids will define an isochron whose age will be dependent upon the time interval between T and the time of formation of the hybrids (T_r) and upon the slope of the line AB. The age given by the isochron T will be anomalously old and the initial Sr^{87}/Sr^{86} ratio will be anomalously low relative to the true age and initial ratio of the intrusion.

If any of the hybrid rocks undergo differentiation, for example a rheomorphic ijolite might differentiate by fractional crystallisation to urtite and melteigite, then the series of differentiates at time T_r the time of rheomorphism and differentiation will lie upon an isochron of zero slope, i.e. they will all possess the same initial ratio. This initial ratio will depend upon the degree of hybridisation which has occurred. The hybrid rocks and their differentiates will at any later time T define anyisochron indicating the time which has emplaced since rheomorphism and differentiation, i.e. the true age of intrusion of the complex. The process is illustrated in Fig. 28.

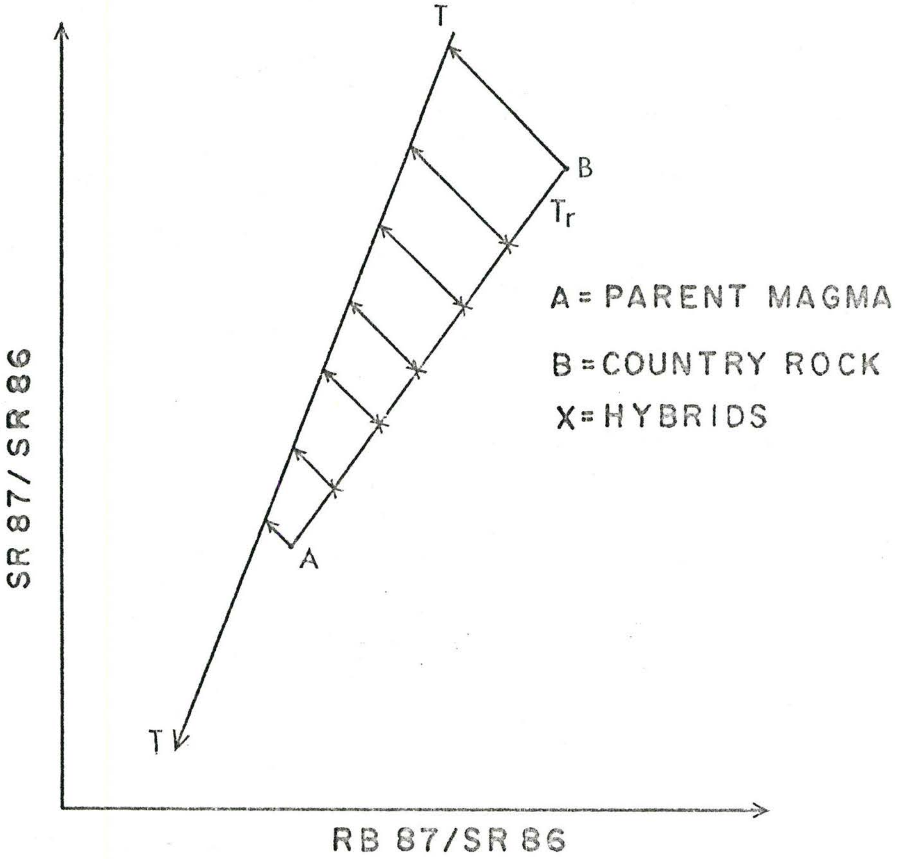


FIG. 27. IDEAL ASSIMILATION.

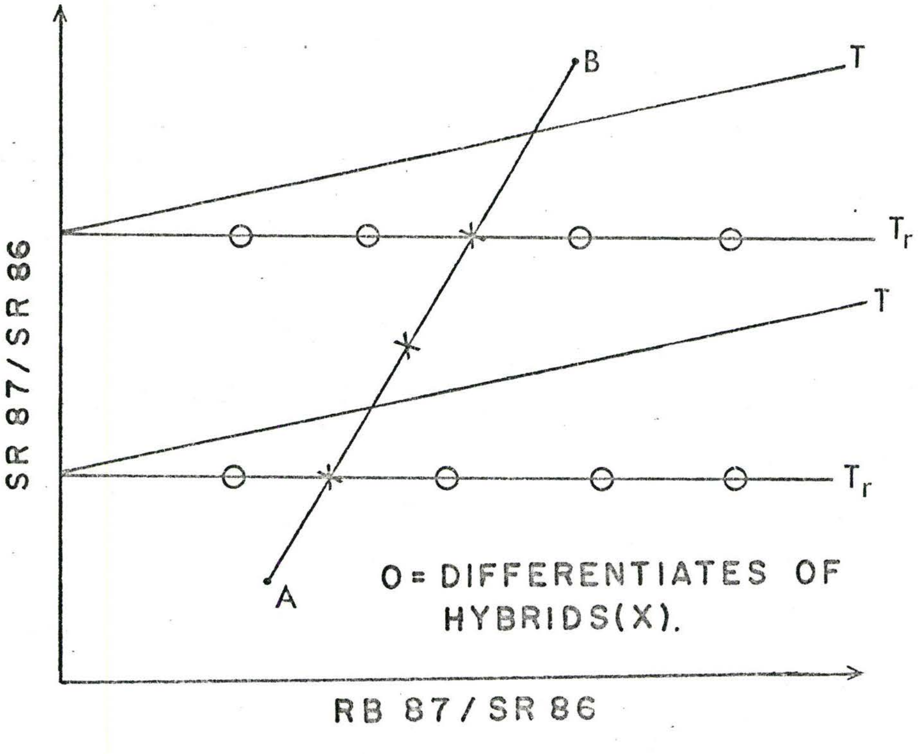


FIG. 28. IDEAL ASSIMILATION TOGETHER WITH HYBRID DIFFERENTIATION.

Model 3 - Assimilation, Rheomorphism and Metasomatism between carbonatite and granite-gneiss

This is a special case of the ideal assimilation model described above. Fig. 29 shows the distribution of a series of hybrids formed between carbonatite (C) and granite-gneiss (G). The hybrids lie upon the straight line CG which is of the type y = mx+c where:

y, the $(Sr^{87}/Sr^{86})_h$ ratio of the hybrid = $\left(\frac{Sr_c}{Sr_c+XSr_g}\right)\left(\frac{Sr^{87}}{Sr^{86}}\right)_c$ +

$$\left(\frac{XSr_g}{Sr_c+XSr_g}\right)\left(\frac{Sr^{87}}{Sr^{86}}\right)_g$$

m, is the slope of the line

x, the Rb^{87}/Sr^{86} ratio of the hybrid = $\frac{(\alpha Rb_c + \beta Rb_g)}{(\alpha Sr_c + \beta Sr_g)}$ x 2.893

c is a constant and equal to $(Sr^{87}/Sr^{86})_c$.

Here Sr_c and Sr_g are the Sr contents of carbonatite and granite gneiss respectively.

Rb_c and Rb_g are the Rb contents of carbonatite and granite gneiss respectively.

$(Sr^{87}/Sr^{86})_c$, $(Sr^{87}/Sr^{86})_g$ are the isotopic compositions of Sr in carbonatite and granite gneiss respectively.

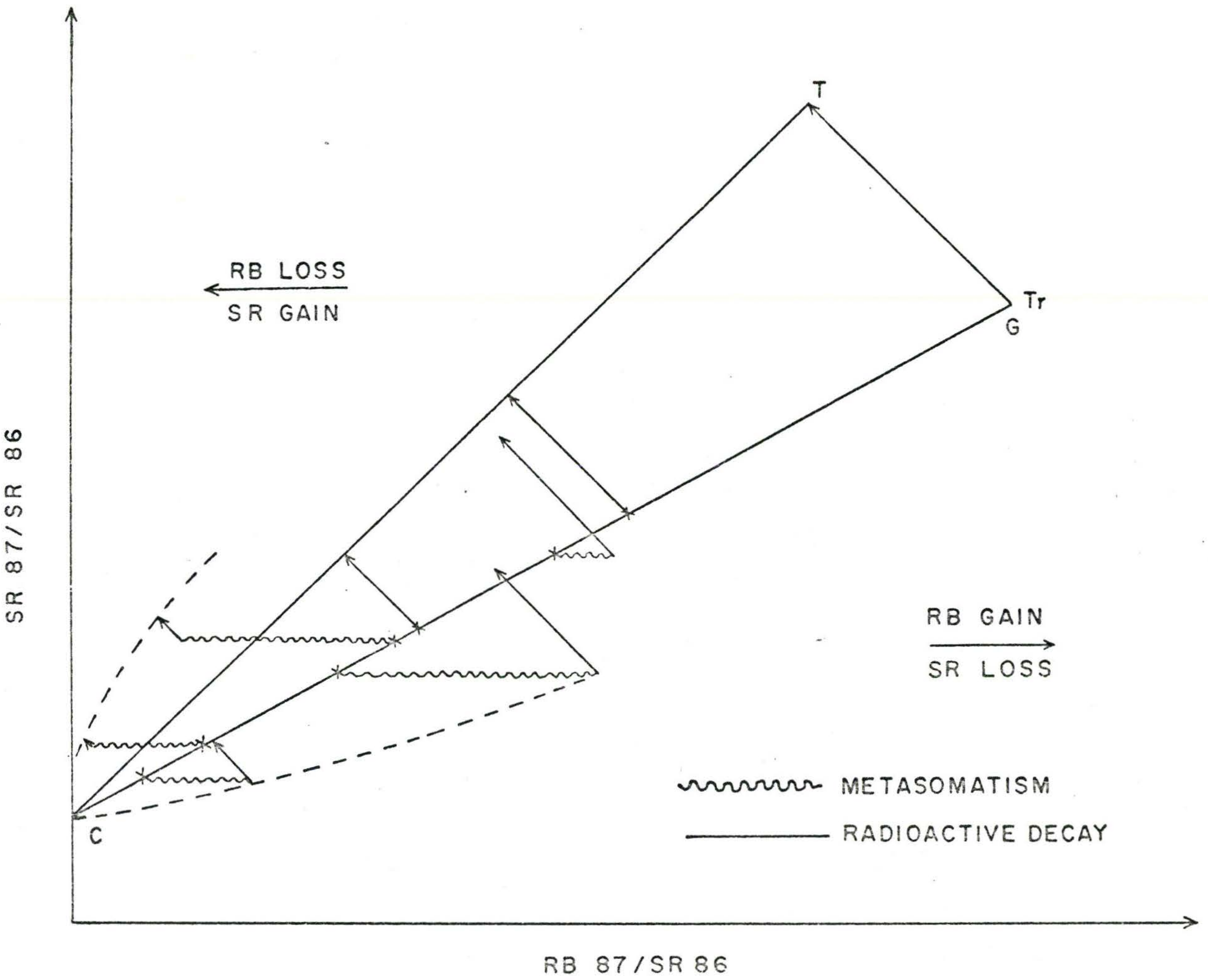


FIG. 29. NICOLAYSEN DIAGRAM FOR IDEAL ASSIMILATION AND METASOMATISM BETWEEN CARBONATITE AND GRANITE.

X is the number of parts weight of granite added to one part carbonatite.

α is the weight fraction of carbonatite Rb and Sr in the hybrid.

β is the weight fraction of granite-gneiss Rb and Sr in the hybrid.

For any value of X, i.e. degree of assimilation between carbonatite and granite-gneiss, the Sr^{87}/Sr^{86} ratio of the hybrid and its Rb^{87}/Sr^{86} ratio can be found at the time of rheomorphism (T_r). The line CG in effect defines an "isochron". At any later time T the whole rock hybrids will form a true isochron which will give an anomalously old age for the complex but the true initial ratio of the parent carbonatite magma. This is because carbonatite contains so little Rb that changes in its Sr^{87}/Sr^{86} with time due to Rb^{87} decay can be ignored. The true age of the intrusion (T_i) is the difference between the isochron T and the "isochron" T_r.

Ideal assimilation is unlikely to be realised in actual carbonatite complexes for a variety of reasons. The ideal model will be subject to modification because the Rb-Sr parameters of the country rock are unlikely to plot as a point source on a Nicolaysen diagram. This is because granite-gneisses are in general heterogeneous bodies in which remnants of ungranitised older metamorphic rocks are frequently found. The whole series may be cut by late stage granitic intrusion, aplites and pegmatites. Thus a wide range in the Sr^{87}/Sr^{86} ratios and Rb^{87}/Sr^{86} ratios of whole rocks may be found. Applying the model to the Fen Area it should be noted that the Telemark granite-gneisses are older than 1000 m.y. and thus at the time of intrusion of carbonatite (550 m.y. see below) would possess Sr^{87}/Sr^{86} ratios which were considerably higher than those of carbonatite.

The range in Rb-Sr parameters of the gneiss might not be very great because the gneiss at the time of metamorphism 1000 m.y. ago would have been isotopically homogeneous, and thus had a uniform Sr^{87}/Sr^{86} ratio. Thus, the slope of the line indicating the Rb-Sr compositions of hybrids between gneiss and carbonatite would be similar to that shown in Fig. 29 because of the great difference in the Rb-Sr parameters of the two end members. Because of the range in the Rb^{87}/Sr^{86} ratio of the gneiss, hybrids would plot on a Nicolaysen diagram as a fan-shaped scatter of points. The fan would originate at the Rb-Sr parameters of the carbonatite and thus the deviation of the Rb-Sr parameters of hybrids from the ideal situation would be minimal for hybrids of low Rb^{87}/Sr^{86} ratio.

Other deviations from the ideal case are possible because of the small volumes of magma involved and the extensive metasomatic effects present. The small volume of magma would certainly not be capable of bulk assimilation of granite-gneiss although partial melting might be possible if prolonged contact of magma with the gneiss occurred. The metasomatic transport of Rb and Sr and other elements would almost certainly be a random process. Thus, considerable deviation of the Rb-Sr parameters of the hybrids from the ideal situation is possible. Fig. 29 illustrates how Rb and Sr gains and losses from the system relative to the ideal case might affect the position of hybrids on a Nicolaysen diagram. It can be seen that the hybrids will lie upon curved lines or be randomly distributed. The position of the rocks relative to the ideal assimilation line CG can be used to determine whether Rb and Sr loss or gain has taken place.

Figs. 30 and 31 illustrate the results of the present investigation of the Fen rocks in terms of a development diagram and a Nicolaysen diagram respectively. Fig. 30 can be used to determine the initial ratios of the rocks at the time of formation of the complex if the age is known. Some previous determinations of the age of the Fen Complex are given in Table 21. Considerable spread in the results is evident, but the age can be taken to be approximately 550 m.y. The intersection of regression lines in Fig. 30 with the 550 m.y. age line can be used to determine the initial ratio of the rocks.

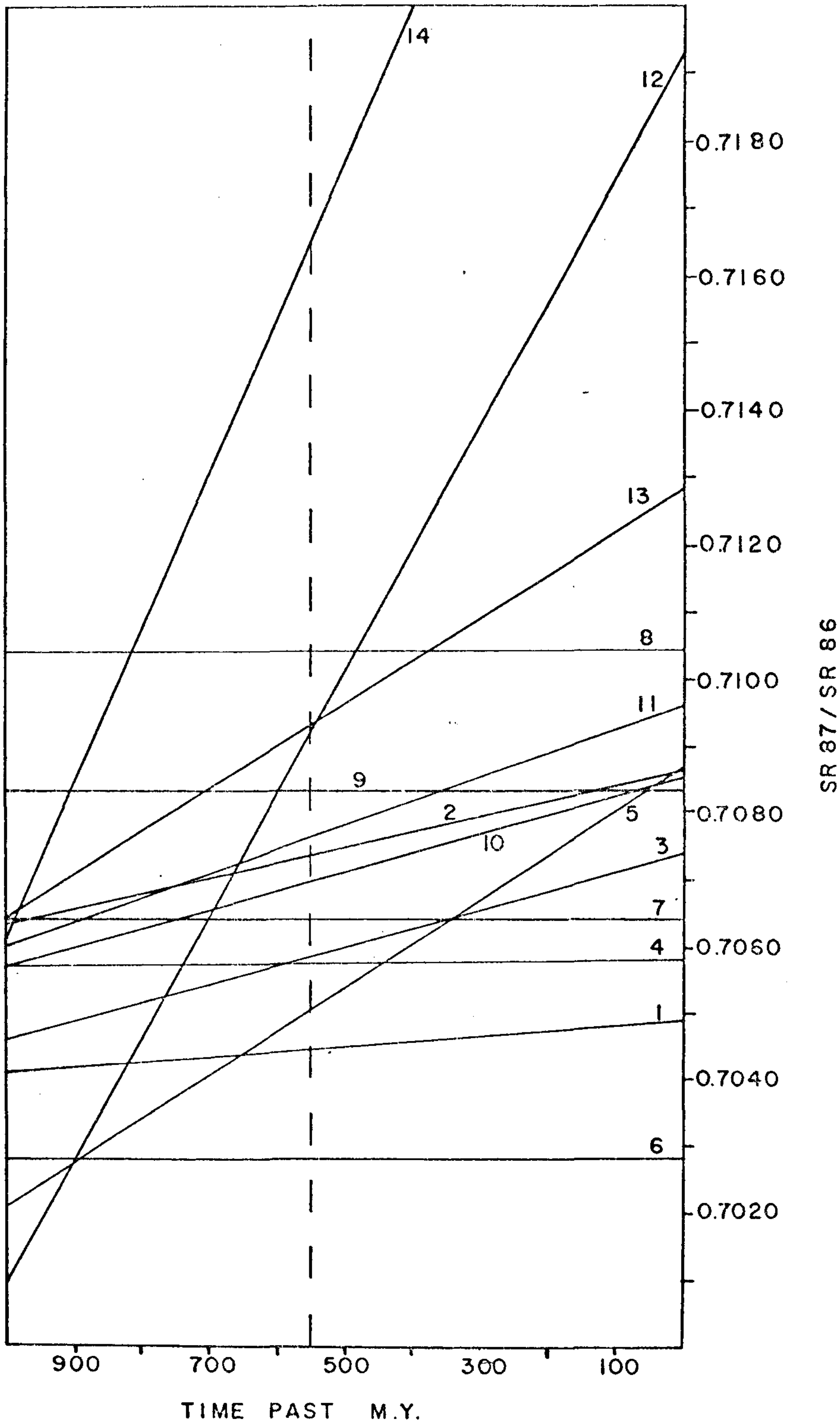


FIG. 30. DEVELOPMENT DIAGRAM FOR ROCKS OF THE FEN ALKALINE COMPLEX. ESTIMATED AGE IS 550 M.Y. (— — —)

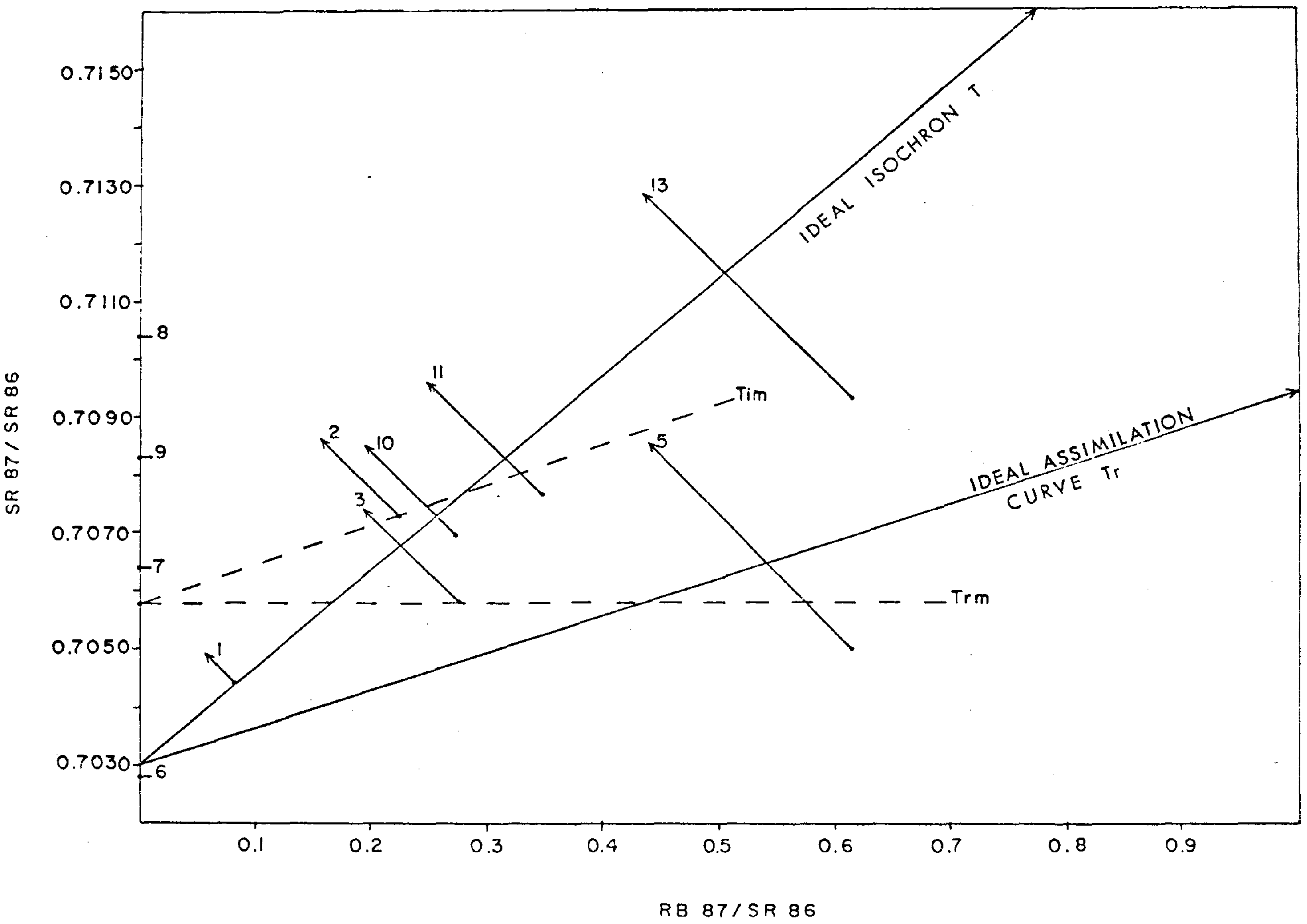


FIG.31. NICOLAYSEN DIAGRAM FOR ROCKS OF THE FEN ALKALINE COMPLEX SHOWING INITIAL PRESENT DAY RB-SR PARAMETERS.

Table 21. Age of the Fen Complex

Method	Sample	Age m. y.	Source
K/AR	Biotite, søvite	565	Faul et al. 1959
K/AR	Biotite, damtjernite	585	Kulp and Neumann 1961
K/AR	Biotite, søvite	590;603	Neumann 1960
K/AR	Biotite, søvite	568	Broch 1965
K/AR	Biotite, damtjernite	573	Broch 1965
K/AR	Feldspar, søvitic melteigite	413	Neumann 1960
Pb-α	Zircon-søvite	460	Neumann 1960
U-Th-Pb	Koppite-søvite	420;570 570;590	Saether 1957

Fig. 31 can be used to determine the Rb^{87}/Sr^{86} ratio of the rocks at the time of intrusion once the initial Sr^{87}/Sr^{86} ratio is known. This is done by projecting the present day Sr^{87}/Sr^{86} ratio back along a line of slope of 45^{o} (which represents the decay path of Rb^{87}) to the initial Sr^{87}/Sr^{86} ratio and then reading the Rb^{87}/Sr^{86} ratio off the diagram. Table 22 gives the initial Sr^{87}/Sr^{86} ratios and the initial Rb^{87}/Sr^{86} ratios of the Fen rocks.

Several conclusions can be drawn from Table 22 and Figs. 30 and 31.

1. The rocks do not lie on an isochron.
2. The rocks are not simply related in terms of a differentiation process from a single parent magma.
3. Søvite (6) has a lower initial Sr^{87}/Sr^{86} ratio than has melteigite, vipetoite and the søvitic melteigites and hence cannot be a residual fraction of a melteigite magma or be the metasomatised product of solid melteigite. The low Sr^{87}/Sr^{86} ratio of søvite (6) is in good agreement with that of 0.7021 determined for the same rock by Powell (1966). Søvite (7) possesses a higher Sr^{87}/Sr^{86} ratio than is normally found in carbonatites which have an average Sr^{87}/Sr^{86} ratio of 0.703 (Powell 1966). This high Sr^{87}/Sr^{86} ratio for a carbonatite is not, however, unique. Deans and Powell (1968) have found similar ratios in some Indian carbonatites and Hamilton (Brown 1964) has described carbonatite from the Songwe Scarp, Tanzania with Sr^{87}/Sr^{86} ratios of 0.709 and 0.712. The high ratios are attributed to the release of radiogenic Sr from the country rocks at the time of carbonatite intrusion.

4. The only development line intersections within close proximity to the age of the complex are those of two fenites (12 and 13) which indicate an age of ca. 540 m.y. and initial ratio of ca. 0.709.

5. If the Sr^{87}/Sr^{86} of the rock which has the lowest Sr^{87}/Sr^{86} ratio in the complex is taken as being comparable with that of the parent magma, e.g. søvite (6) Sr^{87}/Sr^{86}; 0.7028, then the ages of the individual members of the complex calculated using this as initial ratio are impossibly old relative to the true age of the complex (Table 22).

6. If the søvitic melteigites are all considered to be differentiates of a single hybrid magma (T_{rm}, Fig. 31) then using the Sr^{87}/Sr^{86} ratio of the Rb poor sample (4) as an initial ratio, then the ages (T_{im}, Fig. 31) of the søvitic melteigites (3 and 5) are approximately 557 and 430 m.y. respectively (Fig. 31). These ages are within the age established by other methods (Table 21) and are in accordance with the predictions of Fig. 28.

7. Material of high Sr^{87}/Sr^{86} ratio has played a role in the generation of the rocks of the complex.

8. Increasing degrees of fenitisation, e.g. fenite 13 is more intensely fenitised that fenite 12, does not alter the Sr content of the rock but causes a loss of Rb, hence Rb/Sr ratios de-

crease with fenitisation concomitant with the Rb/Sr ratio decrease there occurs a decrease in the Sr^{87}/Sr^{86} ratio.

Genesis of Silicate Rocks

The silicate rocks, melteigite, vipetoite, malignite and søvitic melteigite all have higher Sr^{87}/Sr^{86} ratios than the søvite (6). It is thus not possible to interpret this carbonatite as a residual low temperature fraction of a carbonated ijolitic magma as the high Sr^{87}/Sr^{86} ratio of this magma must be preserved in its differentiates. The high Sr^{87}/Sr^{86} ratios of the silicate rocks and the søvite (7) can be explained by assuming that a parent magma of carbonated ijolite of low Sr^{87}/Sr^{86} ratio was intruded into the granite-gneiss and then underwent a process of selective contamination by radiogenic Sr^{87} in the manner advocated by Pankhurst (1969) i.e. isotopic equilibration. In this type of contamination Sr of high Sr^{87}/Sr^{86} ratio in the country rock is exchanged between two reservoirs and results in an increase in the Sr^{87}/Sr^{86} of the magma until equilibrium is reached. The process implies that no other element is transferred and equilibrium is reached without any effects of assimilation being observed in the intruded magma. Such an interpretation would not seem to be feasible at Fen unless one postulates that søvite (6) is not related in any way to the other silicate rocks and carbonatites or failed to undergo isotopic equilibration.

Such postulates on geological grounds would seem unlikely. The silicate rocks and carbonatites also contain such high amounts of Sr that for equilibration to have occurred then it must have involved large volumes of granite-gneiss.

If the silicate rocks are not considered to be the parent of carbonatite, then it is necessary to consider how carbonatite might be involved in their genesis by processes of fenitisation and rheomorphism of granite-gneiss. The Rb-Sr contents and the Sr isotopic compositions of granite-gneiss and carbonatite can be regarded as estimates of the two extremes between which the Rb-Sr parameters of rheomorphic hybrid might vary. Fig. 31 indicates the Rb-Sr parameters of ideal rheomorphic hybrids between a carbonatite containing 5 ppm Rb, 7000 ppm Sr and Sr^{87}/Sr^{86} ratio of 0.703 and a granite-gneiss containing 225 ppm Rb, 300 ppm Sr and Sr^{87}/Sr^{86} of 0.7175. These values were chosen from analyses of the søvite (6) and the granite-gneiss (14) which is taken to be representative of country rock into which the carbonatite was intruded. Fig. 31 also shows the isochron formed by the hybrids at time (T), 550 m.y. after the time of rheomorphism (T_r). From Fig. 31 it can be seen that the initial Sr composition and initial Rb^{87}/Sr^{86} ratios of the Fen rocks form an array of points above the ideal assimilation line and do not define a straight line. This indicates that the Rb and Sr transferences involved in their genesis were not ideal, elements were preferentially gained and lots. The departure from the ideal system can be expressed in terms of the degree of assimilation of granite-gneiss in carbonatite required to produce the observed initial ratios. Thus Table 22 gives values of (X) the degree of assimilation expressed in terms of the number of parts weight of granite-gneiss assimilated by one part weight carbonatite required to give the initial Sr^{87}/Sr^{86} ratios $X(Sr^{87}/Sr^{86})$ and initial Rb^{87}/Sr^{86} ratio $X(Rb/Sr)$. If assimilation were of the ideal type the two values of X would be equal. As can be seen from Table 22 the irregularity of the two values implies preferential gain or loss of elements. Thus the simple bulk assimilation of granite-gneiss in carbonatite as a means of explaining the observed Sr^{87}/Sr^{86} ratios cannot account for the observed Rb/Sr ratios (and vice versa).

The data can be explained in terms of selective concentration of elements by partial melting and metasomatic processes. If fenites produced in advance of carbonatite magma are partially melted to form a silicate magma which is then 'mixed' with carbonatite, then the resulting silicate rock would possess a high Sr^{87}/Sr^{86} ratio and a low Rb^{87}/Sr^{86} ratio and lie to the left of the ideal assimilation line. This is because carbonatite possesses a very high Sr content, and addition to a partial melt of fenite would result in rapid lowering of the mixtures Rb/Sr ratio, the mixture would have a Sr^{87}/Sr^{86} ratio somewhere between the extremes of the carbonatite and granite-gneiss values. Bailey&Schairer (1966) have demonstrated how partial melting of fenites to give ijolitic rocks could take place, however the process is not as simple as this because of the effect of metasomatism. The metasomatising agents are undoubtedly some type of fluid phase and may be composed of CO_2 and H_2O which act as transporting agents for other elements. Thus the irregular flow of metasomatising agents may cause great variation in the concentrations of Rb and Sr from place to place and to produce a great array of Rb-Sr parameters in the final hybrids.

Thus the results of Sr isotopic studies indicate that the silicate rocks of the Fen complex, viz. melteigite, vipetoite, malignite and søvitic melteigite are the products of partial melting of fenite with mixing of the partial melt with carbonatite. This is in keeping with Brøggers (1921) and Saether's (1957) theory that malignite is a rheomorphic fenite but contrary to their ideas for the origin of the ijolite-melteigite series. The hypothesis is in keeping with Von Eckermann's (1948) theories of the genesis of the Alnö complex.

Table 22. Initial Sr^{87}/Sr^{86} ratios and initial Rb^{87}/Sr^{86} ratios, and apparent ages of Fen rocks.

No.	Rock	Initial Sr^{87}/Sr^{86}	Initial Rb^{87}/Sr^{86}	$X(Sr^{87}/Sr^{86})$	(XRb/SR)	Apparent age $X10^6$
1.	Melteigite	0.7044	0.080	2.6	0.9	2378
2.	Vipetoite	0.7073	0.225	9.8	2.7	2512
3.	Søvitic melteigite	0.7058	0.275	5.6	3.4	1602
4.	Søvitic melteigite	0.7058	0.006	5.6	~ 0	35273
5.	Søvitic melteigite	0.7050	0.615	3.8	9.2	891
6.	Søvite	0.7028	0.001	-	-	-
7.	Søvite	0.7064	0.001	7.2	~ 0	-
8.	Rauhaugite	0.7104	0.002	23.8	~ 0	-
9.	Rødberg	0.7083	0.001	12.4	~ 0	-
10.	Damtjernite	0.7069	0.275	8.6	3.4	2000
11.	Malignite	0.7076	0.350	10.8	4.5	1860
12.	Fenite	0.7092	1.740	17.0	54.5	-
13.	Fenite	0.7093	0.615	17.4	9.2	-
14.	Granite-gneiss	0.7162	2.155	-	-	-

Initial ratios are determined for an age of 550 m.y. for the complex.

Apparent ages are based upon an initial ratio of 0.7028.

Numerous objections to the above theory can obviously be advanced, the most important of these being:

1. Will the heat content of the intruding magma be sufficient to cause partial melting of granite-gneiss or fenite.
2. Will a silicate partial melt mix with a carbonatite liquid or with an immiscible liquid form. Recent experimental work (Wyllie 1966, Kooster van Gross and Piwinski 1969) indicates that immiscibility is possible.
3. Saether (1957) has calculated that a fenite of melteigite or ijolite composition can only be formed if the magma causing the fenitisation is already of ijolitic composition.

Such objections are of course difficult to counter. Unfortunately nothing is known of the temperature distributions between granite gneiss and intruding magma in the deep crust. The temperature differential might be very small and significant partial melting might have occurred. Saether's (1957) calculations were based upon bulk assimilation considerations and did not take into account partial melting and selective concentration of elements. Moreover, the Telemark granite-gneiss is a very heterogeneous body, many partially granitised amphibolite bodies can be found within it and would be major sources of Ca, Mg and Fe.

Damtjernite, Rauhaugite, Rødberg

Field evidence indicates that damtjernite belongs to a later phase of magmatic activity than the søvites and associated ijolitic rocks. Saether (1957) considers that damtjernite is similar to kimberlite, such a view can be definitely discounted as noted in Chapter 1 - the rock is a simple lamprophyre. Rocks similar to damtjernite can be found in other alkaline complexes, e.g. Alnö, Ngualla, Tundulu and in all cases appear to be late stage intrusions. They have been ascribed to reaction between alkaline rest liquids and already crystallised mafic minerals or basalt, and to reaction of liquid basalt with solid alkaline material. Verwoerd (1966) considers that such rocks may be a hybrid formed between peridotite, carbonatite and an alkali fraction generated at depth. The damtjernite at Fen contains numerous xenoliths of ultrabasic rock which appear to be cumulates formed during differentiation of damtjernite at depth. These xenoliths are now rounded and are indications that intrusion of damtjernite took place under fluidising conditions.

Petrographic evidence given by Saether (1957) demonstrates convincingly that rauhaugite and rødberg are formed from damtjernite by metasomatism involving carbonate solutions rich in CaMg and Fe.

The Sr isotopic composition of the damtjernite indicates that it is not simply related to søvite. The isotopic composition of rauhaugite and rødberg are compatible with alteration of damtjernite by carbonate solutions of high Sr^{87}/Sr^{86} ratio which removed Rb from the rock.

Any simple relation of the damtjernite to the rocks of the first cycle of magmatic activity at Fen is difficult to envisage as damtjernite appears to be a very abundant magma at Fen and in the surrounding district. Thus, Ramberg (1964) has, for example, postulated that a 10 km. pipe of damtjernite lies below the complex in order to account for the observed gravity anomalies and Ramberg and Barth (1966) have described a great number of dykes and breccias of damtjernite outside the complex some of which occur many kilometres away.

It is possible to envisage that damtjernite was formed by processes akin to those described for the earlier silicate rocks (they might even be an early differentiate of a damtjernite magma) and which then underwent continued differentiation at depth, but until further evidence becomes available, such hypotheses are merely conjectoral.

Conclusions

The Sr isotopic study of the Fen rocks indicates that rheomorphism of fenites could have played an important role in the genesis of the silicate rocks and supports conclusions reached by several other geologists regarding the genesis of these rocks. Study of one complex does not, however, demonstrate that all ijolitic rocks are generated by such processes. Further studies of complexes which on geological grounds support the theory of rheomorphic ijolites, e.g. Alnö, Nemegosenda Lake, and complexes which show no evidence of rheomorphism, e.g. Napak, Oka, must be undertaken in order that theory be confirmed or rejected. The generation of the small volumes of ijolite rock at Fen by rheomorphic processes also does not imply that the large volumes of nephelinite found for example in East Africa, are generated in a similar manner.

Further work at Fen should involve study of separated minerals and many samples of each type of rock should be analysed in order to determine whole rock isochrons for each petrographic unit.

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APPENDIX I

SAMPLE DESCRIPTIONS AND LOCATIONS

Kimberlites

Swartruggens Fissure, Swartruggens District, Transvaal, S. Africa

Samples 1-9

A calcareous micaceous kimberlite. Phenocrysts of red pyrope, phlogopite and a mineral which is now completely replaced by calcite and serpentine (? olivine), are set in a groundmass of phlogopite, calcite, dolomite and magnetite, together with minor apatite and perovskite. Both generations of phlogopite are replaced along cleavages by a bright green chlorite (kammerite) and show reversed pleochroism. A typical sample of the Swartruggens kimberlite is shown in Fig. 4. Samples 2 and 5 are of yellow ground. In these samples all the primary minerals are replaced by a mixture of serpentine, chlorite, talc and clay minerals.

Wesselton Pipe, Kimberley District, Cape Province, S. Africa.

Samples 10-15

Pipe rock. Phenocrysts of olivine, ilmenite, phlogopite and pyrope set in a fine grained groundmass. Phenocrystal olivines are rounded but are fresh, and are surrounded by reaction rims of magnetite and serpentine. The groundmass is composed of calcite, serpentine, magnetite, apatite perovskite and second generation olivine. The groundmass olivine is euhedral and is often completely replaced by serpentine.

Samples 16-17

Late stage kimberlite dykes. Very fine grained black rocks. Few phenocrysts visible in hand specimen. In thin section are very similar to the coarser grained material of the pipe.

Sample 18

Garnet mica peridotite xenolith. Fresh olivine and enstatite make up the bulk of the rock. The remainder of the rock 5-10% is composed of phlogopite, chrome diopside and pyrope.

Sample 19

Eclogite xenolith. A bimineralic eclogite composed of omphacite and garnet. An intergranular medium of unknown mineralogy surrounds most of the grains.

Premier Pipe, Cullinan, Bronkhortspruit District, Transvaal, S. Africa

Samples 20-22

Highly weathered blue ground. All minerals are completely replaced by serpentine, talc, chlorite and clay minerals.

Monastry Pipe, Marquard District, Orange Free State, S. Africa

Sample 23.

Phenocrysts of magnesian ilmenite and completely serpentinised olivine set in a fine grained groundmass composed of magnetite, serpentine, calcite and apatite.

Dutoitspan Pipe, Kimberley District, Cape Province, S. Africa

Sample 24.

Fresh olivine phenocrysts and phlogopite laths set in fine grained groundmass of calcite, magnetite and serpentine.

Bultfontein Pipe, Kimberley District, Cape Province, S. Africa

Sample 25.

Completely serpentinised olivines and chloritised mica set in a groundmass of serpentine, magnetite and calcite.

Doornkloof Fissure, Barkly West District, Cape Province, S. Africa

Sample 26.

Micaceous kimberlite. Dark rounded phenocrysts of a mineral now completely replaced by calcite, dolomite and serpentine, together with phlogopite laths set in groundmass of phlogopite, dolomite, calcite, apatite and serpentine.

Kirkland Lake, Ontario, Canada

Sample 27.

Micaceous kimberlite. Fresh rounded olivine and phlogopite phenocrysts set in a matrix of calcite, serpentine perovskite and magnetite.

Fen Complex

1. Melteigite-urtite. Melteig farm.

2. Vipetoite. Nigarskåsa.

3-5. Søvitic melteigites. (Hollaites). Samples of varying calcite content from south-west of Kåsen's farm.

6. Søvite. Hydro Quarry.

7. Søvite. Cappelens Quarry.

8. Rauhaugite. Road Cut on highway south of Ringsevja.

9. Rødberg. Tuftestollen.

10. Damtjernite. North-east of Damtjern.

11. Malignite. From stream near Kemperhoig.

12. Fenite. West of Teigen.

13. Fenite. Tuftestollen.

14. Granite-gneiss. Southern Haatvedt farm.