SOME ASPECTS OF THE GEOCHEMISTRY OF GALLIUM IN SILICATE ROCKS AND STONY METEORITES

by

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VOLUME 1

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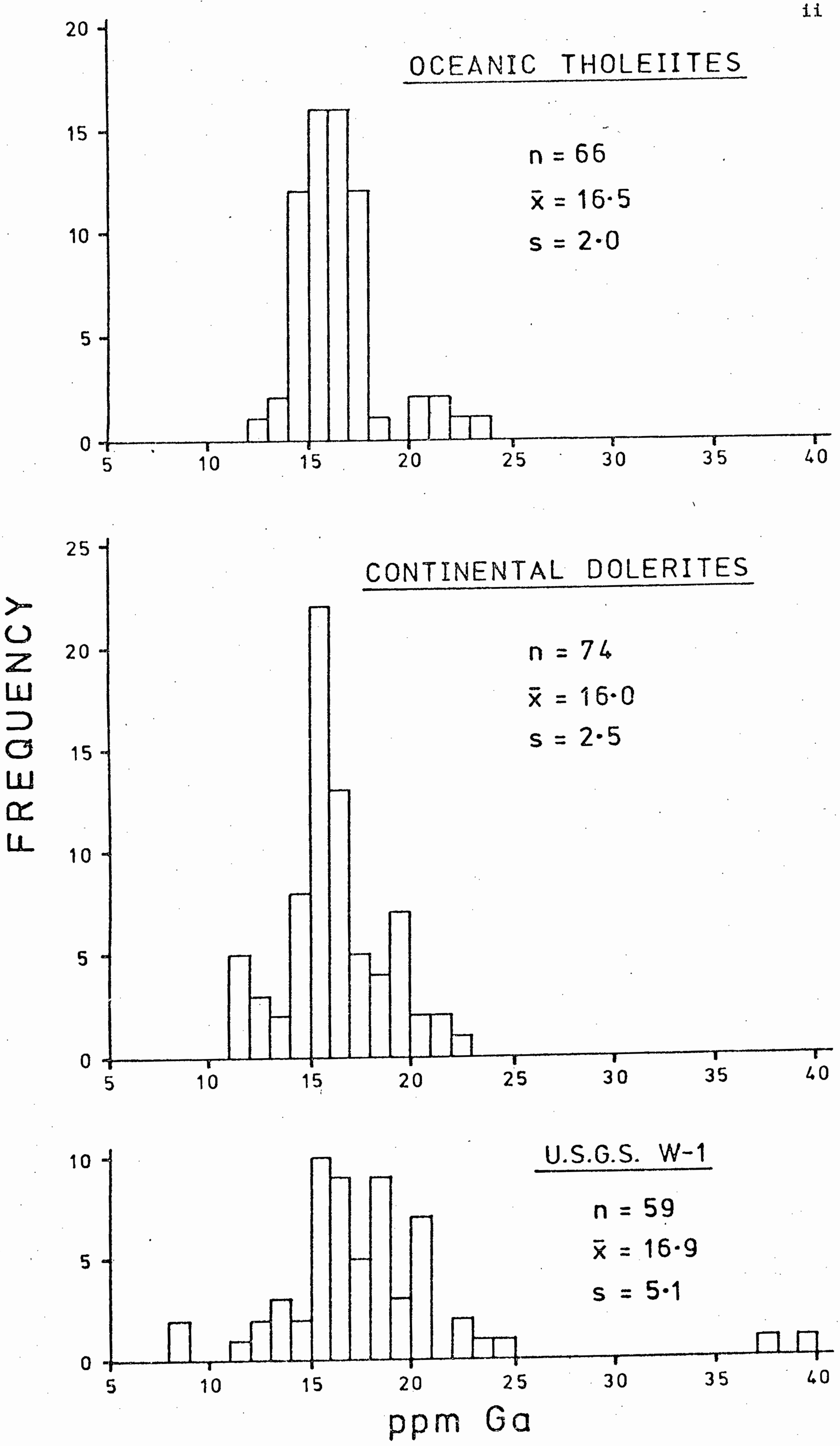
FRONTISPIECE

Frequency distribution diagrams of gallium determinations in oceanic tholeiites and continental dolerites and in the U.S.G.S. standard diabase (dolerite) W-1. Data for the tholeiites and dolerites were determined in this work by a single analytical technique (XRF spectrometry). The data for W-1 have been taken from the literature and were determined by a number of analytical techniques. Disregarding the extreme values reported for W-1, the spread of data for this one rock is still greater than that reported here for sixty-six tholeiites from three different oceans and seventy-four dolerites from four continents in the southern hemisphere. In this work forty-four determinations of gallium in three 4g aliquots of W-1 gave a mean value of 16.5 ppm with a range from 16.1 to 17.1 ppm and a standard deviation of 0.17 ppm (1s).


OCEANIC THOLEIITES
n = 66
$\bar{x}$ = 16·5
s = 2·0
CONTINENTAL DOLERITES
n = 74
$\bar{x}$ = 16·0
s = 2·5
U.S.G.S. W-1
n = 59
$\bar{x}$ = 16·9
s = 5·1
FREQUENCY
ppm Ga
0
5
10
15
20
25
30
35
40

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STATEMENT

This thesis represents in concept and execution my own work.

Certain of the data presented here have been reported previously, with my permission, in the following publications: Erlank and Reid (1974), Fesq *et al.* (1976), Hart *et al.* (1974) and Verwoerd *et al.* (1974).

Dr. Feather was responsible for the development and initial testing of the method described in the paper by Feather and Willis (1976) which is included in Appendix 1. The analytical data in the paper are my work. The concept of using the method to check for errors in XRF analysis as described in Chapter 5.3 is my own.

The development of the Geochemistry Department database was a joint effort by Dr. A.R. Duncan and myself with some programming assistance from C. Hartnady of the Precambrian Research Unit at U.C.T. The rock type codes and classification were put together by myself in consultation with Dr. Duncan and other members of the Geology and Geochemistry Departments.

Most of the Al data used in this thesis have been taken from the literature and are so acknowledged.

A useful paper on the geochemistry of gallium, entitled "Ge-Si and Ga-Al fractionation in Hawaiian volcanic rocks" by R. de Argollo and J.-G. Schilling, was published in the June volume of Geochim. Cosmochim. Acta 42, 623-630 (1978), but was received too late for consideration in this thesis. The data and conclusions are essentially in agreement with those presented here for Hawaiian lavas.

SUMMARY

The objects of the work presented here were: to develop an accurate method for the determination of gallium on a routine basis in rocks and meteorites at concentrations down to or less than 1 ppm Ga with a precision (c.o.v.) at the 10 ppm level and above of 1-2% (1s); to apply this technique to the determination of Ga in rocks and meteorites; by critically examining the high quality data thus obtained, to compare the distribution of gallium in various meteorite types, as well as in igneous, sedimentary and metamorphic rocks, seeking to define, where possible, the fine structure of its distribution and its relationship with aluminium during geological processes; and to evaluate the possibility of using variations in the gallium contents and Ga/Al ratios of rocks both to assist in the interpretation of the geochemical history of differentiated suites and to define regional differences, as has been done with other trace elements.

To achieve these goals an analytical technique for the determination of gallium in silicate rocks and stony meteorites using XRF spectrometry has been developed. The method is applicable on a routine basis and has proved capable of producing data that are both precise and accurate. The detection limit is 0.3 - 0.4 ppm Ga. Gallium has been determined in approximately 100 meteorites and separated fractions, 67 minerals and approximately 1500 rocks of igneous, sedimentary and metamorphic origin.

Although in some instances data are reported for samples in which gallium has previously been determined by other techniques, e.g. Skaergaard, meteorites and Karroo dolerites, the results have nevertheless proved valuable in either confirming the accuracy of the XRF technique, as for the meteorites, or indicating individual samples or suites of samples for which published gallium data are in error, e.g. published data for Karroo dolerites are about 50% too high. New gallium data are reported for a number of igneous complexes in southern Africa, for kimberlites and kimberlitic xenoliths, for rocks from a number of oceanic islands, for rocks from the Barberton Mountain Land, and for rocks from the granite-slate contact at Sea Point, Cape Town.

It has been shown that in only a few instances is the correlation between Ga and (Al + Fe^3) better than that between Ga and Al, and that the general use of the Ga/(Al + Fe^3) ratio in preference to the Ga/Al ratio is not warranted, although the Ga/(Al + Fe^3) ratio can sometimes yield important information.

Evidence is presented to suggest that a considerable proportion of the gallium in carbonaceous meteorites is in the carbonaceous or sulphide fractions. On the basis of Ga, Al and Fe distributions in stony meteorites, it is possible to separate these meteorites into the same classes or groups proposed by other workers on the basis of different criteria. The gallium data suggest that the C4 carbonaceous chondrites are chemically different from the C3 chondrites with which they are usually included.

The variation in the Ga content and Ga/Al ratio of abyssal tholeiites is generally much less than had been previously indicated, and the variation between tholeiites from the Atlantic, Pacific and Indian oceans is no greater than that found for a single ocean.

In order to decide whether gallium data could be useful in geochemical studies it was necessary to examine the distribution of Ga and the Ga/Al ratio in suites of rocks whose geochemical history had already been determined.

Gallium data for various igneous complexes indicated the important effect which changing mineralogy can have on the Ga content and Ga/Al ratio of the rocks. When investigating complexes of unknown history, changes in Ga content and Ga/Al ratio can alert the geochemist to possible mineralogical changes that might have taken place.

The determination of gallium in a number of upper mantle xenoliths, minerals and kimberlites constitutes an important contribution to our knowledge of the distribution of gallium in the earth. The data confirm the depleted nature of common peridotite (CP) xenoliths, and indicate the presence of considerable amounts of gallium in upper mantle ilmenite, in contrast to crustal ilmenite which has very low gallium contents. The enrichment of gallium in metasomatised nodules indicates its association with the metasomatic process and suggests that gallium may be fairly mobile in the upper mantle. The only upper mantle rocks examined in this work which contain sufficient gallium to give rise to MORB tholeiites were the clinopyroxene-rich bands and metasomatised common peridotites found in veined nodules from the Matsoku kimberlite pipe. The enrichment of gallium in kimberlites has been confirmed, and the Ga/Al ratio of kimberlites is dependent on the degree and type of crustal contamination. The Ga/Al ratio of uncontaminated kimberlite is close to 4.0.

On the basis of major and trace element studies, rocks of Karroo (Mesozoic) age from southern Africa have previously been divided into three groups, which are confirmed by the Ga/Al ratios for these rocks. The Ga/Al ratio data suggest that the Parana volcanics from Brazil may also be divided into northern and southern groups, and that the rocks from southern Brazil closely match those from northern South West Africa. The Ga/Al ratio data indicate that rocks from the southern part of the Lebombo monocline and from southern S.W.A. are similar to those from the Central Karroo province, while those from the northern Lebombo are close in composition to the northern Karroo province (Rhodesia). The ratios show further that the Lebombo rhyolitic rocks could not have been derived from the basaltic rocks by fractional crystallization.

The behaviour of gallium during the weathering of granites and shales indicated a separation and removal of Ga from Al during the alteration of feldspars to clay minerals and during the alteration of illite to kaolinite, with a consequent reduction in the Ga/Al ratio. Important evidence on the behaviour of gallium during the alteration of ancient and modern abyssal pillow lavas has been presented. Ga and the Ga/Al ratio are generally unaffected by alteration of the lavas during or after extrusion on the sea floor, but are very sensitive to epidotisation caused by the metasomatic introduction of elements into the rocks, which results in an increase in both Ga content and the Ga/Al ratio. Gallium increases with increasing degree of fenitization, and the behaviour of gallium during fenitization is similar to that reported during albitization. The increase in gallium during fenitization is, however, much less than that found for Zn, Cu or Sr. In kimberlites gallium was not affected by thermal metamorphism, nor was it lost to the wall-rocks during intrusion of kimberlite magma.

Gallium can be useful in distinguishing between different rock groups on a regional basis, and in tracing and interpreting the geochemical history of a rock suite. One of the advantages of using gallium is its relative immobility compared with many other trace elements, and the fact that very low concentrations of the element are present in intercumulus material. It became clear during this investigation that the Ga/Al ratio is usually of much more use to the geochemist than the abundance data on gallium alone.

Because of its relatively small range of concentration in most common rock types, gallium will be useful to the geochemist in studying igneous, metamorphic and sedimentary processes only if the data are of the highest quality.

FOREWORD

Many of the tables in this thesis have been printed by computer because of the large quantity of data presented, not only to save costs but primarily in an attempt to minimise the errors that would have occurred during typing. In this way it is hoped that errors have been kept to a minimum.

The printers available on the U.C.T. computer were capable of printing only in capital letters (upper case), and it has therefore not been possible to use upper and lower case lettering in those tables printed by the computer.

Most of the many frequency distribution diagrams (histograms) presented have been drawn by computer using a Calcomp plotter and a program written by the author. A few X-Y plots were drawn using a program developed in the Geochemistry Department by H.S. Smith and modified by A.R. Duncan.

THROUGHOUT THIS WORK THE Ga/Al RATIO WILL BE REPORTED TO ONE OR TWO DECIMAL PLACES, AND IT WILL BE TAKEN AS UNDERSTOOD THAT THE RATIO HAS BEEN MULTIPLIED BY 10^4, i.e. a Ga/Al ratio reported as 2.19 or 2.2 in the text represents values of 2.19×10^{-4} or 2.2×10^{-4}. For convenience, brevity and readability the factor 10^{-4} has been omitted in the text. In the tables the Ga/Al ratio is correctly shown as having been multiplied by 10^4.

Valence states of elements, e.g. Fe, are given as Fe^2 or Fe^3, and cations are indicated as Fe^{2+} or Fe^{3+}.

In Tables 32 and 38 modal values were reported only for different rock types or meteorites for which 15 or more samples had been analysed. For fewer samples the data points were generally so widely spread over the chosen class intervals that a modal value was not meaningful. Chosen class intervals were 1 ppm Ga and 0.2 for the Ga/Al ratio.

Some abbreviations and symbols used in the text or tables have the following meanings:

s.d. or s = standard deviation or root mean square (RMS) error
s_c = standard deviation for counting (XRF analysis)
C_i = coefficient of variation (in per cent) = c.o.v.
μ/ρ or m.a.c. = mass absorption coefficient
c.p.s. = counts per second
alk. fel. = alkali feldspar
amph = amphibole
ap = apatite
cpx = clinopyroxene
gt = garnet
hnbl = hornblende
ilm = ilmenite
mt = magnetite
ol = olivine
opx = orthopyroxene
plag = plagioclase
pyx = pyroxene
XRF = x-ray fluorescence spectrometry
OS = optical emission spectroscopy
INAA = instrumental neutron activation analysis
RNAA = radiochemical neutron activation analysis
MS = spark source mass spectrometry

ID = mass spectrometric isotope dilution analysis

AA = atomic absorption analysis

C_L = detection limit

For IUGS rock classification: A = alkali feldspar, Q = quartz, P = plagioclase, F = felspathoids, M = mafic and related minerals.

D.I. = differentiation index (Thornton and Tuttle, 1960), except when stated otherwise.

CHAPTER 1

INTRODUCTION

"The literature on gallium is very extensive...... Only a small proportion of the many determinations of gallium in rocks and minerals has been made by the most precise and accurate procedures. These results show that generally less precise spectrographic procedures give, on average, values of adequate accuracy. In view of this and also the quite low dispersion of gallium in common rocks and minerals, the average results of the less precise analyses often constitute abundance data of reasonable quality. Individual determinations or whole series of determinations by these methods are sometimes inaccurate, however, and it remains difficult to assess questions such as the extent to which differences in concentrations recorded for various areas represent genuine regional variations as distinct from systematic errors. Furthermore, the low dispersion of gallium leads to an interest in relatively small variations in processes such as magmatic differentiation, and these variations tend to be obscured in many investigations through the use of imprecise methods."

This quotation from the section on gallium by Burton and Culkin (1972) in the Handbook of Geochemistry summarises a number of ideas which led to the work presented in this thesis. The literature on gallium is indeed extensive. However, most of the papers were published before the 1970's. Probably the majority of the data was obtained using optical emission spectrography, because although gallium occurs at fairly low concentrations in common rocks and minerals, generally less than 70 ppm, it has a number of sensitive lines in the emission spectrum of the DC arc which allow its determination in most samples. Unfortunately the vast majority of spectrographic determinations of gallium were only semi-quantitative, i.e. with a coefficient of variation (C_1) of 30-50%, and even the best data had a c.o.v. of only 7-10%. In most instances this meant that the variation in gallium due to analytical error was equal to or greater than the actual variations in the rocks and minerals, which lead to the frequent comment on the gallium distribution, if any was made, that "gallium showed little significant variation with differentiation", e.g. Wilkinson (1959), although the gallium content in question may have varied from 15 to 25 ppm. It is to the credit of the early geochemists that they appreciated the problems associated with analytical error, but the use of a relatively imprecise analytical technique prevented the elucidation of the finer details of the behaviour of gallium during geochemical processes, and lead geochemists generally to regard gallium as one of those elements that was of little use in evaluating or determining such processes.

In the late 1960's and the 1970's x-ray fluorescence spectrometry (XRF) replaced optical emission spectography as the main analytical tool in many geochemical laboratories, and with its introduction there followed a marked decrease in the number of papers reporting gallium data. The reason for this was simple. In optical emission spectography the gallium spectrum was automatically recorded on the photographic plate together with lines of other elements, while in XRF analysis the gallium lines would be measured only if the instrument was specially set up to determine gallium, and, as already stated above, most workers considered its determination a waste of time and effort. XRF analysis, however, is capable of producing both accurate and precise data, even at concentrations below the 10 ppm level. Recently a few papers have appeared in which geochemists have begun to appreciate that perhaps gallium can be a useful element, e.g. Floyd and Winchester (1978), who have used Ga and its inter-element ratios to identify and discriminate between altered and metamorphosed volcanic suites.

Meteorites are the one group of samples for which really good gallium data are available in any quantity, and most of the data were obtained using radiochemical neutron activation analysis. This is not a technique that can be routinely applied in most laboratories.

During the 1960's and early 1970's the Department of Geochemistry at the University of Cape Town developed a general XRF analytical scheme for the determination of both major and trace elements in rocks and meteorites. The scheme was based mainly on the work of Norrish and his co-workers at the CSIRO in Adelaide and the ANU at Canberra. Routine methods were developed for trace elements such as Zn, Cu, Ni, Rb, Sr, Zr, Ba, Co, Cr and V, and the quality of the data was proved by comparison of meteorite data with that of other workers and by participation in the lunar program. The Department had also built up over the years an extensive collection of meteorites and rock samples from the mid-ocean ridges, oceanic islands, many igneous complexes, kimberlites and the upper mantle, and rocks of Mesozoic age from four continents in the southern hemisphere, which were available for analysis.

The objects of the work presented here were: to develop an accurate and precise XRF method for the determination of gallium on a routine basis in rocks and meteorites at concentration levels down to or less than 1 ppm Ga with a precision (c.o.v.) at the 10 ppm level and above of 1-2%, which would fit into the general analytical scheme within the Department; to apply this technique to the determination of gallium in a number of different types of rocks and meteorites; and, by critically examining the high quality data thus obtained, to compare the distribution of gallium in various meteorite types, as well as in igneous, metamorphic and sedimentary rocks, seeking to define, where possible, the fine structure of its distribution and its relationship to aluminium during geological processes; and to evaluate the possibility of using such variations in the gallium contents and the Ga/Al ratios of rocks to assist in the interpretation of the geochemical history of differentiated suites and to define regional differences in rock suites, as has been done with other trace elements.

To achieve these goals, gallium has been determined in about 100 meteorites and separated fractions, 67 minerals and approximately 1500 rock samples of igneous, metamorphic and sedimentary origin.

Although in many instances data are reported for samples in which gallium had been previously determined by other techniques, e.g. Skaergaard, B.I.C., meteorites and Karroo dolerites, the results have nevertheless proved valuable in either confirming the accuracy of the XRF technique, as for the meteorites, or indicating individual samples or suites of samples for which the published gallium data are incorrect. The published gallium data for Karroo dolerites, for example, are high by about 50%.

New gallium data are presented for a number of igneous complexes in southern Africa, for kimberlites and kimberlitic xenoliths, for rocks from a number of oceanic islands, for rocks from the Barberton Mountain Land, and for rocks from the granite-slate contact at Sea Point, Cape Town.

In order to decide whether Ga data could be useful in geochemical studies, it has been necessary to examine the Ga and Ga/Al ratio distribution in suites of rocks whose geochemical history has already been determined.

This thesis falls naturally into four main sections: a detailed description of the analytical technique (Chapters 3 and 4); a section on meteorites (Chapter 6); a section on the gallium content of minerals, the distribution of gallium in different rock types, and inter-element ratios with gallium (Chapters 8 to 10); and a section dealing with gallium in rocks from the abyssal oceans, oceanic islands, igneous complexes, the upper mantle, ancient greenstones, and its behaviour during weathering and metamorphism (Chapters 11 to 21).

CHAPTER 2

GENERAL STATEMENT ON THE CHEMISTRY AND GEOCHEMISTRY OF GALLIUM

The existence of an element similar to aluminium was predicted by the French scientist Lecoq de Boisbaudran in 1860 and independently by D.I. Mendeleev in 1869. Such an element was discovered and described in 1875 by de Boisbaudran who detected a new chemical element in sphalerite from the Pyrenees. He named the element gallium in honour of his country, Gallia (France).

Gallium (Ga) is located in the third group of the periodic table. Its atomic number is 31, atomic weight 69.7, and there are two stable isotopes found in nature, ^{69}Ga (60.4%) and ^{71}Ga (39.6%). There is no information on the natural fractionation of these isotopes in geological processes.

The Ga atom has 18 electrons in the outermost level, which relates it to Zn, an element with similar electron structure and chalcophile properties. But, unlike Zn and the other transition elements where electrons are added to the inner orbital, Ga has a third valence electron in the outermost electron layer (4p). This places Ga in the same group as Al, s^2p^1, the difference being that in Ga the penultimate M shell consists of 18 electrons, rather than the 8 electrons in the L shell of Al.

Fe also plays an important role in the geochemistry of Ga, often occurring as Fe^2 or Fe^3 and frequently accompanied by Al and Zn. The similarity of the cycles of Al, Fe and Zn and their extensive isomorphism in various crystal lattices, places Fe in the group of elements having an important influence on the crustal abundance and distribution of Ga. Cr can also be included in the group and possibly Ti as well. Some fundamental data relating to Ga and associated elements are given in Table 1.

As a solid, Ga resembles Zn, showing a bluish lustre and a semi-brittle fracture.. Ga melts at 29.8^{o}C and boils at about 2200^{o}C. Liquid Ga metal, when free of oxide, is almost indistinguishable from Hg. However, the surface film that forms immediately on contact with air prevents it from coalescing, and this rapid oxidation limits the number of applications that could be envisioned for a metal that is liquid at near room temperature. The adherence of the oxide layer to most surfaces gives the appearance of wetting. Other unusual properties of this element are its exceptionally low vapour pressure even at high temperatures, i.e. 0.003 mm Hg at 1000^{o}C; the density of the liquid which is greater than that of the solid (Ga expands on solidification); its high heat conductivity and thermal stability; and its ability to remain a liquid indefinitely at temperatures considerably below its normal freezing point. It can occasionally be held without freezing for short periods of time at liquid nitrogen temperature (77^{o}K).

Most commercially produced Ga is derived as a byproduct from Zn ores and bauxite. Although the purification of Ga to 99.9999% purity is relatively simple, it is a very expensive process, and the high cost of very pure Ga has limited its commercial use. Ga has nevertheless been found useful in electronic devices where advantage has been taken of its property of forming semiconductors with Sb, As and P; in pressure-volume-temperature studies because of its wide liquid range and low vapour pressure; and as a heat exchange medium because of its thermal stability, high heat conductivity, low vapour pressure and wide liquid range.

The valence states of Ga in various compounds are 1, 2 and 3, but the Ga^{3} compounds are the most stable, and in nature Ga occurs only as Ga^{3}. A particularly important property of Ga is its ability to combine with both O (partial or complete ionic bonds) and S (covalent bonds). An equally important property is its ability to form complex anions with O and F. The tendency of elements to form oxygen complexes is determined by the degree of covalence of their bonds, which increases with increasing alkali content of the medium, and Ga, Al and other elements form oxygen complexes more readily in alkaline media, whereas in acidic media the amphoteric elements remain preferably as positively-charged ions.

Ringwood (1955b) concluded that during magmatic crystallization there is an equilibrium state in which complex-forming ions are distributed between two structural positions, i.e. both as free ions and as complex centres. Because of its lower ionic potential, it can be expected that for any given medium the amount of free Ga ions should be greater than the amount of free Al ions. This difference, which apparently has some influence on the simultaneous isomorphous replacements of the (GaO_4)-(AlO_4) and Ga^{3+}- Al^{3+}, Fe^{3+} types, increases the probability of cationic Ga substitution. Although Ga has been shown to form complex fluoride ions, in nature there is an almost complete absence of Ga in minerals where Al is combined with F. This is ascribed to the lower stability of the Ga fluoride complexes relative to that of the corresponding Al fluoride complexes.

A discussion of the distribution and behaviour of Ga during sulphide formation does not form part of this work. However, one of the only two independent Ga minerals known to date is Gallite ($CuGaS_2$), found only at Tsumeb (S.W.A.) and Kipushi (Zaire), with Ga contents from 29-37%. The other Ga mineral is the hydroxide Soehngeite ($Ga(OH)_3$). The relationship between Ga and Zn in the reducing environment of sulphide mineralization is well known, and Ga contents in sphalerite up to 0.1% have frequently been reported.

Ga is a widely dispersed element and is almost always present in rocks and minerals at concentrations less than 500 ppm, but usually at concentrations less than 70 ppm. Due to the similarity of its crystallochemical properties to those of the principal rock-forming elements Al and Fe and its extensive isomorphism with them, Ga does not form independent deposits. The bulk of Ga in nature is therefore dispersed in many minerals, mainly in those listed in Table 37.

Al may enter crystal lattices as the cation Al^{3+} and as the complex $(AlO_4)^{5-}$. The cation occurs in an octahedral (6-fold co-ordination) position (Al_{VI}) and establishes an ionic bond with O. The complexed Al occurs in 4-fold co-ordination (Al_{IV}) and the bond is predominantly covalent. Ga will replace Al in either state, but the Al-O bond is slightly shorter and less covalent than the Ga-O bond.

The substitution most likely to occur is the Ga^{3+} - Al^{3+} diadochy, and the minerals with this substitution generally contain higher amounts of Ga (e.g. muscovite and chlorite). On the other hand excellent samples of the substitution of the $(GaO_4)^{5-}$ complex for the $(AlO_4)^{5-}$ complex are provided by the feldspars, nepheline and sodalite. The isomorphism of the complexes is very widespread, and the bulk of Ga in rocks (50-75%) occurs as an isomorphous substitution for Al in 4-fold co-ordination. The isomorphism of Ga with Fe is apparently not as marked as that with Al, although this aspect has not yet been sufficiently investigated. However, Fe^{3+} has similar ionic radii to those of Ga^{3+} in both 4- and 6-fold co-ordination. Cr^{3+} has the same ionic radius as Ga^{3+} in 6-fold co-ordination.

The question whether Ga preferentially replaces Al^3 or Fe^3 when they are in either 4-fold or 6-fold co-ordination is unresolved at the present time. Burton and Culkin (1972) summarise the position for Al by saying that preferential substitution of Ga for 6-co-ordinated Al is not an over-riding factor. Other factors that have to be taken into account are electronegativity (Ringwood, 1955a), ionisation potentials (Ahrens, 1964), and bonding energies (Nockolds, 1966). Burns and Fyfe (1967) suggested that attention should be focussed on thermodynamic parameters governing the free energies of distribution or difference in two states, and not the parameters of any single state.

In the case of Fe^3 in 4- or 6-fold co-ordination it seems from the data in the literature that Ga substitutes preferentially for Fe^3 in 4-fold co-ordination (e.g. magnetite) rather than 6-fold co-ordination (e.g.

ilmenite) in crustal materials. However, data presented in this work for upper mantle ilmenites indicate the presence of significant amounts of Ga, in contrast to crustal ilmenites.

The situation is very complex, in that Ga can substitute for Cr^3, possibly Ti^4, and also for Si in silica tetrahedra. It is also possible that Ga may substitute for Fe^2 in minerals such as diopside, hedenbergite and anthophyllite. Interesting work carried out by Huggins et al. (1977) on Ti-containing silicate garnets indicated that experimentally determined preferences for the tetrahedral over octahedral sites in garnets are in the order $Ga > Al > Fe > Ti \gg Cr$. The distribution of Al, Fe and Ti between octahedral and tetrahedral sites only approached equilibrium at temperatures in excess of 1200°C. This is in contradiction to the radius ratio rules (Goldschmidt, 1954) which suggest that Ga should favour octahedral co-ordination, although in 4-fold co-ordination its radius ratio relative to oxygen (Table 1) is very close to the theoretical value of 0.41 separating tetrahedral from octahedral co-ordination.

Another very important parameter governing the distribution of Ga between various minerals is its partition coefficient between the liquid magma and individual minerals. Little work has been done on this aspect of the geochemistry of Ga which constitutes a serious gap in our knowledge. Goodman (1972) determined partition coefficients for Ga between pyroxene and groundmass and between plagioclase and groundmass in a number of basic volcanic rocks from oceanic islands. Mean values for partition coefficients calculated from Goodman's data are 0.99 between plagioclase and liquid, and 0.41 between pyroxene and liquid. Corresponding values for Al are 1.91 for plagioclase and 0.27 for pyroxene. Goodman found a partition coefficient of 0.04 for Ga between olivine and liquid. Paster et al. (1974) attempted to calculate partition coefficients for minerals from the Skaergaard, but their mineral separates were not very pure, resulting in uncertainties in the partition coefficients of ± 50%. They reported partition coefficients for

Ga in plagioclase of 1.7 and in magnetite of 2.0. Their value for plagioclase is very much higher than that of Goodman, which is thought to be more correct. The value of 2.0 for magnetite is probably correct. The partition coefficient for ilmenite is thought to be similar to that of olivine, namely 0.05. The partition coefficient for Ga between amphibole and liquid has been taken as 0.9 in this work.

A knowledge of partition coefficients is essential when considering possible trends in Ga concentration and Ga/Al ratio during fractional crystallisation or partial melting. From the data mentioned above it may be predicted that plagioclase fractionation causes little or no change in the Ga concentration in the liquid, but does lower the Al concentration resulting in an increase in the Ga/Al ratio. Pyroxene fractionation results in an increase in Ga in the liquid and a relatively greater increase in Al, with a resultant slight decrease in the Ga/Al ratio. Olivine fractionation causes an increase in both Ga and Al in the same proportion and therefore no change in the Ga/Al ratio. Magnetite fractionation causes a marked decrease in the Ga content of the liquid with essentially no change in Al, with the result that the Ga/Al ratio of the liquid decreases.

Goodman also studied the relationship between the Ga content and the composition of feldspars, and the relationship between Ga and Fe^3 in pyroxenes. He found a good correlation between Ga and Fe^3 in clinopyroxenes and concluded that both Fe^3 and Ga probably occurred in 6-fold co-ordination in the M.1. clinopyroxene site. Goodman found that although Ga was enriched in the plagioclases, the Ga/Al ratio was low indicating that Al was enriched over Ga. He also found that there was good inverse correlation between the Ga content of the plagioclase and the anorthite content. Using his data, it is possible to write the following equation for the relationship:

$$\text{ppm Ga in plagioclase} = 15 + 0.36x(\%\ \text{albite})$$

This is of course applicable only to his data. The increase in Ga content with increasing albite content in the plagioclase can be related to the melting points of plagioclase. Goldsmith (1950) synthesised Ga feldspars and showed that these have lower melting points than natural plagioclases.

	Melting points °C
$CaAl_2Si_2O_8$	1500
$NaAlSi_3O_8$	1118
$NaGaSi_3O_8$	1015

Melting point criteria lead to the prediction that Al would be preferred relative to Ga when competing for lattice sites in earlier products of magmatic crystallization. Ga should therefore tend to accumulate in later products of differentiation and in residual materials. This explanation also accounts for the fact that Ga is not related to the amount of Al present in the feldspars, and that anorthitic plagioclases have a much lower Ga/Al ratio than albitic feldspars. As a result of the early crystallization and fractionation of anorthitic feldspars, an initial increase in the Ga/Al ratio of rocks during igneous differentiation can be expected. This phenomenon is found for a number of igneous complexes examined later in this work.

The geochemical cycle of Ga may be summarised as follows. Among common rock-forming minerals Ga is generally concentrated above its crustal abundance (18 ppm) only in some feldspars and amphiboles, feldspathoids, micas, chlorite and magnetite. Its concentration is usually low in pyroxenes and particularly low in olivine and quartz. These features reflect the close coherence of Ga and Al in most geochemical processes and the less close but important relationship between Ga and Fe^3.

It follows that the Ga content of ultrabasic rocks is generally low, with most of the Ga being present in pyroxenes and amphiboles. The chief Ga carrier minerals in basic, intermediate and acid rocks are feldspars, but the highest concentrations are found in muscovites and biotites. The relative affinity of some common minerals for Ga is usually $>$ muscovite $>$ biotite $>$ plagioclase $>$ hornblende $>$ potash feldspar $>$ pyroxene.

In alkaline rocks the bulk of the Ga is found in nepheline and feldspars, while the highest concentrations are found in biotites and sodalites.

The differentiation products of one magmatic event generally show an increase in Ga content of the rocks with increasing differentiation, with sometimes considerable enrichment in the late stages. The Ga/Al ratio may stay constant or increase or decrease depending on which minerals are being fractionated and in what proportion to one another. In this respect the Ga/Al ratio can yield significant information. Alkaline rocks usually show an increase of Ga with differentiation, while subalkaline rocks show little change or possibly a slight decrease with differentiation. Ga may be strongly enriched in alkaline pegmatites and associated minerals.

A noticeable Ga enrichment is observed in greisens, while skarns contain variable amounts of Ga depending on their mode of origin. The high-temperature pneumatolytic minerals cryolite and cryolithionite do not contain detectable Ga.

In hydrothermal processes Ga is chiefly associated with sphalerites, and generally low-temperature sphalerites contain more Ga than high-temperature types.

The average Ga content of sedimentary rocks is about 15 ppm, but varies considerably in different types of rock.

Weathering processes result in the redistribution of Ga. Ga accumulates in hydroxides and hydrosilicates, but sometimes is completely separated from Al, as in halloysites.

In soils the Ga content ranges from 5 to 50 ppm, and the usual trend is for Ga to increase with depth.

Ga has been detected in coal ash in the concentration range 8-1000 ppm (mean $=$ 40 ppm Ga).

In metamorphic rocks both the concentration of Ga and the Ga/Al ratio are in general similar to those in unmetamorphosed material. During albitisation and fenitisation Ga increases relative to Al, and Evans (1964) in his study of Connemaran rocks found that both the Ga concentration and the Ga/Al ratio increased with increasing degree of metamorphism.

Any Ga present in carbonate rocks is present almost entirely in clay impurities. Carbonatites are very low in Ga.

The small amount of data available on Ga in natural waters indicates that Ga is only slightly mobile in natural waters. It appears that Ga may accumulate in sea water relative to Al as was predicted by Goldschmidt (1954).

Further details on the general geochemistry of Ga may be found in papers by Vlasov (1966), Borisenok and Saukov (1960), Ronov and Migdisov (1965), and Burton and Culkin (1972).

Two other important properties of Ga in rocks should be mentioned. Vincent (1974) summarised the distribution of trace elements in minerals from the Skaergaard Intrusion. He stated that the distribution of Ga among the coexisting mineral phases is very well defined. Calculation of the modal contributions of each separate mineral to the Ga content of the rock shows almost 100% agreement with independent analysis for Ga of the whole rock sample, so that almost none of the element resides in the intercumulus material. Similar results are reported in this work. Winchester and Floyd (1977) and Floyd and Winchester (1978) proposed the utilization of the seven elements, Ti, Zr, Y, Nb, Ce, Sc and Ga, which they generally regarded as immobile during secondary alteration processes, including spilitisation, submarine alteration and metamorphism, as an aid to discrimination between different volcanic magma series and their metamorphosed equivalents. Evidence for and against the "immobility" of Ga during secondary alteration processes will be presented in this work.

Finally, one point must be stressed again. The maximum spread of the Ga concentration in rocks is about 100 ppm, although most rocks have Ga contents from <0.3 to 40 ppm (Fig. 42a). Therefore a change in the Ga concentration of only 2-3 ppm can mean a relative change of perhaps 10-20%, which is considerable. It is therefore imperative that precise and accurate data be made available, otherwise analytical error will be sufficient to obscure natural variations in the Ga content and the Ga/Al ratio.

CHAPTER 3

SAMPLE PREPARATION

The sample preparation technique used in this laboratory for trace element analysis by XRF is basically that described by Norrish and Chappell (1967).

A sufficiently large bulk sample of the rock (0.5 - 4 kg, depending on grain size) is passed through a jaw crusher (Mn steel jaw plates) to give −6 mm (−¼ inch) chips, and then split. 75-150g are ground in a carbon steel ball mill shaken in a paint mixer, or in an agate vessel using a Siebtechnik vibratory mill, so that the material is at least −120 #. A subsample of 4-6g, depending on the type of rock, is taken from the crushed powder and ground for 60 minutes in an automatic agate mortar, after which the powder is predominantly −300 #.

According to Kleeman (1967) this means that $\sim 10^7$ grains of rock are sampled before grinding to −300 #. Again according to Kleeman, this ensures a sampling error of c.o.v. = 1% (68% probability) for each mineral present in the rock at concentrations greater than 0.1%, or a c.o.v. = 0.5% (68% probability) for all minerals present at concentrations greater than 0.5%. The highest concentrations of Ga in common rock-forming minerals (Burton and Culkin, 1972) have been found in albite (120 ppm Ga), nepheline (140 ppm Ga), muscovite (400 ppm Ga), biotite (150 ppm Ga), and magnetite (120 ppm Ga). In the worst case, muscovite at 0.1% of the rock, the random sampling error for Ga would be 1% of 0.4 ppm Ga, or 0.004 ppm Ga. For 99% confidence limits, this amounts to 0.012 ppm Ga, which is negligible.

The fine powder is briquetted in a hand press with a backing of a 50:50 mixture of bakelite powder and boric acid at a pressure of 15 tons p.s.i. For acid rocks containing free quartz it is sometimes necessary to add one drop per gram of powder of distilled water or a solution of 2% Mowiol (N90-88), a water-soluble plastic available from Hoechst AG, to assist binding of the powder. Experience has shown that this has no effect on the analyses, due to the very small quantity of material actually added to the rock, about 0.02% in the case of Mowiol solution.

Details of the sample preparation techniques used for meteorite samples are given in von Michaelis et al. (1969a) and McCarthy (1971).

In trace element analysis the correct choice of material from which grinding vessels are made is of paramount importance. When Ga is to be determined, tungsten carbide vessels must not be used. In Fig. 1, XRF scans across the Ga wavelength region are given for an anorthosite from the B.I.C. Separate aliquots of –6mm chips were ground in a carbon (black axle) steel vessel, a stainless steel and a tungsten carbide vessel. The degree of tungsten contamination is obvious, and causes interference on the Zn K_β line and first background position in the determination of Ga.

CHAPTER 4

ANALYTICAL TECHNIQUE

4.1 INTRODUCTION

There are a number of analytical techniques that can be used for the determination of Ga in rocks and meteorites. Amongst others, instrumental neutron activation analysis (INAA), spark source mass spectrometry (MS), mass spectrometric isotope dilution (ID), atomic absorption (AA), optical emission spectroscopy (OS), colorimetric analysis, and x-ray fluorescence (XRF) have been used. The most frequently used method for rocks has been OS, while for meteorites INAA has been used by most recent workers.

Some desirable attributes of any analytical technique may be listed as follows:

Sensitivity
Ability to determine several elements simultaneously
Freedom from contamination and reagent blanks
Precision
Accuracy
Speed
Cheapness of equipment
Throughput of samples
Automation

For Ga, which has a low concentration dispersion in common rocks, probably the most important factors are sensitivity, freedom from contamination, specificity, precision and accuracy. If a large number of samples is to be analysed, then cost and speed are also important.

Ga is probably one of the most frequently reported, and least used, elements in geochemical literature. Only a very small proportion of the many Ga determinations have been made by the most precise and accurate procedures, and analyses by OS constitute the major part of the data (Burton and Culkin, 1972).

Generally, OS, while having reasonable sensitivity, gives at best relatively imprecise (c.o.v. = 5-10%) data which can suffer from considerable bias or systematic errors. As will be shown later, errors of up to 300% can arise. The method has the advantages of being relatively cheap and quick, and requires only small quantities of sample.

ID is probably the most inherently accurate and precise of the instrumental techniques available today, but is not commonly used for the determination of Ga.

INAA can be very accurate, but it is necessary to make an ion-exchange separation to achieve this accuracy. This makes it not only expensive but relatively slow, and not everyone has access to a reactor.

AA does not have the sensitivity necessary for a general method applicable to rocks because of the high dilution factors resulting from the dissolution of the sample.

Two of the most exciting and promising techniques are the ICP (inductively coupled plasma) used as a source for OS, and also the use of the glow discharge source for OS (K. Laqua, pers. comm.). The latter is probably the more attractive because it is not necessary to dissolve the sample, but only to mix it with an electrical conductor, e.g. Cu or graphite powder. However, much research needs to be done on the ICP source before it fulfils its potential, and the glow discharge source has not yet been proved for trace element analysis at low levels.

Burton et al. (1959) determined Ga in over 200 terrestrial materials using a sensitive spectrophotometric technique in which the precision was better than 2% (c.o.v.) at 20 ppm Ga, while at the 1 ppm level the s.d.(1s) was ± 0.02 ppm. The accuracy, however, was poor. Both G-1 and W-1 gave essentially the same values at 21.3 and 21.5 ppm Ga respectively, compared with recommended values of 19.6 and 16.0 ppm Ga, indicating considerable bias.

The remaining technique is XRF spectrometry. XRF has a number of advantages which recommend it as a general purpose analytical technique for the determination of Ga in rocks and meteorites. It will be shown that XRF has sensitivity (C_L = 0.3 ppm Ga), speed (5-30 mins/sample), accuracy, precision, freedom from contamination, and the cost per sample is low.

Many geochmical laboratories these days have an XRF spectrometer as their basic analytical tool, because of its ability to determine most of the major, minor and trace elements important to the geochemist. XRF is essentially complementary to INAA and MS.

4.2 THIS WORK

The method used in this work will be presented in detail for two reasons. The accuracy of trace element analysis using XRF has been found, from bitter experience, to be critically dependent on the detail and care with which the necessary corrections for peak overlap and matrix effects are made. If others are to use the method effectively, it is essential that these details be available to them. Secondly, one of the main objects of this work was to produce first-class data that are both accurate and precise. It is necessary, therefore, that it be shown not only that the analytical method is capable of producing such data, but that all necessary precautions were taken to prevent bias or systematic error in the data presented here.

Although Ga has been determined in rocks and meteorites by a number of workers using XRF (Parker, 1969; Carmichael et al., 1968; Thomas and de Laeter, 1972; Compston et al., 1970; Goodman, 1972; Reed, 1972), in only four cases are full details of the methods given (Thomas and de Laeter, Carmichael, Parker, and Reed). Two of these papers describe the application of XRF to the determination of Ga, Ge and Ni in iron meteorites. Goodman (1972) used a method somewhat similar to that to be described here, but the coefficient of variation of his technique was 6% at the 20 ppm Ga level, and he mentioned no corrections for interfering elements.

The method described here was developed for the determination of Ga in rocks, minerals and meteorites at concentrations down to 0.3 ppm Ga.

The method was first used for the determination of Ga in chondrites and achondrites using the rocks G-1 and W-1 as reference standards. A preliminary but careful scan of the wavelength tables indicated little chance of line interferences taking place, except for Zn and Cu, with possibly Hf, on the background positions. Wavelength scans of G-2 and W-1, Fig. 2, seemed to confirm this fact, with no lines being visible apart from Zn K_β, Ga $K\alpha$ and Cu K_β.

In this work a "doped" sample or "doped" blank refers to a sample or blank to which a known amount of an element or elements has been added.

Interference blanks were prepared from Specpure chemicals Fe_2O_3 and SiO_2, and doped separately with Zn, Ga and Cu. These doped blanks were then measured to allow interference factors to be calculated for each element on the other peak and background positions. Samples were run measuring intensities at Zn K_β, B1, Ga K_α, B2 and Cu K_β. At this early stage of the work the possible interference of Hf was neglected, Hf being present in stony meteorites at levels undetectable by XRF, and in G-1 and W-1 at about 5 and 3 ppm Hf respectively. Possible error in G-1 could amount to less than 0.5% relative, which was considered negligible. Highly satisfactory results for the meteorite analyses were obtained (see Chap. 5).

The next step was the extension of the method to the analysis of rocks and minerals. It was realised that some of the rocks to be analysed would contain Hf up to the 100 ppm level, and that corrections would have to be made for Hf interference. Table 2 and Figs 2 and 3 indicate the interferences that are likely to occur, and initially it was decided to measure intensities at Zn K_β, B1 (38.05°), Ga K_α, B2 (39.60°), Hf $L_{\beta 1}$ and Cu K_β. Inspection of Fig. 3 indicated that the two background positions would be those least likely to interference. Possible interference by Ba $K_{\beta 1,3}$(4) was considered but rejected, as it was thought that a fourth order line would be completely removed by the use of pulse height selection. Subsequent work with samples such as NIM-S, containing about 2600 ppm Ba, resulted in strongly negative nett peak counts at the Hf position, indicating an error on one of the background positions. A blank sample doped with 6350 ppm Ba showed clearly that a fourth order reflection of Ba $K_{\beta 1,3}$ was in fact being detected (Fig. 4), and the background position was changed to 39.40° 2θ, which then yielded satisfactory results for samples with Ba contents up to 3000 ppm.

Perusal of Table 2 indicated that interference could occur from W, Pt, Ta, Pb, Ir and Os (all first order lines), and possibly also from second order lines of Zr, Nb and Th. The intensity ratio for first : second : third : fourth order reflections is 100 : 35 : 10 : 2.5. In most rocks the concentration levels of Pt, Ir and Os are so low that any interference can be neglected, as is the case with Ta.

The amount of interference caused by Pb, Ba, W, Ta, Nb, Th and Zr was determined (Table 3). Blank samples were doped with Th (2000 ppm), Zr (2400 ppm) and Nb (2100 ppm), but in no case could any interference be detected. Of the remaining elements, W, Ta and Pb can cause interference, the level of which was measured using doped blanks. At the 54 ppm Pb level no detectable interference (i.e. $<$ 0.4 ppm Ga) was measured. However, a blank sample doped with 1110 ppm Pb yielded 6.8 ppm Ga (0.0061 ppm Ga per ppm Pb), which meant that some acid rocks containing 50 ppm Pb would be in error by about 0.3 ppm Ga. W is not normally present in rocks to any significant level, but it can be introduced at fairly high concentrations (a few hundreds of ppm) by grinding in tungsten carbide vessels during the crushing process. The nett result in the determination of Ga may or may not be serious depending on the degree of W contamination. About 330 ppm W gives a negative concentration of 0.5 ppm Ga, resulting from interference on B1 causing too high a background intensity. Grinding in any vessel other than agate should be avoided wherever possible, tungsten carbide vessels introducing Co contamination as well as W, and steel vessels introducing Cr, Ni and Mn contamination depending on the type of steel used. In the very few samples in which Ta occurs at high concentrations, the Ga concentration must remain uncertain (Fig. 5). From measurements on a doped blank, 230 ppm Ta results in 2.8 ppm Ga being determined, i.e. about 0.012 ppm Ga per ppm Ta.

4.2.1 Instrumental Conditions

The best x-ray tube for exciting the Ga K spectrum is one with a Mo target. The use of a Cr tube is possible, but will result in considerable reduction in intensity. Both W and Au tubes cause strong line interference from the characteristic tube lines. Reed (1972) recommended the use of a thin Ni filter placed over the window of the Mo x-ray tube to help reduce the background level in the Ga $K\alpha$ wavelength region, without absorbing too much of the Mo radiation itself. A Ni filter was tried in this work, but while indeed improving the peak to background ratio and thus potentially improving counting statistics, the overall intensity loss was such that there was in fact no improvement in counting statistics relative to measurements made without the filter. While the thickness of the Ni filter is probably extremely critical in determining maximum sensitivity, it was felt that further experimentation was not warranted. A filter was therefore not used for this work as one of the main objects was to be able to determine very low concentrations of Ga in meteorites and ultrabasic rocks.

The choice of analysing crystal was a difficult one. It is possible to use either a LiF(200) or LiF(220) crystal, the former yielding twice the intensity of the (220) but having poorer dispersion. The greater dispersion of a (220) crystal would result in less line interference, but to achieve the same counting statistics it would be necessary to count for twice the time. In the case of low Ga concentrations, this would have meant unrealistically long counting times, and with the dispersion of LiF(200) being adequate (Figs 2-4), the crystal was chosen for this work. It was felt that the correction factors for average rock types were sufficiently small not to jeopardise the accuracy and precision of the method. A fine collimator (150 μm) was used with the LiF(200) crystal to keep line interference to a minimum.

At this wavelength region (Ga Kα = 1.34Å), both the scintillation detector and the flow proportional detector operate below their best sensitivities (Jenkins and de Vries, 1970, p.66). On the spectrometer used for this work, a Philips PW1220, it is possible to use both detectors in tandem. The scintillation detector measures about 60% of the combined count rate, and the flow counter about 40%. Increasing the measured count rate from 60%, using the scintillation detector only, to 100% using both detectors was therefore possible, and both detectors were used in this work. All samples were measured under vacuum to improve intensities further. Samples were rotated during analysis. The pulse height analyser was set to pass 95% of the Cu Kβ radiation, a setting which resulted in the optimum peak to background ratio being obtained to give the best counting statistics.

The best counting statistics and detection limits were obtained by running the x-ray tube at 95 kV and 21 mA (generator maximum = 2kW). In the early stages of this work it was possible to run the instrument at these settings, but subsequently the instrument became unstable at these settings and the maximum voltage that could be maintained was 80 kV. Most of the work was therefore run at 80 kV and 25 mA, although the best sensitivity is achieved using as high a kV as possible.

Instrumental settings are set out in Table 4.

4.2.2 Counting Times

As has been stated previously, the object of this work was to determine the concentration of Ga with an error of less than 2%, if possible. In XRF analysis the counting error varies with counting time, such that the longer the counting time the lower the counting error. In order to halve the counting error, it is necessary to count four times as long, as the error is dependent on the square root of the counting time, according to the equation

$$\mathcal{E} = \frac{1}{\sqrt{RT}}$$

where $\mathcal{E}$ = standard deviation

R = countrate

T = time

(Jenkins and de Vries, 1970, p.95)

The Ga concentration in the samples analysed in this work varied from not detectable (<0.3 ppm) to 100 ppm Ga. In addition, differences in mass absorption coefficients of the samples could result in two samples having the same gallium concentrations requiring different counting times to achieve similar counting errors.

In order to make the best use of the instrumental time available, it was decided to use a set of six different counting times (see Table 5) resulting in a total counting time per sample that varied between 8 and 40 minutes. Those samples with high Ga concentrations could be counted for the shorter times and those with low concentrations for the longer times. To determine which set of counting times should be used for each sample, all samples were first counted on a "test" run using very short counting times, code 80 in Table 5. A computer program was used to calculate what the counting statistics would be if the sample was counted for each of the six sets of counting times, and the results together with the detection limits and an estimate of the Ga concentration were printed in a table (Table 6). From this table a set of counting times was chosen such that, if possible, the projected counting error (s_c) would be 1.7% or less. As each sample was to be counted at least twice, the final counting error should be $1.7 / \sqrt{2} = 1.2\%$ or better. For low Ga samples it was not possible to achieve counting errors of this level and they were counted using code 1400, giving absolute errors ($1s_c$) of about 0.1-0.2 ppm Ga for a single determination.

At low concentration levels the best counting statistics are obtained if the peak and background are measured for the same length of time. Wherever possible, therefore, and using the available time settings on the instrument, the counting time for the Ga peak was made equal to the sum of the counting times on the two background positions.

This work was aimed at the determination of Ga, but it was necessary to count Zn, Hf and Cu peaks as well in order to make accurate interference corrections. In the case of Zn, Hf and Cu the strongest interference is caused by Hf lines. Hf was counted for the same time as a background position, while Zn and Cu were usually counted for shorter times. The counting errors for these elements are therefore larger than on the Ga peak itself. However, when the intensities are low, the interference is very low and a slightly larger error in the measurement is not important. Conversely, when the intensity is high and interference more significant, the counting error is smaller and therefore the correction more accurate.

4.2.3 Determination of Background

An examination of Figs 2-6 is sufficient to indicate that the determination of background in this wavelength region is not simple. It is not possible to measure a background at angles lower than 37° 2θ, because at about this angle there is a sudden increase in the background level (Fig. 7). The reason for this jump in background intensity is uncertain, but it is probably associated with second order reflections of the Mo $K_{\beta 1}$ line and its

4.2.4 Determination of Interference Factors

For the determination of Hf, Zn, Ga and Cu interference factors, three other angle positions were measured at 37.20, 40.00 and 40.85° 2θ (Fig. 7). It will be noticed in Figs 3, 4 and 7 that there is a small peak at the Cu K_β position in all the blank samples. This is due to Cu contamination in the x-ray tube, and the intensity of this tube peak is inversely proportional to the mass absorption coefficient of the sample. In order to obtain the true background intensity under this peak, a best fit second order polynomial curve was fitted to the intensities measured at 39.40, 39.90, 40.00 and 40.85° 2θ, and the intensity at 40.44° (Cu K_β) calculated from this polynomial.

Similarly, the true background intensity at the Zn K_β position was calculated from a curve fitted through intensities measured at the angles 37.20, 38.05, 38.90, 39.89 and 40.00° 2θ. The reason this was necessary for the Zn position was that some vacuum pump oils contain Zn, which tends to build up on samples that are in the instrument for long periods of time, such as the blanks used here. On early runs this calculation was unnecessary as there was no measurable Zn intensity in the blanks (Fig. 7), but Zn began to show on later runs. The cost of making new blanks each time was prohibitive, and therefore corrections had to be made for Zn contamination.

To determine the Ga interference correction factors, ratios were calculated from the blank samples relating the intensities measured at Ga K_α, B1, B2 and Hf $L_{\beta1}$ respectively to the sum of intensities measured at 37.20, 40.00 and 40.85°. Measurements were then made on a Ga-doped blank and the ratio factors used to calculate the background intensities at B1, Ga K_α, B2 and Hf $L_{\beta1}$. Nett counts were calculated at each position and the ratio of the nett counts at B1, B2 and Hf $L_{\beta1}$ to the nett counts on the Ga peak gave the correction factors for Ga on these three positions. For each run the average of at least five measurements was taken. A similar procedure was adopted for Zn using 39.40, 39.90 and 40.00 as the background angles. For Hf the background angles used were 37.20 and 40.85, and for Cu 37.53, 38.05 and 38.90. Correction factors were calculated by computer for Zn on B1, Hf on Zn, B1, Ga, B2 and Cu, and for Cu on B2 and Hf. The magnitudes of these interferences are given in Table 7. The most important corrections are for Zn on B1, Ga on B2, Hf on B1, Ga, B2 and Cu, and Cu on Hf.

4.2.5 Determination of Ga in Samples

Once the background and correction factors had been determined, all samples and standards were counted at the four element and two background positions, and also at the Mo K_α Compton peak position to determine the mass absorption coefficient (see later). Using a computer program written for the purpose, all intensities were converted to counts per second, corrected for dead-time and sample position in the instrument, and the mass absorption coefficient (μ/ρ or m.a.c.) calculated.

Using the equations of the lines relating 1/m.a.c. to background factors, Fig. 8, background factors were calculated for each sample. The following iterative calculation was then made to determine the nett peak intensities for Zn, Ga, Hf and Cu after correction for both background and line interferences. Depending on the degree of interference on the background positions, the number of iterative cycles varied from 2 to 5, averaging 3 or 4. Samples such as NIM-L required 5 iterations.

4.2.6 Iterative Calculation Procedure

```
     B1* = B1
     B2* = B2
   7 BGD = B1* + B2*
     B1* = B1
     B2* = B2

     ZN* = ZN - BGD x ZNBGFAC
     GA* = GA - BGD x GABGFAC
     HF* = HF - BGD x HFBGFAC
     CU* = CU - BGD x CUBGFAC

     If HF* is zero or negative, go to 1

     CU* = CU* - HF* x HFCORFACCU
```

```
1  If CU* is zero or negative, go to 2

   HF* = HF* - CU* x CUCORFACHF
   B2* = B2* - CU* x CUCORFACB2

2  If HF* is zero or negative, go to 3

   ZN* = ZN* - HF* x HFCORFACZN
   B1* = B1* - HF* x HFCORFACB1
   GA* = GA* - HF* x HFCORFACGA
   B2* = B2* - HF* x HFCORFACB2

3  If ZN* is zero or negative, go to 4

   B1* = B1* - ZN* x ZNCORFACB1

4  If GA* is zero or negative, go to 5

   B1* = B1* - GA* x GACORFACB1
   B2* = B2* - GA* x GACORFACB2
   HF* = HF* - GA* x GACORFACHF

5  BKG = B1* + B2*

   If |BGD - BKG| ≪ 0.0001 x BGD, go to 6

   Go to 7 and repeat above calculation

6  Calculation of background at Ga for determination of counting
   errors and detection limit

   BGD2 = (B1* + B2*) x GABGFAC + HF* x HFCORFACGA

   Continue with calculations.
```

B1, B2, ZN, GA, HF and CU represent measured intensities in c.p.s.

B1*, B2*, ZN*, etc. represent <u>nett</u> intensities in c.p.s.

ZNBGFAC, etc. represent background factors for each element.

HFCORFACCU, etc. represent correction factors for Hf on Cu, etc.

Once the nett intensities had been calculated for each standard, the following calculation was made:

$$\text{GAFAC} = \frac{\text{ppm Ga}}{\text{GA}^* \times \text{m.a.c.}}$$

GA* = nett Ga intensity in c.p.s.

m.a.c. = mass absorption coefficient

Once all standards had been processed, the average value of GAFAC (GAFAC*) was calculated and used for the determination of Ga in the samples, using the equation:

$$\text{Ga ppm} = \text{GA*} \times \text{m.a.c.} \times \text{GAFAC*}$$

The detection limit for Ga was calculated using the equation:

$$\text{DTLMT} = 3 \times \text{m.a.c.} \times \text{GAFAC*} \times \sqrt{(\text{BGD2}/\text{TIMEPK})}$$

where TIMEPK = counting time on Ga peak in seconds.

Conventionally the background intensity is divided by the total counting time on the background, assuming that both the peak and background are counted for the same time. Because in this work peak and background were not always counted for the same time, the program determined the shorter of the two counting times and used the shorter time in the calculation of the detection limit. This ensured that any bias in the calculation was towards a higher detection limit rather than a lower.

The counting error on Ga was calculated using the usual equation incorporating counting times on peak and background (see Equation 5.11, page 100, Jenkins and de Vries, 1970).

During the calculation of the nett Ga intensity, it was necessary to calculate also the nett intensities of Zn, Hf and Cu. It was therefore simple to calculate factors for these elements similar to GAFAC* and to use these factors to determine the concentration of Zn, Hf and Cu at the same time as Ga. Mention has been made earlier of the presence of Cu tube contamination, and for the accurate determination of Cu a correction was made for the tube contamination, which was m.a.c.-dependent and therefore varied from sample to sample.

A computer program was written to do the calculations, and print out the results. Information fed into the program included correction factors for sample position in the spectrometer, dead-time, and number of counts measured on the Mo K_α Compton peak, line interference factors, slopes and intercepts for the lines relating background factors and 1/m.a.c., slope and intercept relating time on Mo K_α Compton peak and m.a.c., factors for conversion of Zn, Hf and Cu intensities to ppm, and a constant representing Cu contamination from the x-ray tube. For each sample the information required was name, position in spectrometer, counting time code, six intensity measurements, counting time on Mo Compton peak and per cent Al_2O_3 (when known). For standards, the same information, except per cent Al_2O_3, was required together with the Ga concentration in ppm. Information included in the printout was sample name, Ga/Al ratio, Ga ppm, counting error expressed both as ppm and % relative, detection limit, counting time code, concentrations in ppm and detection limits for Zn, Hf and Cu, number of iterations, m.a.c. and time measured on the Mo K_α Compton peak (Fig. 9). If no Al_2O_3 data was supplied, then the Ga/Al ratio was printed out as ".00".

4.2.7 Determination of Mass Absorption Coefficient (m.a.c.)

In XRF analysis the concentration of an element is related to its nett peak intensity according to the equation:

$$\text{Concentration} = \text{Intensity} \times \text{m.a.c.} \times F \qquad (1)$$

where F is a constant derived from standard samples and dependent on the instrumental conditions used for the determination. F is calculated from a standard sample by rewriting equation (1) as:

$$F = \frac{\text{concentration}}{\text{intensity} \times \text{m.a.c.}} \qquad (2)$$

It is obvious therefore that the final accuracy of the results is dependent as much on the accuracy of the mass absorption coefficient as on the accuracy of the intensity measurement and the concentration. In this study particular attention has been paid to the determination of the m.a.c., and many interesting points have come to light.

The m.a.c. may be determined in three ways. The first and least accurate (probably) is the calculation of the m.a.c. using data from tables and a knowledge of the major element composition. The drawbacks of this method are the stated accuracy of the m.a.c. tables ($\sim$2-4%) and the fact that major element data are not always available.

Probably the most accurate method, if used carefully and correctly, is the transmission method of Norrish and Chappell (1967). A sufficiently penetrative radiation, e.g. Nb K_α, is allowed to pass through a known weight of sample pressed into a circular hole of known diameter in a perspex slide placed in front of the scintillation detector, and the intensity measured with and without the sample in position. The m.a.c. for Nb K_α radiation may then be calculated using the equation:

$$\text{m.a.c.} = \ln \frac{I_o}{I} \times \frac{\text{area}}{\text{mass}}$$

where I_o = intensity of incident radiation, and I = intensity after absorption, area = area of hole in slide in cm^2, and mass = mass of sample taken in g.

This method, while accurate, is very time-consuming since it must be carried out at least twice on each sample to ensure accuracy. Consequently, it is not often used for routine analysis. It is used in this laboratory only when the third method (to be described) is not applicable, or to check the accuracy of the results so obtained, or on specially important samples (e.g. standards and lunar samples).

The third method, commonly used in this laboratory and in many others, is the method of Reynolds (1963, 1967) which makes use of the fact that the m.a.c. of a sample is inversely related to the intensity of the scattered tube radiation, in particular the Mo K_α Compton peak, from a Mo tube. The Compton peak is caused by incoherent scattering by the sample of the Mo K_α line from the Mo x-ray tube. It will be shown that this method, subject to certain conditions, is capable of producing m.a.c's with an accuracy equivalent to those obtained by the transmission method, i.e. $\sim$1%.

In his original paper, Reynolds (1963) recommended the use of a

LiF(200) analysing crystal together with an Y_2O_3 filter placed in front of the detector. Since that time crystals with better dispersion, such as LiF(220), have become available and are to be preferred for reasons given later. Fig. 10 illustrates the spectrum obtained from pure quartz using a LiF(220) crystal, that has twice the dispersion of LiF(200), both with and without a Y_2O_3 filter. It is obvious that use of a crystal of lower dispersion, e.g. LiF(200), would result in some cross-tailing of the Mo K_α peak under the Compton peak. As the Mo K_α lines is not as sensitive to changes in m.a.c. as the Compton peak, this would result in errors. For this reason only a LiF(220) analysing crystal is used in this laboratory for the determination of m.a.c. using the Compton peak method.

Normally the intensity of the Mo K_α Compton peak is measured at an angle corresponding to the maximum intensity of the peak. However, during the analysis of lunar samples, some of which contained up to 200 ppm Y, it was noticed that the m.a.c's determined by the transmission technique and the Compton peak method did not always agree. When there was a discrepancy, the Compton peak method always yielded a lower m.a.c. Investigation showed that the Y $K_{\beta 1}$ peak was almost exactly superimposed on the Compton peak causing too high an intensity to be measured, resulting in a low estimate of the m.a.c. (Fig. 11). Fig. 12 gives an expanded view of part A of Fig. 11. It is clear that even for a sample containing 2000 ppm Y there is a part of the Compton peak (marked with an arrow) where the intensities of the Compton peaks of the two samples, pure quartz and quartz + 2000 ppm Y, are almost equal. This angle is about 0.15° 2θ lower than the maximum of the Compton peak, and corresponds to the lowest intensity between the Y $K_{\beta 1,3}$ and $K_{\beta 2,4}$ peaks, as shown in Fig. 11(B) using a W tube. When the lunar samples were re-run measuring the Compton peak at the off-set angle, there was good agreement between the transmission and Compton peak methods. Another element that can cause interference on the Compton peak is Nb, the Nb K_α line occurring at an angle of 30.4° 2θ. It is only in exceptional rocks that this type of interference occurs, e.g. NIM-L (980 ppm Nb). Other elements causing interference are U ($UL_{\beta 1}$ at 29.3° 2θ) and $ThL_{\beta 3}$ at 30.7° 2θ), e.g. in SY-1 (2500 ppm U and 1300 ppm Th). All m.a.c's are now measured in this laboratory using a Mo tube, Y_2O_3 filter, LiF(220) analysing crystal, and the off-set angular position on the Compton peak.

To prove the accuracy of the Compton peak method, the m.a.c. of a number of international standard rocks was determined by the transmission method (using Nb K_α radiation) as carefully as possible, including the use of an expanded form of the dead-time correction equation:

$$R_{true} = \frac{R_{obs}}{1 - (R_{obs} \times t_D + (R_{obs}^2 \times t_D^2/2))} \qquad (3)$$

to correct I and I_o for dead-time losses, where

R_{true} = true count rate in c.p.s.

R_{obs} = observed count rate in c.p.s., and

t_D = dead-time in seconds.

The Compton peak intensity was measured for 26 briquettes comprising 18 standard rocks and minerals, and the time required to acquire 400,000 counts, corrected for dead-time, was plotted against the transmission m.a.c's. A reduced major axis regression line (which assumes errors in both measurements) was fitted to the data points (Fig. 13). The intercept on the m.a.c. axis was -0.0003. The maximum relative error of any of the points compared to the best fit line was 1.91%, while the average relative error was 0.82%. As the error on the transmission determinations was probably about 1%, the agreement between the two methods was most satisfactory, and proved that the use of the Compton peak method for determining m.a.c's for accurate trace element analysis was justified.

For comparative purposes, the m.a.c's for the standards were calculated from the recommended major element concentrations (Flanagan, 1973) using five different sets of m.a.c. tables from the literature. Intercepts on the m.a.c. axis, maximum deviations from the best fit lines, and average percentage deviations from the lines are shown in Table 8. It is obvious that the best agreement with the Compton times occurs when the transmission data are used, with the average percentage deviation being about half that obtained using calculated m.a.c's. For comparison with Fig. 13, the plot of the Philips data against Compton time is shown in Fig. 14.

It was necessary to confirm that a m.a.c. determination made using the Mo K_α Compton peak (at 0.73Å) would still be correct at the Ga K_α wavelength (1.34Å). It is not possible to determine the m.a.c. at the Ga K_α wavelength by the transmission method, as the very small amount of sample required to allow measurable transmitted intensity precludes the making of a disc in the perspex slide. It is possible to make discs of sufficient thinness to measure Rb K_α radiation (0.93Å), and in Table 9, abstracted from a paper by Feather and Willis (1976), m.a.c's for a number of samples measured at five different wavelengths are shown together with various ratios.

Hower (1959) stated that in the wavelength region shorter than the absorption edge of the highest atomic number major element, which in most rocks is Fe, the ratio (m.a.c. S_1) / (m.a.c. S_2) for two samples is constant for all wavelengths, although the absolute values of the m.a.c's vary considerably for different wavelengths. Therefore, provided that Fe is the highest atomic number major element, the determination of the m.a.c. using the Mo K_α Compton peak (0.73Å) will be valid for the correction of m.a.c. effects at the Ga wavelength (1.34Å) as well, both wavelengths being shorter than the Fe absorption edge at 1.74Å. The data in Table 9 support this statement.

There are, however, some samples for which the Compton peak method cannot be used for the analysis of Ga, for reasons other than line interference. Usually these are samples in which a major or minor element absorption edge occurs between the Compton peak and the Ga K_α wavelengths. Typical examples are samples having high Sr concentrations, such as NIM-L (4500 ppm Sr) (see Table 9), or high Th concentrations, such as SY-1 (1300 ppm Th). If samples have trace elements in this wavelength region (0.7-1.0Å) at concentrations higher than 1000-1500 ppm, the accuracy of the m.a.c. as determined by the Compton peak method must be suspect. It is then necessary to determine the m.a.c. at the Rb K_α wavelength by the transmission method.

Table 9 shows that the error for NIM-L would be 5.5% if the m.a.c. for the determination of Ga was measured using the Compton peak method.

The Mo x-ray tube was already being used for the determination of Ga with the LiF(200) analysing crystal. As the spectrometer can hold up to three analysing crystals at a time, it was possible to have the LiF(220) crystal mounted together with the LiF(200) crystal, and to use the Mo K_α Compton peak for the determination of the m.a.c. during the Ga run. This resulted in a considerable saving of time as the sample had to be loaded into the instrument only once for both measurements. Another advantage was that if the sample was for some reason not at the correct height in the instrument, the effect of making the two measurements together was to cancel out any errors due to varying distance from the x-ray tube.

It was not possible to measure the Compton peak with the yttrium filter as this would have absorbed too much of the Ga radiation. The result was some cross-tailing of the Mo K_α peak under the Compton peak for low m.a.c. samples (Fig. 10), altering the slope of the line relating time to m.a.c. such that it made an intercept on the m.a.c. axis of about 1.0, and also affecting very high m.a.c. samples. The slope and intercept of the line were calculated from measurements on a number of standard samples, and were fed into the computer program which used the information to calculate m.a.c's for unknown samples. Satisfactory results were obtained as shown in Table 10 and Fig. 15 comparing m.a.c's determined by the Mo K_α Compton peak method using an yttrium filter and during a Ga run. The samples shown cover the range of m.a.c's found in rocks and meteorites. Above a μ/ρ_{Rb} of about 22, which applies only to meteorites and some minerals such as ilmenite and magnetite, it is best to determine the m.a.c. separately using the yttrium filter or the transmission method.

4.2.8 Alternate Means of Background Determination

Before discussing the accuracy and precision of the method, the reader's attention is drawn to another means of determining the background intensity at a peak position, as described in a paper by Feather and Willis (1976) (see Appendix 1).

In brief, the background intensity at any wavelength shorter than the Fe absorption edge was found to be linearly related to the reciprocal of a m.a.c. appropriate to that wavelength region, e.g. m.a.c. Rb K_α. It followed that if the m.a.c. was known, then the background intensity at a peak position could be calculated from the equation of the line relating 1/m.a.c. and background at the peak wavelength. The equation of the line was determined by plotting intensities at each required position against 1/m.a.c. for a number of blank samples, obtaining the best fit line to the points and calculating its equation. It is obviously extremely important to ensure that the 'blank' samples contain no traces of the elements being determined, otherwise the equations of the best fit lines will be incorrect.

All that is then required to determine the concentration of an element in an unknown sample is to measure its m.a.c. and the intensity at the peak position. From the equation of the background line, the background intensity is calculated, the nett peak intensity found and the concentration of the element determined in the normal way. <u>It should be noted that it is</u>

no longer necessary to measure background positions.

For the determination of Ga, this method has important implications. Firstly, it is not necessary to count the background positions. Secondly, the only element actually interfering on the Ga K_α line is Hf, with an interference factor of 5.5% of the nett Hf peak. The Hf peak itself suffers interference from the Cu K_β peak to the extent of 3.4% of the Cu peak intensity. If the determination of Ga is the only interest, the contribution of Cu on the Hf peak can be ignored as the cumulative error for the effect on the Ga peak is negligible. Consider the data in Table 11 as an example. For EG-4489, ignoring Cu correction on Hf, the Hf correction on Ga amounts to 3.6 c.p.s. or 1.4% of the Ga peak. The error in ignoring the Cu interference on Hf is 0.3 c.p.s. or $\sim$0.1% of the Ga peak. Depending on the accuracy required, it may even be acceptable to ignore the Hf contribution on the Ga intensity. Theoretically, therefore, it should be possible to reduce the number of positions counted from six to either two or one. The saving in time would make the method extremely attractive. If both Ga and Hf were to be determined, it would be necessary to count the Cu peak as well as Hf and Ga.

It was noted earlier that Pb also caused interference on the Ga peak to the extent of 0.0061 ppm Ga per ppm Pb. Figure 4 shows that the Pb L_L line in fact straddles both the Ga peak and B2, so that the interference on the Ga peak is to some extent cancelled out by a slightly higher background intensity, when using the conventional method of analysis.

Using the new method described above, this is not the case, and in fact the Pb interference increases to 0.0132 ppm Ga per ppm Pb, or double the amount (Table 3). Of course there is no reason now why the Pb content should not be determined instead of, say, Zn, and a proper correction made. It would still mean that only two, three or four measuring positions (Ga, Hf, Cu, Pb) are required instead of the six used in this work. Using conventional methods of background determination, it is not possible to determine Pb with a Mo tube. The poor dispersion of LiF(200) prevents accurate background measurements and LiF(220) causes "spurious" or "ghost" reflections on the Pb peak position (Willis, 1968).

The accuracy of the new method is still somewhat uncertain. At high concentrations, above 50-100 ppm, the accuracy is 1-2% (Feather and Willis, 1976) and perfectly adequate for most purposes, but at lower concentrations the accuracy deteriorates (Table 12).

The reason possibly lies in the accuracy of the m.a.c. determinations. Using the new method, any error in the m.a.c. is compounded in the final result. For example, if the m.a.c. for a sample is too high, because the reciprocal m.a.c. is related to the background intensity the reciprocal of the m.a.c. will be too small and so the background intensity will be too low, resulting in a nett peak that is too large. To determine the concentration, the nett peak, which is too large, is multiplied by a m.a.c. that is also too high, resulting in a compounded error giving a concentration that is high. Equally, if the m.a.c. was low, the final result would also be low. In the conventional method, any error in the m.a.c. is of course present in the final result, but it is not compounded. The effect of instrumental drift is also magnified using the new method.

In essence, the final accuracy of the new method relies even more heavily on the accuracy of the m.a.c. than the conventional one, and also on the stability of the instrument.

Ga data for some international rock standards determined by the "no background" method are given in Table 12 (column 2). At concentrations above ~5ppm Ga, the agreement with the data determined by the conventional method is good.

4.3 EFFECT OF PARTICLE SIZE ON DETERMINATION OF GALLIUM

A possible cause of bias in XRF analysis is the so-called particle size effect or mineralogical effect. This is usually only a problem when the particle size is fairly large (+100 #), the wavelength $> \sim 3$Å, and the element being determined is concentrated in a single phase or mineral. If the mineral in which the element is concentrated is finer than the bulk of the sample, high values will result, while if the mineral is coarser than the bulk of the sample, low values will be obtained, because the coarse grains are shielded by the finer material.

To test the effect of particle size on the determination of gallium in rocks, a rock sample, OK 227, was ground for varying times in an automatic agate mortar. The rock chosen was a gabbro-picrite, an olivine cumulate, which would be a good test of particle size effects as the plagioclase would contain the bulk of the gallium in the rock while the olivine would contain none. The starting material was -120 # and after grinding for 60 minutes the powder was less than 300 #.

The results are plotted in Fig. 16. The mean of twelve different briquettes was calculated, and all Ga values plotted within $\pm 3s_c$ (counting statistics) of the mean, indicating that there was no statistically discernable difference between briquettes. Close scrutiny of the plot in Fig. 16, however, suggests the possibility that the determined values tend to decrease slightly with decreasing particle size.

The problem of particle size effects was recognised in this laboratory many years ago, and all briquettes are made with samples ground to -300 #, especially as they are used for the determination of sodium which does require a very small particle size for accurate measurement.

Particle size effects should therefore not be a cause of bias in the results presented here.

4.4 STANDARDISATION

In common with most other instrumental methods of analysis, e.g. optical emission spectrometry, XRF spectrometry is not an absolute analytical technique, in that unknown samples must be compared to standards of known element concentrations. In common practice resort is made to the use of standard rocks, such as the USGS rocks, whose elemental concentrations are well known (for some elements). It is also possible to use artificially prepared standards which usually consist of mixtures of specially pure chemical compounds, or pure quartz or silica doped with known amounts of trace elements. The experience in this laboratory during the past ten years is that the use of artificial standards is sometimes successful and sometimes not, and we have preferred to use natural rock standards whenever possible. Norrish and Chappell (1967) state that adding an element in the form of an oxide or salt can lead to errors arising from micro-absorption effects, especially in the wavelength region ~1-3Å (Ga K_α 1.34Å). This can be due both to differences in particle size between the sample and added compound and to the fact that, in this instance, the Ga is present in an oxide molecule if Ga_2O_3 is added, whereas in the rock sample it is present in a different molecule or molecules.

The precision of the method presented here is 1-2%, and to ensure accuracy of the same level, it was necessary to use standards having an accuracy of better than 0.4 ppm Ga at the 20 ppm level. It is the writer's opinion that it is not possible by dry grinding alone, the only technique available at the time, to guarantee to mix or dilute samples down to the 20 ppm Ga level with the required accuracy. Even if such accuracy could be attained, there was still a strong possibility of bias due to micro-absorption effects. It was therefore decided to use the USGS rock standards for standardisation purposes. Having made this decision, it was necessary to assign usable values to each of the USGS rocks.

Flanagan (1973) presented a list of recommended values, averages or magnitudes for a large number of elements in "international" rock standards and minerals. The data are extremely useful, but must be used with great care, and there is the drawback that no individual values are given. In a new compilation, Flanagan (1976), the individual values for the USGS standard rocks are reported.

If the Ga contents in the two standard rocks G-1 and W-1 are considered, Ahrens and Fleischer (1960) recommended averages of 18 and 16 ppm Ga respectively. Fleischer and Stevens (1962) and Fleischer (1965, 1969) found no reason to change these values. However, in Flanagan (1973, 1976) the recommended value for G-1 changed to 19.6 ppm, while W-1 remained unchanged at 16.0 ppm Ga. From inspection of Table 12, it is apparent that Flanagan (1973, 1976) has taken de Laeter's (1972) isotope dilution values for the USGS rocks as being the definitive values. To the writer's knowledge no one else has used the isotope dilution technique for the determination of Ga in rocks, and while the stable isotope dilution technique is known to give accurate results for elements such as Rb and Sr, there are problems associated with its use for the determination of Ba, for example, (Philpotts, pers. comm.). In principle the writer considers it wrong to assume the results of a single analyst using an untried method as being definitive, until such time as his data are supported by further work.

In the absence of original data in Flanagan's (1973) report, a list of data for the concentration of Ga in the eight USGS standard rocks G-1, W-1, GSP-1, AGV-1, BCR-1, PCC-1 and DTS-1 was compiled. In addition to the individual analyses reported in Ahrens and Fleischer (1960), Fleischer and Stevens (1962), Fleischer (1965, 1969), and Flanagan (1967, 1969), data have been taken from twenty other papers in the literature. Altogether data from 92 papers have been collated. The data are summarised in Table 13 and individual determinations plotted in Figs 17-19. For ease of plotting, the data values have been rounded to the nearest ppm, but the calculations shown in Table 13 were made using the original values.

From the data plotted in Figs 17-19 the problem arose of how best to arrive at a "preferred", "proposed" or "usable" value for these rocks. Roubault et al. (1966) calculated means and standard deviations for each element for the three French standard rocks using all available results. All results which differed from the mean by more than one standard deviation were then rejected and the remaining values used to calculate "preferred" means. Abbey (1970) found that for major elements considerably more (80-85%) than two-thirds of the data lay within one standard deviation of the mean. In calculating "usable values" for the trace elements, Abbey (1972, 1973) arbitrarily decided, when 10 or more results were available for a particular standard, to reject the 20% of the results farthest removed from the mean of all available results. The mean of all remaining results was taken as a "usable value". When between 5 and 9 results were available for a standard, all results were accepted and the crude average taken as the "usable value", but with the reservation that it was less certain and might well change when more results became known.

In this work a combination of the two methods was used in attempting to arrive at preferred values for Ga in the USGS standard rocks. First, the means and standard deviations using all available results were calculated for each standard. All results lying outside the range of $\pm$ 1s of the mean were rejected, but an attempt was made to retain at least 85% of the results. The mean of all remaining results was taken as the "preferred value". For G-1, W-1 and GSP-1 both criteria were satisfied. For G-2, AGV-1 and BCR-1 the distributions of the data points in Figs 17-19 were considered when deciding which of those results outside the $\pm$ 1s range to accept. For PCC-1 and DTS-1 the reported results range from 0.1 ppm to 22 ppm Ga. As Laul et al. (1970) and de Laeter (1972) have pointed out, it would be expected that the Ga content of these ultrabasic rocks would be extremely low. Accordingly, only those results less than 1 ppm Ga were accepted, and the average used as the "preferred value".

Mr. T. Steele (pers. comm.) of the National Institute for Metallurgy, Johannesburg, has devised another method of calculating "preferred values". His method involves calculating the mean and standard deviation of all values, and rejecting those results falling outside the range of mean ± 2s. A new mean and standard deviation are calculated using the remaining results, and again those results falling outside the acceptable range of new mean ± 2s are rejected. The calculation is repeated until no further results are rejected. When the method was applied to the data presented here, three iterations were required for G-1, AGV-1 and BCR-1; for G-2 and GSP-1 four iterations were necessary; and for W-1 six iterations.

The results of all three methods are presented in Table 14, and the mean of the three results for each standard used as the preferred average in this work.

Ahrens and Fleischer (1960) usually used averages when reporting trace element values for G-1 and W-1, which were classed as either "recommended", when the analytical data were satisfactory, or "magnitudes" when it was not so good. The use of simple averages is satisfactory when the number of values is large and the distribution symmetrical, as for G-1 and W-1 in Fig. 17. Although there are one or two values, e.g. 37 to 39 ppm Ga, that are far removed from the main body of data, because of the fairly large number of values, the high results do not greatly affect the means. For G-2, however, the number of values is smaller, and there are four values that are rather high with only one low value outside the main body of data. In this case the average is biased towards the higher values to the extent of about 4%.

There is unfortunately no international agreement on how to handle standards data in order to arrive at "preferred values", which is a pity. It is to be hoped that one of the international organisations will set up a discussion group that could set accepted rules for the handling of data that is of such crucial importance to the practising analyst, geologist and geochemist.*

In the absence of any set guidelines, the handling of standards data must be to some extent subjective. It is hoped that the means used to arrive at the preferred values in this work are less subjective than most.

In Figs 17-19 the analytical technique used for each determination is indicated, and a study of the results obtained by different methods is interesting. Most of the determinations have been made by optical emission spectroscopy with neutron activation analysis the next most frequently used method. For OS there is a clear-cut bimodal distribution of the data, although not so obvious in the case of G-1. This is particularly so for data from Flanagan (1969) where the analyses by three USGS laboratories show a marked systematic difference in their results for Ga. The difference is consistent for all four standards G-2, GSP-1, AGV-1 and BCR-1. In Figs 17-19 the preferred averages tend to fall between the two modes of OS data.

Fleischer (1969) commented that the INAA results tended to be high compared with other techniques. This observation is confirmed by the data presented here, particularly for the acid and intermediate type rocks, indicating that there may be some interference in the technique that is not taken into account. The XRF analyses tend to be rather widely scattered about the preferred averages.

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* Note added in proof: This is now being done.

CHAPTER 5

QUALITY OF THE DATA

5.1 GENERAL

The duration of the analytical runs on the spectrometer varied from about ten days to six weeks. Because no normalisation to a reference sample was made in the computer program, the overall accuracy and precision of a run was dependent on the stability of the instrument. In order to monitor the drift occurring during a run, a blank sample heavily doped with copper was run every three to four hours on B1, Cu $K_{\beta 1}$ and the Mo K_{α} Compton peak. In this way it was possible to monitor any changes taking place in peak counts (using Cu $K_{\beta 1}$), background counts and Compton peak times. In addition to the Cu-doped sample, a briquette of W-1, and later a doped sample, was counted once with every twenty to thirty samples. Depending on the counting times for the samples, this resulted in W-1 being counted once or twice a day.

In practice the stability of the instrument was quite remarkable, as indicated by the plots for W-1 and a Ga-doped blank used in place of W-1 for the October 1974 run, in Fig. 20. In not a single instance was the calculated Ga content outside the range of $\pm 3s_c$ counting statistics (99% confidence limits), while it was usually within $\pm 2s_c$ (95% confidence limits), indicating that there was no significant drift or bias and that at all times the measured concentrations were within the range expected from counting statistics alone. It is considered that much of the precision of the final results is due to the fact that both nett intensities and m.a.c. (by Mo K_{α} Compton peak) were measured at the same time; if, for example, a slight increase in the intensities occurs, i.e. nett peaks, it is accompanied by a slight increase in the Compton peak, which, being inversely related to the m.a.c., results in a slightly lower m.a.c. Therefore, when the peak intensity and m.a.c. are multiplied together as in equation (1), any drift will tend to cancel out.

5.2 PRECISION

The majority of the measurements made in this work were carried out at three separate times, and it was important that there should be no bias between the results from different runs. Altogether three separate briquettes (each 4g) of W-1 were run during this work, as shown in Table 15. In no case was there a greater difference than 0.1 ppm between the three briquettes which were used as standards for the various runs. When the W-1 briquettes were run as standards, as opposed to being run as monitors, counting times using code 800 were used giving a relative counting error of 1.2% (Table 6). The briquettes were run at the start of a run, in the middle and again at the end of the run, usually three times on each occasion. Monitor determinations using W-1 were counted using code 480 giving a counting error of 1.7%. In addition to W-1 other standard samples, e.g. G-1, G-2 and BCR-1, were run at the same time, and reference to the data in Table 15 indicates no bias between runs. In all cases the results are within $\pm$ $3s_c$ of the mean, except for G-2 where the results are within $\pm$ $4s_c$ for briquette 1, i.e. any differences are those that may be expected from counting statistics alone.

It appeared therefore that all results obtained were within the precision calculated from counting statistics alone. In the case of individual unknown samples, all samples were counted twice in the first instance. The Ga content was calculated and the two results compared. If the difference between the two results was less than four times the $1s_c$ error due to counting statistics, the results were accepted. If the difference was greater than four times the counting error, the sample was recounted as many times as necessary to achieve an acceptable result. In Table 15 the data in column "sigma" are the maximum difference between the determined Ga concentrations divided by the counting error ($1s_c$) for a single determination. The value of sigma for each sample was checked to ensure it was less than 4.

5.3 ACCURACY

It is well known, but frequently forgotten, that although the precision of an analysis may be good, it does not necessarily follow that the accuracy is also good. The result may in fact be biased due to some factor in the technique affecting the final answer. Before discussing the accuracy as a whole of the technique used here, the precautions taken to avoid bias in individual samples will be described.

In this XRF technique there are three likely sources of error that could introduce bias into the final result: errors in the determination of the m.a.c., "counting errors", and interference on peaks and backgrounds by elements other than Zn, Hf and Cu. Possible errors in the determination of the m.a.c. have been discussed earlier, and in all samples where errors were suspected, the m.a.c. was determined either by the transmission method or by calculation from tables when no further sample, other than the briquette, was available. Included in the term "counting errors" are the occasional bad count on the instrument, e.g. due to spikes on the mains, mis-setting of the counting time, and mis-punching of computer cards for the calculation program, i.e. errors other than those due to counting statistics which are random. The possible interferences on peak and background positions by unmeasured elements have already been discussed.

The means of checking for these possible errors is a novel one, and arose out of the work by Feather and Willis (1976) and the alternative method for determining Ga already described. The method of checking for errors has been so useful that it is strongly recommended that it be used whenever trace elements are determined by XRF analysis.

Essentially the method involves plotting all backgrounds for individual samples against their reciprocal m.a.c's. By "all" backgrounds is meant the calculated background for Zn, Ga, Hf and Cu, as well as the individual measurements of B1 and B2. As the backgrounds for Zn, Ga, Hf and Cu are all calculated by multiplying the sum (B1 + B2) by different factors, it follows that if the Ga background is in error, the others will be too. Therefore only plots for B1, Ga background and B2 are shown here. Some typical plots are shown in Figs 21-23, in which data for 883 samples have been plotted. The diagrams are easily plotted by computer. An option was built into the calculation program by which the background intensities and reciprocal m.a.c. for each sample were written to a disc file. Following the calculation section of the program, a program from the BMD package, BMDO2D, (Dixon, 1976), was used to plot the data on the line printer of the computer.

Inspection of Figs 21-23 indicates that most of the points, as expected, cluster around a straight line relating intensity to 1/m.a.c. It is also immediately obvious that certain samples do not, and it is these samples that are checked further in an effort to find out why they do not fit the general trend.

The first possibility checked is that punching errors occurred. If duplicate points for a sample plot in the same place, it is unlikely that punching errors were made. If no punching mistakes were made, then either the m.a.c. is incorrect or the background intensities are in error. Again, as each sample was measured twice, if the two points plot together, then it is unlikely that a bad count was the cause of the error.

In general, if a point lies to the right of the trend line, then the m.a.c. will be in error by being too low, i.e. 1/m.a.c. is too high.

If a point lies to the left of the trend line, then either the m.a.c. is too high or there is interference on one or both of the background positions, or perhaps both of these alternatives are true.

In Figs 21-23 four samples plot to the right of the trend line, JJG106-108 and ilmenite. As indicated earlier (Fig. 15), samples with exceptionally high m.a.c's, such as ilmenite, will tend to give low m.a.c. values when measured without an yttrium filter, so that it was expected that the ilmenite sample would plot where it did. When the m.a.c. was redetermined by the transmission method, the point fell on the trend line.

In the case of the three samples JJG106-108, one possible explanation was that the briquettes were not infinitely thick for Mo K_{α} radiation (about 4g of sample is required) and that some of the Mo K_{α} radiation was being reflected from the bakelite/boric acid backing (very low m.a.c.), yielding low m.a.c. values for the samples. On enquiry, Dr. J.J. Gurney (pers. comm.) indicated that only 2-3g sample had been available for these samples. These briquettes were therefore not infinitely thick for Mo K_{α} radiation (therefore giving an incorrect m.a.c. measurement), but would be so for Ga radiation (1g being sufficient). No further material was available for these samples, but fortunately they had been analysed for major elements. The major element data were used to calculate the m.a.c's and the points then plotted correctly on the diagram (Fig. 24). To check that a 1g briquette was infinitely thick for Ga K_{α}, both a 1g and a 4g briquette of sample E26, an intermediate lava, were measured with the results given below:

	ppm Ga	m.a.c.
4g briquette	20.4	15.77
1g briquette	17.6	13.54

When the correct m.a.c. for the sample, i.e. 15.77, was used for the 1g briquette, a value of 20.5 ppm Ga was obtained, in excellent agreement with the result for the 4g briquette.

Of the points lying to the left of the trend line, sample KL13 will be considered first. This sample is a rhyolite from northern S.W.A., and it should be noted that, although the sample falls off the trend line for B1 in Fig. 21, it does not do so for B2 in Fig. 23, indicating the presence of an element causing interference on B1. Table 2 suggested Ta or W as the likely elements and a wavelength scan (Fig. 25) showed the presence of an exceptionally high concentration of W. According to Prof. A.J. Erlank (pers. comm.), this sample was not ground in tungsten carbide. In contrast, sample BRA2, for which B1 was also in error, showed the presence of a considerable concentration of Ta (Fig. 5). The other sample that has consistently fallen off the trend line is NIM-L. As indicated earlier, the m.a.c. as determined at the Rb K_α wavelength by the transmission method seems to be correct. NIM-L is known to contain ~20 ppm Ta, which would cause B1 to be slightly high, but as B2 is also high, this is not the complete explanation. A wavelength scan for this sample is shown in Fig. 2, indicating the high concentration of Hf in this sample.

To ensure that the interference correction procedure was working correctly, a sample doped with exceptionally high concentrations of Zn, Ga, Hf and Cu, relative to average rocks (Fig. 6) was counted with the results shown in Fig. 26. The background points for this sample, counted eight times, straddle the general trend line very closely, indicating that for high concentrations of the elements concerned, where any errors would show up most strongly, the correction procedure worked satisfactorily. The reasons for NIM-L falling off the trend line are at present unknown.

The final sample to be discussed is the kimberlite phlogopite nodule 199, and this sample plots a very considerable distance off the trend line for both B1 and B2. It would seem therefore that the m.a.c. is in error. The Compton peak method had in fact placed the sample at a position marked with an 'X', and the transmission m.a.c. gave the value for its present position. In Fig. 25, which shows a wavelength scan for this sample, there appears no reason for error in the background measurements. The sample is known to contain very high concentrations of Ba (~1%) and Sr (~0.2%) (Dr. J.J. Gurney, pers. comm.). In addition, being a mica, it was very difficult to grind finely, and it is possible that some type of diffraction effect is taking place affecting the background intensity relative to rocks. In any case, one would be most reluctant to report data for such a sample, and it is omitted from this compilation. For the record, the value determined for Ga was 18.5 ppm, which is not inconsistent with the size of the peak in Fig. 25. If the m.a.c. is incorrect, this would reduce to about 13 ppm Ga.

The preceding comments show the value of plotting 1/m.a.c. against background intensity, not only for this work but for any trace element work done by XRF, in highlighting errors that would not otherwise be obvious, thereby helping to maintain a high standard of accuracy.

The problem in deciding on the question of the overall accuracy of an analytical technique is always a difficult one, and in the final result is always highly subjective. One of the common ways of estimating the accuracy of an analytical technique is to compare results obtained on international standards with recommended values, when they are available, and also to compare results with those of other workers on the same samples when this is possible. Both approaches will be discussed here with regard to some international rock standards and meteorites.

Table 14 compares the results obtained in this work with the preferred averages for eight USGS rock standards. The mean correction factor required to change the values from this work to the preferred average values is very close to one (1.004), indicating an absence of bias in the results. There are nevertheless fairly large differences in the results for GSP-1 and BCR-1. The reasons are unknown. In the case of BCR-1, the difference may reflect the large proportion of INAA results used in calculating the average value. In the case of GSP-1, the spread of the data points in Fig. 18 is so large and symmetrical that no comment is possible. Our bottle of GSP-1 is known to be inhomogeneous with respect to Zr and Th, but it is unlikely that it would be so for Ga.

In this work it was possible to determine Zn, Cu and Hf, as well as Ga, and if the data for these elements are accurate, it lends support to the question of the accuracy of the Ga data. Data for Zn, Cu and Hf in some standard rocks have been tabulated in Tables 16-18. In spite of the fact that for Zn and Cu the K_β lines were used, which resulted in far less sensitivity and greater counting errors than those obtained using the K_α lines, the agreement for the USGS rocks is excellent. For the French standards GA, GH, GR and BR, the agreement for the Cu results is fair, but for Zn the agreement is very poor for GA, GH and GR. The reason is uncertain, but it may be due to Zn contamination from the vacuum oil as these briquettes date from 1965, before the problem of contamination was recognised. The data for Hf are in satisfactory agreement with those from the literature, allowing for the rather large error (0.5 ppm,$1s_c$) for this method. The literature data for NIM-L are very poor, five analyses ranging from 148-274 ppm Hf. For the counting times used here the precision is rather poor, but could be improved if required. In any case XRF is not the best method of determining Hf in rocks, but could be used when the concentration is above 10 ppm Hf.

It is concluded that the accuracy and precision (1-2%) of the analytical method presented here holds for the determination of Ga in rocks at concentration levels above about 10 ppm Ga. At concentration levels less than 5 ppm the precision will depend on the concentration, varying from 2% at the 5 ppm level to 50% at the detection limit of 0.3 ppm Ga.

From Table 14 it appears that the accuracy at the 1 ppm level is still satisfactory, but the data obtained on meteorites in this work will be compared with those obtained by other workers as a further check on the accuracy at low concentrations.

Gallium is an important element in meteorite geochemistry, and its concentration in meteorites has been determined by many workers, using mainly radiochemical NAA or INAA. Comparative Ga concentrations in individual meteorites have been tabulated in Tables 19-24 and all data have been summarised in Table 25. When comparing meteorite data, the problem of possible sample inhomogeneity must be considered, and therefore it is preferable to compare the averages obtained for different classes of meteorites, when this is possible, rather than individual samples. In considering the data in Table 25, it should be borne in mind that the data of Greenland (1965) were amongst the earliest presented, and it is clear that he experienced some difficulties, especially with the carbonaceous and enstatite chondrites for which his data appear to be higher than that obtained by other workers.

It should also be borne in mind that not all of the workers analysed the same meteorites, and this also has an effect on the average values obtained. The point is well illustrated if one considers the carbonaceous chondrites class C3. There is a distinct difference between the Ga contents of the C3-0 and C3-V sub-classes, and depending on the number of each class analysed, the average for the C3 class as a whole may vary considerably. In the data reported in this work there are four meteorites for which the Ga data appear anomalous for their type. The individual results are discussed later, but in Table 25 the anomalous values are reported separately so as not to distort the averages, e.g. C3-V, E6 and aubrites.

Bearing these points in mind, the agreement between the meteorite data presented here and that from the literature is excellent at all levels from 18 ppm Ga in the E4 enstatite chondrites, down through the 5 ppm level of the H- and L-group chondrites, to the 1 ppm level in the howardites, with no evidence of consistent bias towards either high or low results relative to those of other workers.

It is clear that the analytical technique presented here yields data that compare favourably with those for the international standard rocks and those for meteorites, the two instances where meaningful comparisons can be made.

The technique can, therefore, be used with confidence to determine the gallium content of common rocks, minerals and meteorites, always bearing in mind the few exceptions that have already been discussed, i.e. samples containing unusually high concentrations of W, Ta, U, Th, Ba and Pb.

Before moving on to a discussion of the data presented in this work, it is necessary that an important point be emphasised. For the vast majority of samples analysed in this work, the Pb content is unknown, and it has therefore not been possible to make a correction for the effect of this element on the measured gallium concentration, except in a few instances. In order to be consistent from one group of rocks to another, it was decided to make no correction for Pb, except in the case of the standard rocks. In most samples the lead content is unlikely to be greater than 50 ppm Pb, which means that the maximum error would be 0.3 ppm Ga. Some exceptions are the syenites from the Nejoio Ring Complex in Angola where the lead content rises to 70 ppm Pb. As the gallium content of these rocks is approx. 40 ppm Ga, the relative error introduced by ignoring the Pb correction is only about 1%. In general, the relative error will vary from zero for basic rocks to a maximum of 1.5% for granitic type rocks. It should be borne in mind, therefore, that there could be a systematic error of up to 0.3 ppm Ga in the acid rocks relative to the basic rocks. The error is considered to be sufficiently small to be ignored.

CHAPTER 6

GALLIUM IN STONY AND STONY-IRON METEORITES

6.1 GENERAL

Data are presented on the Ga content of one hundred and ten bulk samples of seventy-seven meteorites (fifty-four chondrites and twenty-three achondrites) and thirty non-magnetic or silicate portions of twenty-eight meteorites (twenty chondrites and eight mesosiderites), probably the most complete suite of stony and stony-iron meteorites ever analysed for Ga in one laboratory using a single technique.

The data contribute to the knowledge of the geochemistry of Ga in the following ways: (i) eleven of the twelve classes of chondrites and achondrites listed by Mason (1972), together with the mesosiderites, have been analysed, a fairly comprehensive coverage; (ii) in most classes a number of meteorites have been analysed; (iii) although Ga has been determined in thirty-one of the meteorites by other workers, thirty-six new analyses are presented; and (iv) the use of a single technique of high accuracy and precision enables meaningful comparisons to be made both within and between groups.

There are very many papers in the literature that deal, at least in part, with Ga in meteorites. The most recent reviews were published by Baedecker and Wasson (1970) and Burton and Culkin (1972) and include publications up to 1970. Since that time a number of papers have been published, especially on the achondrites, which are not mentioned by Baedecker and Wasson, and for which only five analyses of howardites and eucrites are included by Burton and Culkin. No data were available for the less common types of achondrites. It was, therefore, considered appropriate to this study to summarise the data at present available on Ga in stony meteorites and the non-magnetic portions of mesosiderites.

As discussed in the previous chapter, comparisons of Ga determinations on individual meteorites have been presented in Tables 19-24. Except for the consistently high data of Greenland (1965) for the carbonaceous chondrites, the data are remarkably consistent, especially when the number of different laboratories is considered. This consistency may be due, in part, to the common use of a single analytical technique, radiochemical neutron activation analysis.

All available data for the different classes of stony meteorites have been summarised by analyst in Table 25 for comparative purposes. Four apparently anomalous values obtained in this work are reported separately in Table 25 under the classes C3 and C3-V, bronzite chondrites, E6 and aubrites. The data have been condensed in Table 26 to give concentration ranges and mean values for the individual classes of meteorites. Anomalous (?) values appear in brackets. Table 26 represents the present extent of our knowledge of the distribution of Ga in the stony meteorites.

Before discussion of these tables and the data in detail, it may be advantageous to summarise also the present knowledge of the distribution of Ga in meteoritic minerals, including the metal phase. As stated in the introduction, Ga exhibits chalcophile, siderophile and lithophile behaviour in meteorites, although in terrestrial materials it tends to be mainly lithophile and, in some cases, chalcophile.

Tables 27-29 summarise our present knowledge of the distribution of Ga between the various minerals and phases found in meteorites. The only data for Ga in individual minerals are those of Mason and Graham (1970) and Allen and Mason (1973), whose study constitutes an extremely important contribution to our knowledge. It is to be hoped that with the improvement of analytical techniques such as the ion microprobe, which will allow analysis of mineral grains for trace elements *in situ*, more data will be forthcoming. The information would be of considerable help to our future understanding of the geochemistry of meteorites.

Tables 27-29 indicate that chromite and bulk metal (in enstatite chondrites) contain the maximum Ga (~ 60-70 ppm) found in minerals. Ni-rich taenite also has a high Ga content (~ 30 ppm). The metal fraction of the ordinary chondrites contains ~14 ppm Ga. The data indicate that on average the sulphides in the H and L chondrites contain ~ 7 ppm Ga, while in the highly reduced enstatite chondrites the sulphide fraction contains only about 0.5 ppm Ga. The very variable Ga content of plagioclase in various meteorite types is extremely interesting and further work is required to confirm and extend these findings. Sulphide minerals contain between 0 and 14 ppm Ga. It is possible that the magnetite found in the carbonaceous chondrites also contains high Ga values, similar to the magnetite in terrestrial rocks. All other minerals analysed to date contain less than 2 ppm Ga and contribute very minor quantities to the total Ga content in chondritic meteorites.

Table 30, taken from Mason (1972), summarises the mineralogy of meteorites. Information for the shergottites has been added. It is predictable from this information and from Table 29 that the achondrites should have, in general, very low Ga contents, consisting as they do mainly of pyroxenes, olivine and low-Ga plagioclase. Experimental work confirms this prediction.

The Ga data determined in this work are listed in Table 31 A-L. All 'finds' have been indicated with an asterisk, and where more than one sample of an individual meteorite was available, the data for each are given. The table includes the Ga concentration determined in each sample, the Ga/Al ratio, Al concentration, the detection limit in ppm, one standard deviation error ($1s_c$) in the Ga determination expressed as both ppm and percentage, and the class to which the meteorite belongs where this is known. The classification used is that of van Schmus and Wood (1967) and Van Schmus and Hayes (1974) for the chondrites, and class names from Table 30 (Mason, 1972) for the other meteorites. The mesosiderites have been sub-divided according to the scheme of Powell (1971).

If the data in Tables 25 and 26 are considered in conjunction with those in Table 31, a few results are anomalous. The Ga content of Coolidge falls well outside the range found by most other workers for C3-V carbonaceous chondrites. However, Coolidge is the only C4 meteorite analysed in this work and should perhaps form a further sub-class of the carbonaceous chondrites. Karoonda, the only other C4 analysed for Ga (Matza and Lipschutz, 1977), is also anomalous, and will be discussed in detail later. Coolidge is a find and is apparently considerably weathered (Jarosewich, 1966), a fact that may have affected the Ga content. Another anomalous Ga value is that for Beardsley (H5) of 9.8 ppm Ga, a value comparable with those of the E6 chondrites, and which might indicate that the sample was mislabelled. However, the same sample was analysed by von Michaelis (1969) for major and trace elements, and both K and Rb were high for an H5 chondrite (e.g. 11.5 ppm Rb compared with the group average of 2.9 ppm), which seems to indicate that some contamination may have occurred. Major element data definitely place it as an H-group chondrite. Beardsley was reanalysed twice when the anomalous value became apparent, and the repeat analyses yielded the same value as previously obtained.

A further anomalous concentration found was that for Blithfield (E6), 5.5 ppm Ga compared with the group mean of 11 ppm. This meteorite is a find and will be discussed in a later part of this chapter (6.5). Shallowater (aubrite) has a Ga content of 6.3 ppm, anomalously high for an achondrite. However, its very high metal content (9%) could account for the high Ga value.

In addition to bulk analyses of meteorites, separated non-magnetic fractions of some H, L and enstatite chondrites and mesosiderites were analysed and the data are included in Table 31. Sulphide minerals were not removed from these fractions prior to analysis. It is very difficult to ensure that all metal has been removed from the non-magnetic fraction, and because of the very high Ga content of the metal relative to that of the silicate and sulphide fractions, the presence of a small amount of metal can produce a considerable bias in the Ga content of the non-magnetic fraction.

The values presented for the H and L chondrite non-magnetic fractions in this work are essentially the same as, or even slightly lower than, the group means calculated using the values of all workers, which is a tribute to the care with which von Michaelis (1969) carried out the separations. Of the two enstatite chondrite fractions analysed, the value for Hvittis agrees well with those reported by other workers, but the value for St. Marks is probably slightly high due to incomplete separation of the metal fraction. However, since no other analyses have been made of separated fractions of E5 chondrites, this value may be correct. Fouche and Smales (1967) obtained similarly high values for E4 chondrites, which they considered to be contaminated by metal.

Wasson <u>et al</u>. (1974) reported unpublished values for Ga in the silicate fractions of the mesosiderites Estherville and Patwar and indicated that work would be published on the non-magnetic portions of mesosiderites, but do not appear to have done so. No other work has been done on Ga in the non-magnetic portions of mesosiderites and it is not possible to compare the data presented here with those of other workers.

The data presented here are summarised in Table 32 and histograms are given in Figs 27-36. The data in Table 26 and Fig. 27 indicate that Ga in achondrites is very much lower than in chondrites and mesosiderites. In the chondrites Ga has a very wide range from about 3 ppm to 20 ppm, with the enstatites having the higher concentrations. The H and L group chondrites have a very restricted range of concentrations and almost identical mean values (Table 32, Fig. 29). The carbonaceous chondrites have a somewhat greater range and higher concentrations (Table 32, Fig. 32). There is no significant difference in the Ga concentration ranges of the non-magnetic fractions of the H and L chondrites and of the mesosiderites.

6.2 CLASSIFICATION OF METEORITES USING Ga, Al AND Fe CONCENTRATIONS

Although much of the Ga in meteorites is present in the metal or sulphide phases which are essentially Al-free, it is nevertheless quite useful to plot Ga against Al, as is commonly done for terrestrial rocks. This has been done in Fig. 37, and several interesting features are apparent. It is possible to differentiate unambiguously between a number of the main groups of meteorites. The achondrites, except for the nakhlites, the anomalous aubrite Shallowater, and Shergotty, all cluster at the left of the diagram with Ga contents of less than 2 ppm. The bronzite and hypersthene chondrites form a discrete cluster, with the hypersthene chondrites having a slightly higher Al content. The groups cannot be separated on this diagram. Plotted with data for Orgueil (C1) taken from the literature, the carbonaceous chondrites also form discrete groups in terms of the classification according to Van Schmus and Hayes. Coolidge, the only C4-V, plots separately from the C3-V chondrites. The enstatite chondrites extend across the diagram with a small range in Al but a large range in Ga, but Blithfield plots in the middle of the bronzite chondrites. The calculated bulk concentrations for mesosiderites cluster in two groups, generally different from any others but with the sub-group 1 tending to overlap with C3-V carbonaceous chondrites.

If the non-magnetic fractions are also plotted on this diagram, then those of the mesosiderites fall in a field distinct from any other.

The non-magnetic fractions of the bronzite and hypersthene chondrites tend to overlap. The non-magnetic fractions of the enstatite chondrites plot in the achondrite field, with the non-magnetic fraction of Hvittis plotting directly on the Ga-Al trend line of the achondrites.

The groups or classes that are difficult to separate on this diagram are the H and L chondrites, the C1 and E6 chondrites, and the subgroup 1 mesosiderites and C3-V carbonaceous chondrites. In Fig. 38 Ga is plotted against total Fe, the other major element with which Ga is associated. It is possible to get an unequivocal separation between those groups which could not be separated on the Ga-Al diagram. The mesosiderites, because of their very high Fe contents, are well separated from the C3-V carbonaceous chondrites; the H and L chondrites are separated by their different Fe contents, with no overlap; and the C1 and E6 classes are also well separated by their differing Fe contents.

The C3-V carbonaceous chondrites overlap with the L group chondrites, but are well separated from them on the Ga-Al plot. It seemed logical, therefore, to plot the three elements Ga-Al-Fe together on a ternary diagram to investigate the possibility of achieving separation of the various classes of meteorites on a single diagram. The ternary plot is shown in Fig. 39. The ppm Ga values have been multiplied by a factor of 4, the percentage Al by 3, and percent Fe by 1.

This diagram separates the H and L group chondrites, the C1 carbonaceous and E6 chondrites and the mesosiderites and the C3-V carbonaceous chondrites. There is a slight overlap between the C3-O carbonaceous chondrites and the L group chondrites. The separation between the howardites and eucrites is small but distinct, the eucrites plotting above 90% Al and the howardites below 90% Al. The anomalous aubrite Shallowater plots between the E6 chondrites and C1 carbonaceous chondrites and the single nakhlite falls in the mesosiderite field. The non-magnetic (troilite + silicate) fractions of the mesosiderites plot in the Al corner of the diagram, and it is interesting to note that the lunar mare basalts (Taylor, 1975) plot in the same field. The silicate fractions (no troilite) of the mesosiderites plot between the mare basalts and the Fra Mauro basalts, with that for Patwar falling between the eucrites and howardites.

It has therefore been shown that just as Ga and Ge can be used to classify the iron meteorites into groups (Baedecker and Wasson, 1970), so can Ga be used, in conjunction with Al and Fe, to divide the stony meteorites and mesosiderites into the various groups or classes suggested by Van Schmus and Wood (1967), Van Schmus and Hayes (1974) and Mason (1972). Unfortunately, most analysts determine either trace elements or major elements, but seldom both together, in meteorite analysis. The data presented here were determined in the same laboratory on the same aliquots or portions of meteorites and are therefore directly comparable. The plots shown here are critically dependent on the correct relationship between the three elements Ga, Al and Fe. In many meteorites there can be a considerable difference in the Fe and Al contents depending on the proportion of metal in a particular sample, and this will also affect the Ga content. For this reason composite data for Ga, Al and Fe from the literature have not been plotted on the diagrams. In this context XRF spectrometry is an ideal analytical technique for the analysis of meteorites, enabling the accurate, fast and relatively simple determination of both major and trace elements. The only problem is the relatively large amount of sample required, 2-3g. On the other hand, this has the advantage of analysing a more representative sample than is commonly the case when much smaller aliquots are taken.

There are a number of interesting points that have come to light while considering the data so far, and these will now be considered in detail.

6.3 CARBONACEOUS CHONDRITES

There have been considerable differences of opinion on the classification of the carbonaceous chondrites in the past, but the consensus as stated by Van Schmus and Hayes (1974) is that there are four groups: C1, C2, C3-0 and C3-V. Although no C1 chondrites were analysed in this work, data for Orgueil taken from the literature (Fouche and Smales, 1967; and von Michaelis et al., 1969b) have been combined with those from this work and those from Van Schmus and Hayes (1974). In Fig. 37 there is a negative correlation between Ga and Al in carbonaceous chondrites which is quite marked. This could be accounted for by increasing metal content, except that metal is absent, or almost absent, from carbonaceous chondrites.

There is a very variable amount of volatile matter in the carbonaceous chondrites and Van Schmus and Hayes preferred to use data normalised relative to Si to avoid distortion of the relationships between non-volatile elements. The same procedure has been adopted in this study. In Fig. 40 Ga/Si is plotted against Al/Si, Fe/Si, C/Si and S/Si for all carbonaceous meteorites analysed in this work, together with Orgueil and Karoonda. The negative correlation between Ga and Al is still obvious. There is a slightly positive correlation between Ga and Fe, although the line of best fit is almost horizontal. It is also obvious that the two C4 meteorites, Coolidge (C4-V), a find, and Karoonda (C4-0), a fall, which were originally classed as C3 meteorites, do not plot with the other C3 meteorites. When the data for Coolidge were found to be displaced from those of the C3-V group, it was at first considered to be the result of weathering leading to a loss of Ga. However, with Karoonda, a fall, being similarly displaced from the C3-0 group of meteorites, the Coolidge data may be correct, and the C4 carbonaceous chondrites are perhaps different from the C3 chondrites.

With Ga inversely related to Al and only following Fe to a very slight extent, the question arises as to which fraction contains the bulk of the Ga in the carbonaceous chondrites. One possibility is that Ga is concentrated to some extent in the volatile fraction.

Fig. 40 shows plots of normalised Ga versus both C and S. C is positively correlated with Ga, although there is considerable variation in the C content of the C3-V meteorites, and both C4 chondrites are depleted in C relative to the C3 chondrites. The correlation is even stronger between Ga and S with less variation within groups, and this plot also shows the displacement of the C4 chondrites relative to the C3 chondrites. The evidence suggests that in the carbonaceous chondrites a considerable portion of the Ga is present in the carbonaceous and sulphide fractions. This observation, coupled with the fact that the C4 chondrites are generally more recrystallized (Van Schmus and Wood, 1967), may account for the low Ga values found in these meteorites relative to the C3 chondrites, i.e. they may have lost some Ga by volatilisation during a period of reworking.

An interesting experiment in this regard has recently been made by Ikramuddin and Lipschutz (1975) and Ikramuddin et al. (1975) in which samples of Allende were heated in a low pressure environment at 500°C and 1000°C for seven to twenty-nine days. At 500°C there was no loss of Ga and at 1000°C only a minor loss when compared with more volatile elements such as Bi, Tl and In. Unfortunately no accurate measurements were made on S or C, although C will certainly be lost and S tends to be released over a narrow temperature range.

Assuming part of the Ga is in the volatile fraction, it is interesting to calculate residual values from the C-Ga and S-Ga graphs. Both Karoonda and Coolidge have a Si content of about 15.5%, equivalent to 15.8% on a volatile-free basis. Taking the intercepts on the Ga/Si axes for S/Si and C/Si equal to zero, and calculating the Ga concentration in ppm for a Si concentration of 15.8%, gives Ga values of 2.7 and 4.3 ppm respectively, which lie in the range of the non-magnetic fractions of the

H and L group chondrites.

Obviously much more work needs to be done on the individual meteorite minerals and fractions, especially of the carbonaceous chondrites.

The Ga concentrations in the four groups of carbonaceous chondrites, C1 (~10 ppm), C2, C3-V and C3-0, are not clearly separated (Fig. 31, Table 31A), although the C3-V chondrites have distinctly lower values than the others. However, the Ga/Al ratio (Fig. 32) clearly distinguishes between the four groups with no overlap, the C1 chondrites having a Ga/Al ratio greater than 10.0.

The Ga data presented here confirm, as do many other properties, the sub-division of the carbonaceous chondrites into four sub-groups, and also that there is more variation in the C3-V chondrites than in the C3-0 chondrites. The Ga data further suggest that there may be a significant difference between the C3 and C4 meteorites, confirming results from Van Schmus and Hayes (1974) and McCarthy (1971).

6.4 BRONZITE AND HYPERSTHENE (H AND L) CHONDRITES

So much has already been written about Ga in these chondrites that little more need be said here, except that the data confirm those determined by other workers. There is little difference in the Ga contents of the two groups (see Table 31B-E and Fig. 33). Because of the similarity in their Al content (1.07% and 1.15% respectively), the only way to distinguish between the two groups in this work was by their Fe contents (Figs 38, 39). Because of the fairly high Ga content of the metal fractions (14 ppm), the non-magnetic and silicate fractions should have a lower Ga content than the bulk meteorites, as found in this work (Tables 31 and 32). The Ga contents of the silicate fractions determined by Chou and Cohen (1973) and Chou et al. (1973) appear to be high, as their averages are higher than those of the bulk meteorites.

6.5 ENSTATITE CHONDRITES

The enstatite chondrites are highly reduced and therefore contain a considerable proportion of Fe metal, which in turn has a high Ga content, in the range 41-71 ppm (Table 27). Because the silicate fraction has an exceptionally low Ga content (0.3-1.2 ppm), the proportion of metal in the meteorite will determine the total Ga content of the meteorite. Fig. 41, in which Ga has been plotted against Al and total Fe, shows a strong positive correlation between Ga and Fe and a negative correlation between Ga and Al, with the non-magnetic fractions of St. Marks and Hvittis falling on the same trend line for Ga-Al as the bulk meteorites.

Fouche and Smales (1967) analysed separated fractions of the enstatite chondrites and found 29% metal in Abee, 25.5% in Indarch, and 20% in the E6 chondrites, and a corresponding decrease in the Ga content of the metal fractions of 70, 63 and 57 ppm Ga respectively. Using these data, it is possible to calculate the Ga content of the enstatite chondrites analysed in this work. The agreement between calculated and determined values is good, c.f. Baedecker and Wasson (1975).

Compared to the H and L chondrites, the enstatite chondrites are interesting because almost all the Ga is in the metal phase, whereas in the H and L chondrites Ga is partitioned to a greater extent into the silicate phase (about 30%). Because Ga is essentially siderophile in the enstatite chondrites, the silicate fraction is strongly depleted in Ga and the Ga/Al ratio is much closer to that found in the achondrites than that in the ordinary chondrites.

An unusual meteorite in this group is Blithfield, which has a very low Ga content relative to the other E6 chondrites, although it lies on the same Fe-Ga trend line in Fig. 39 as the other meteorites. Blithfield is also unusual because the Fe is present as troilite rather than metal (McCarthy, pers. comm.). Moss _et al_. (1967) determined Ga in the sulphide phase of Khairpur (E6) and found it to be zero, and Allen and Mason (1973) measured 1 ppm Ga in troilite from Khairpur. It would be interesting to determine the Ga content of the sulphide fraction of Blithfield in which there is little metal. Blithfield has the same Ga/Al ratio as the L group chondrites, but is otherwise chemically dissimilar because of its much lower Ca concentration and higher Mg and Si contents.

Ikramuddin et al. (1976) carried out similar heating experiments on a sample of Abee as those of Ikramuddin et al. (1975) on Allende. The results for Ga were slightly different for the two meteorites, and not quite as might have been expected. About 35% of the Ga was lost from Abee only at 1000°C, whereas in Allende 10-15% was lost at 900 and 1000°C. Another interesting result from the experiment was the loss of S, as a result of sulphide decomposition, at 1000°C from Abee compared with 700°C for Allende.

6.6 ACHONDRITES

Since the latest review of Ga in meteorites a considerable amount of work has been done on the achondritic meteorites. The present study has included all the different classes of achondrites, except shergottites and angrites, and the data are in excellent agreement with those of other workers. In Fig. 37 data points taken from the literature have been plotted for Angra dos Reis and a shergottite. Both are mineralogically anomalous: Angra dos Reis is the only meteorite consisting of more than 90% augite, while the shergottites consist of equal proportions of augite and pigeonite, with plagioclase, magnetite and ilmenite. Angrites have a similar Ga/Al ratio to that of the other basaltic achondrites, whereas the shergottites have a very high Ga/Al ratio (~ 5), similar to that of the ordinary chondrites. The very high Ga content of the shergottite makes it unique among chondrites other than the enstatites.

It is clear from Figs 27 and 37 and Table 26 that the eucrites, howardites, diogenites and angrites are strongly depleted in Ga and have exceptionally low Ga/Al ratios of about 0.2-0.6 (Figs 28 and 36), compared with both terrestrial rocks and other meteorites. The basaltic achondrites, eucrites and howardites, are considered to have formed by different processes (McCarthy et al., 1972), the eucrites (and diogenites) by igneous differentiation, and the howardites by mixing of different proportions of the two end members, eucrites and diogenites. In Fig. 37 all three groups fall on a line which could be a mixing line or could result from fractionation. McCarthy et al. (1972) proposed mixing proportions, for the two samples of Frankfort analysed here, of 38% eucrite and 62% diogenite for Frankfort (F) and 30% eucrite and 70% diogenite for Frankfort (T). Calculation of the Ga content of these two meteorites on this basis, using data from Table 26, gives values of 0.68 ppm Ga compared with a measured value of 0.7 ppm and 0.57 ppm compared with a measured value of 0.6 ppm Ga, respectively.

It has already been pointed out that the separated silicate portion of Hvittis plots on the achondrite Ga-Al trend line, as does that of St. Marks, if it is assumed that 1% of metal remains in the separated silicate portion of this meteorite.

The enstatite achondrites (aubrites) are another interesting group of meteorites, and it has been suggested by Mason (1962) and others that they may represent the silicate portion of the enstatite chondrites. Keil (1969), however, concluded otherwise, and the data presented here for Norton County and Cumberland Falls indicate that it would be difficult to relate them to the non-magnetic fractions of Hvittis or St. Marks. In Fig. 41 Ga-Al and Ga-Fe are plotted for the non-magnetic fractions of Hvittis and St. Marks and the three enstatite achondrites. Neither the Ga-Al data nor the Ga-Fe data of the enstatite achondrites coincide with those of the non-magnetic fractions of Hvittis and St. Marks. McCarthy (1971) also found difficulty in applying the proposal of Wasson and Wai (1970) that the enstatite chondrites and achondrites form a genetic relationship. It is interesting to note, however, that Shallowater, which has 9% metal (Hey, 1966), lies on a Ga-Fe mixing line between the other two enstatite achondrites and the E5 chondrites. If it is assumed that the metal fraction contains 60-65 ppm Ga, i.e. similar to that of enstatite metal (Table 27), then the Ga content of Shallowater is calculated to be between 5.5 and 6.0 ppm Ga, in fairly close agreement with the measured value of 6.3 ppm. It is possible that the sample of Shallowater analysed in this study contained a slightly higher percentage of metal.

The enstatite achondrites, therefore, probably represent a silicate composition different from that of the enstatite chondrites but mixed with metal of a similar Ga content to that in the enstatite chondrites. Further work on different fractions in Shallowater would be useful to enable a proper interpretation to be made of the data.

Laul et al. (1972) suggested that the nakhlites and shergottites may have originated in parent bodies that had similar compositions, and also that the shergottites and L-group chondrites may have a common origin. In support of this suggestion, these three groups of meteorites and Chassigny have similar Ga/Al ratios (Fig. 37). Boynton et al. (1976) have suggested that similar processes were responsible for the generation of the source liquids of Chassigny and the nakhlites. The data presented here support this idea.

6.7 MESOSIDERITES

In this work the non-magnetic fractions of seven mesosiderites and the silicate fraction of another were analysed. The silicate portion of Bondoc was analysed on an "as received" basis, as were the non-magnetic fractions of Estherville and Mt. Padbury. The other samples were prepared by Simpson (1978). Three of the non-magnetic fractions contain very high concentrations of troilite (Powell, 1971; and Simpson, 1978). These are Vaca Muerta (16.7%), Patwar (18.9%) and Mt. Padbury (8.3% troilite) (Table 33).

Wasson et al. (1974) stated that the Ga content of the metal from the mesosiderites falls in the same range as the H-group chondrites (Table 27), and also reported the Ga contents of the metal fractions of a number of mesosiderites.

In Table 33 information is listed that allows the calculation of the Ga content of the bulk mesosiderites and also of the silicate (no troilite) fractions. Data for the proportions of metal (Simpson, 1978) were used, except for Estherville and Mt. Padbury for which respectively Powell's (1971) and McCall's (1966) values were taken. Although there was almost certainly a considerable difference between the metal content of the Estherville samples as determined by Powell and that analysed here, the maximum difference is likely to be less than 10% absolute, which would cause an error in the Ga content of the bulk meteorite of less than 1 ppm Ga. A further error could arise from the fact that the Ga content of the metal is not constant throughout the meteorites. It was nevertheless still considered worthwhile to calculate Ga values for the bulk mesosiderites and the silicate fractions as no other data were available. Calculated values for bulk meteorites and silicate fractions are reported in Table 31K, and the data have been plotted in Figs 27, 28, 37 and 39 and included in Table 32.

In order to calculate the Ga content of the silicate fraction, it was necessary to correct for the considerable sulphide content of some of the mesosiderites. The Ga content of the metal fraction of the mesosiderites is similar to that of the H and L chondrites ($\sim$13 ppm). It was therefore assumed, in the absence of other data, that the Ga contents of the mesosiderite sulphide fractions were also similar to those in the sulphide fractions of the H and L chondrites, i.e. ~7 ppm Ga, rather than those in the enstatite chondrites (~ 0.5 ppm).

As the Ga content of the metal is not nearly as high as that of the enstatite chondrites, and as the metal/silicate ratio in the mesosiderites is approximately unity, the effect of the Ga content of the metal on that of the bulk meteorite is not as marked as for the enstatite chondrites, with the result that the bulk Ga content is in the range 5-10 ppm. The range for the non-magnetic fractions is 2-5 ppm Ga and that for the silicate fraction is 0.5-5 ppm. The calculated value of 0.7 ppm Ga for the silicate fraction of Patwar and the 0.5 ppm measured value for the silicate fraction of Bondoc appear anomalous compared to the other calculated values. Bondoc is extremely inhomogeneous (Simpson, pers. comm.) and it is possible that the powdered sample received may consist of nearly pure pyroxene.

Although the Al contents of the silicate fractions are similar to those of the Ca-rich achondrites, the calculated Ga contents are considerably higher (Fig. 37), except for Patwar, Mt. Padbury and Vaca Muerta, which have Ga values similar to the howardites and eucrites. In general, both silicate and non-magnetic fractions occupy fields in the Ga-Al diagram that are different from all other meteorites or meteorite fractions.

Powell (1971) divided the mesosiderites into three groups based on differences in textural and mineralogical characteristics. All of the mesosiderites analysed here belong to group 1, except Mincy and Vaca Muerta, which are group 3, and Emery which is still unclassified, although Wasson _et al_. (1974), having studied the metal fraction, found Emery to be on the borderline between groups 1 and 2/3. Bondoc is also unclassified because no major element data are available.

It is interesting to note that on the Ga-Al diagram the bulk, non-magnetic and silicate fractions of the group 3 mesosiderites are always distinguished from the group 1 meteorites by their higher Ga contents. On this basis Emery would be classified as a group 3 mesosiderite for all fractions. Unfortunately no group 2 mesosiderites have been analysed in this study, and further work must be awaited before it will be possible to confirm whether Ga can be used to separate mesosiderites into sub-groups as it can for other meteorites. On the ternary diagram (Fig. 39) the three group 3 mesosiderites are clearly separated from the group 1 meteorites by their higher Ga contents.

The mesosiderites analysed here form part of a thesis in preparation by Simpson (1978) and will not be discussed further.

6.8 CONCLUSION

Data for Ga in a number of meteorites have been presented. It has been demonstrated that by using Ga, Al and Fe, it is possible to separate the meteorites chemically into the same classes or groups as proposed by various workers on the basis of other criteria. This could be very useful when attempting to classify meteorites that are on the borderline between classes using textural, mineralogical and petrological data. It has been confirmed that the mesosiderites, bulk, separated silicate and non-magnetic fractions, are distinct from all other types of meteorites. The subdivision of the C3 carbonaceous chondrites into C3-0 and C3-V is likewise confirmed, and there is evidence to suggest that the C4 chondrites might be chemically different in terms of Ga and other elements from the C3 chondrites. There is evidence which suggests that a considerable proportion of the Ga in the carbonaceous chondrites is located in the carbonaceous and sulphide fractions. Blithfield is shown to be distinctly different from other E6 chondrites. On the basis of their Ga contents, it is difficult to relate the enstatite achondrites to the enstatite chondrites. The Ga contents of the howardites are in agreement with the proposal that they could be mixtures of varying proportions of eucrites and diogenites, but also indicate that the howardites could have been derived by fractionation, or by mixing of a range of fractionated materials.

CHAPTER 7

DATA HANDLING AND STORAGE

In this work approximately 1600 samples have been analysed for Ga, usually in groups related to the locality from which the rocks came and only occasionally in groups determined by the rock type. Handling and storing this quantity of data was not a simple matter, especially when it was necessary to handle it in different ways, e.g. by rock type, or by broad sub-division such as oceanic or continental, or by smaller grouping such as a specific igneous intrusion or single island. A database was established in collaboration with Dr. A.R. Duncan to aid in data manipulation, and a brief description is included in the appendix. Mr. C. Hartnady of the Pre-Cambrian Research Unit at the University of Cape Town assisted with some of the programming. All the data included in this work have been stored in the database which was used extensively in extracting data according to various criteria. Without the use of the database, the task would have been extremely difficult.

The single biggest problem in establishing the database was the classification of the various samples into correct rock types. The classification as recommended by the IUGS Subcommission on the Systematics of Igneous Rocks was followed for the plutonic and hypabyssal rocks (Streckeisen, 1973, 1976). As yet no IUGS classification is available for volcanic rocks, and it was decided to adopt a classification based on Streckeisen (1967) similar to that used for the plutonic rocks. For volcanic rocks it was necessary to have two divisions depending on whether a rock had been classified on the basis of chemical or mineralogical criteria. Modifications of the IGS classification code (Harrison and Sabine, 1970) were used for sediments, minerals and meteorites.

The classification is hierarchical and is shown in Table 34. It is by no means complete at the present time as only those rock types that have been required are included. Other rock names or types can be added when necessary. Table 35 lists the sub-divisions and rock types sorted by name for easy reference. It is possible also to sort and list by type number, but this table has not been included here.

By using the various supporting programs with the database, it was a simple matter to select or extract data sets, either on the basis of rock type, using the specific code number, or by locality (e.g. oceanic or island or igneous complex) using the information built into the database number, or both.

CHAPTER 8

GALLIUM IN MINERALS

Ga has been determined in a number of mineral separates and the data are reported in Table 36. For most of the samples no Al data are available. Data for Ga and the Ga/Al ratio in some important rock-forming minerals have been abstracted from the literature and are reported in Table 37, and data from this work included for comparison.

In acid, intermediate and, frequently, basic rocks, the bulk (50-70%) of Ga is concentrated in feldspars, which are also the principal rock-forming minerals of these rocks. It is only in microcline, the plagioclases, some feldspathoid minerals, the micas, chlorite, epidote, tourmaline, and the ore minerals magnetite, chromite, titanomagnetite and spinel, that Ga occurs in concentrations significantly above its crustal abundance of 18 ppm.

The range of Ga values reported here for plagioclase from various rock types (19-32 ppm) is well within that reported by Burton and Culkin (1972) of 10-110 ppm Ga. The exact compositions of the plagioclase samples are not known, but for the B.I.C. samples Wager and Brown (1968) report that the range in plagioclase composition for the Critical Zone, sample ET3/169, is An_{79} to An_{76}, while for the Main Zone, sample 5087, the range is An_{76} to An_{54}. Mathias (1956) reported the plagioclase composition for the biotite norites to be from An_{50} to An_{60}. The composition of plagioclase DS-50 is An_{50-55} (A.R. Duncan, pers. comm.). The composition of the plagioclases from the three NOR- samples is An_{40} to An_{48}. Although the plagioclase samples come from very widely differing areas and igneous bodies, it is nevertheless apparent that those plagioclases with a lower anorthite content have a higher Ga content. This is in accord with the theoretical work of Goldsmith (1950) on synthetic feldspars, although no consistent relationship between Ga and anorthite content is apparent in the literature. The results are also in accord with those found by Goodman (1972).

Of the six pyroxene samples, three have Ga contents of ~3 ppm, while the other three have 4-5 ppm Ga. It is possible that the higher values represent slight impurities in the separates. The samples were available only in briquette form and the purity is not known. However, all the samples fall within the range of 1-12 ppm Ga reported by Burton and Culkin (1972) for pyroxenes.

The six pyroxene samples form mineral pairs with corresponding plagioclases, and it is interesting to note the ratios of the Ga contents for the various plagioclase-pyroxene pairs.

Sample	Ga ratio (plag/pyx)	Rock type
ET3/169	6.8	pyroxenite
5087	5.8	norite
ME-6	6.8	biotite norite
ME-7	6.7	biotite norite
ME-9	3.9	biotite norite
DS-50	4.4	dolerite

The ratio for the first four samples is fairly consistent, and the low ratio for ME-9 would seem to confirm that the pyroxene sample for this rock was impure, leading to a high Ga content. However, the ratio for the Karroo dolerite DS-50 is almost as low. The number of mineral pairs is too small to be able to make definite conclusions regarding the constancy of partitioning of Ga between plagioclase and pyroxene.

The single orthopyroxene analysed has a very low Ga content of 0.9 ppm, and a Ga/Al ratio of 1.7 which is lower than any reported by Burton and Culkin (1972) for orthopyroxenes.

The Ga contents of the two hypersthenes NOR-1 and NOR-2 seem rather high at 13-14 ppm. Burton and Culkin (1972) report a range for Ga in orthopyroxenes from 1.5 to 30 ppm, and from 2 to 10 ppm in hypersthenes. Howie (1955) reported a range for orthopyroxenes from the charnockite series, Madras, of 5 to 30 (mean = 13) ppm Ga. Philpotts (1966) reported a range from 10 to 25 (mean = 15) ppm Ga in orthopyroxenes from Quebec rocks, mainly norites. Philpotts also reported a range from 10 to 20 (mean = 14) ppm Ga in clinopyroxenes. Philpotts reported no difference in the Ga content of clino- or orthopyroxenes, in contrast to Howie who found twice the amount of Ga (13 ppm) in orthopyroxenes as in clinopyroxenes (6 ppm) with corresponding differences in the Ga/Al ratios. Bell (1953) reported a range from 1 to 8 ppm Ga for pyroxenes, with only spodumene having a high Ga content of 33 ppm. Burton et al. (1959) reported a range from 5 to 7 ppm Ga in pyroxenes.

The data of Philpotts and Howie are, therefore, much higher than those of Bell and Burton and co-workers. The data of Philpotts and Howie were determined by Nockolds and Allen. The same analysts determined the Ga contents of Messum rocks for Mathias (1956, 1957). In Chapter 13.7 the Messum data are shown to be high. Nockolds and Allen (1956) also determined the Ga content of Karroo dolerites, and in Chapter 16 their data are shown to be high by about 50%. The data of Philpotts and Howie may therefore be higher than others as a result of systematic error in the analyses.

In Table 38 the range for Ga in 14 pyroxenites is given as 1.3-6.3 with a mean of 3.3 and median of 3.0 ppm. Although these are ultrabasic rocks, it does suggest that the hypersthenes might be contaminated. The two hypersthenes analysed in this work were separated from rocks containing magnetite, and although every attempt was made to separate the magnetite completely (A.J. Erlank, pers. comm.), it is possible that some magnetite was included in the hypersthene grains. Assuming the magnetite contained 100 ppm Ga, it would require the presence of about 10% magnetite to account for the increased Ga content relative to other clinopyroxenes. Such a degree of contamination is unlikely, but some finely divided magnetite could be disseminated in the hypersthene. An attempt was made to detect magnetite by XRD analysis. Unfortunately the strongest magnetite reflection (2.53Å) occurs very close to two weak hypersthene reflections (2.51 and 1.56Å), and it was not possible to confirm the presence or absence of magnetite. No feldspar peaks were found.

The two rocks NOR-1 and NOR-2 from which these hypersthenes were separated have fairly high Ga contents (32 ppm and 24 ppm respectively) and the separated plagioclases also have high Ga contents. It is possible that the measured Ga contents of the hypersthenes are correct.

Erlank (1971) reported that the rock ET3/169 (Table 55B) from which the plagioclase and pyroxene reported in Table 36A were separated, contained 20% plagioclase, 80% pyroxene (mostly orthopyroxene) and about 0.02% alkali feldspar. Burton and Culkin (1972) report values for Ga in alkali feldspar ranging from 8 to 20 ppm with a mean of 14 ppm. The mean Ga contents of alkali feldspars reported in Table 37 are similar. It is possible to calculate the Ga contributions of the individual minerals to the bulk rock for ET3/169, as follows:

	Mineral ppm Ga	Rock ppm Ga
Plagioclase (20%)	20.4	4.1
Pyroxene (80%)	3.0	2.4
Alkali feldspar (0.02%)	~14.0	0.0
	Total:	6.5

The measured Ga content of ET3/169 is 6.3 ± 0.2 ppm at 95% confidence limits, in good agreement with the calculated value. The good agreement confirms the conclusions reported by Vincent (1974), namely that almost no Ga resides in the inter-cumulus material.

Of the two upper mantle clinopyroxene megacrysts from kimberlite, sample M(A), which crystallized at 1340-1395°C, has an average Ga content and Ga/Al ratio, but sample JJG248 (1030°C) has a very high Ga/Al ratio. Some upper mantle pyroxenes contain exsolved ilmenite which contains approximately 20 ppm Ga. However, JJG248 contains only 0.5% TiO_2. The high Ga/Al ratio for this sample can not therefore be due to the presence of ilmenite. These samples are discussed further in Chapter 14.2.

Five upper mantle garnets were analysed for Ga. Two samples were garnet megacrysts separated from kimberlite, one garnet was separated from an eclogite, and two from peridotite xenoliths.

All the Al in garnets is in 6-fold co-ordination. As discussed in Chapter 2, considerations of the ionic radius of Ga and its radius ratio compared with that of oxygen would lead to the expectation that Ga would preferentially enter those minerals in which Al is in 6-fold co-ordination. Huggins et al. (1977) reported, however, that in garnets Ga showed greater preference for tetrahedral sites compared with octahedral sites than did Al. This evidence would suggest that the Ga/Al ratio in garnets should be low. Four of the garnet samples have Ga/Al ratios in the range 0.5-0.8, and the fifth has a ratio of 1.2. These are among the lowest ratios found in this work. The low ratios are in contrast to the data of Howie (1955) who reported a value of 40 ppm Ga and a Ga/Al ratio of 3.0 in a garnet from Madras, but confirm the data of De Vore (1955), Bell (1953) and O'Hara (1961) who found mean values for Ga in garnets of 4, 6 and 6 ppm respectively, and corresponding Ga/Al ratios of 0.4, 0.56 and 0.5. All the garnets analysed by these three workers were obtained from schists or gneisses, whereas those analysed in this work are of upper mantle origin and from a high pressure environment. The reason for the high Ga content of the

Monastery garnet is uncertain, but this sample is discussed further in Chapter 14.2.

Ga has been determined in a single sample of epidote. The value of 34 ppm Ga is well within the range reported in the literature of 4-57 ppm. A sample of a zeolite (heulandite), separated from a basalt, contained 5 ppm Ga. This is close to the lowest value reported in the literature, 4-75 ppm Ga (Shaw, 1957).

Only a few values for Ga in corundum have been reported, namely "not detected" by Pearson (in Shaw, 1957) in a corundum of metamorphic origin, 99.7 ppm Ga in corundum of unknown origin from N. Carolina (Burton et al., 1959) and 0.01-0.05% Ga in corundum samples from Russia (Vlasov, 1966). The single determination on corundum made in this work of 100.2 ppm Ga is very close to that of Burton and co-workers. The origin of the sample analysed here is uncertain, but is probably metamorphic.

Ga was not detected (<0.3 ppm) in an olivine sample, confirming that Ga is excluded from the olivine lattice.

Two samples of schorl tourmaline from very different rock types were analysed and Ga found to be present at the 29 and 37 ppm levels. Burton et al. (1959) reported 14 ppm Ga in a tourmaline sample, and Bell (1955) 27 ppm Ga, giving an average of 21 ppm. Butler (1953) reported extremely high values for Ga in tourmalines separated from adamellite, pegmatite and topaz-fels, namely 150-800 ppm Ga. These values seem unrealistically high, although Vlasov (1966) reports the presence of 260-310 ppm Ga in pegmatitic tourmalines from Russia. Neiva (1974) reported Ga in schorl tourmalines from granites (62-75 ppm), associated aplites (50-90 ppm) and pegmatites (75-90 ppm).

Some of these high values may be the result of poor analytical technique. Butler (1953) used an optical spectrographic method in which the sample was mixed with carbon and arced at 8 amps for the first 30 seconds of the burn. Butler stated that he measured the Ga line at 4215Å, which does not exist. Butler also arced to completion and used the Ga 2943Å line, which is a line commonly used by spectrochemists for the determination of Ga, but which may be sensitive also to interference by Fe 2943Å in schorl tourmalines. He made a visual estimate of line intensities and compared these with line intensities of spectrograms of artificial standards to obtain concentrations. It is not clear from Butler's paper which line he actually used to determine Ga in tourmaline, but his data must be open to question and should be disregarded. Neiva (1974) determined Ga in Nockold's laboratory, and the data are likely to be high, as mentioned earlier for other minerals.

Ga was also determined in biotites and perthitic feldspars separated from fresh, partly weathered and weathered samples of three granites from the Cape Peninsula, but these data will be discussed in Chapter 17. At this point it is sufficient to record that the range of Ga values in the biotites was 57-66 ppm Ga and in the feldspars 13-17.5 ppm, in agreement with other data in the literature. Only the data for the minerals from the fresh rocks are reported in Table 36.

Five chromites (18-58 ppm Ga) and five magnetites (49-54 ppm Ga) from the B.I.C. were analysed for Ga, and the results are discussed in detail in the section on the rocks from the B.I.C. (Chapter 13.4). The Ga contents of the magnetites can be considered normal and similar to those reported by other workers, but the values found for the chromites are mostly much higher than other values reported in the literature, by factors of two to three.

Ga contents are reported for five ilmenites and one spinel from kimberlite. The ilmenite data are extremely interesting. Wager and Mitchell (1951), Vincent and Nightingale (1974), Howie (1955) and Burton <u>et al</u>. (1959) all reported low Ga values for ilmenite, ranging from "not detected" to 9 ppm Ga. The five ilmenite values reported here range between 16 and 21 ppm Ga, at least a factor of two higher than previously reported results. Wager and Mitchell, Vincent and Nightingale, and Howie all reported that Ga preferentially entered magnetite, substituting for Fe^3 in 4-fold co-ordination, rather than ilmenite where Fe^3 is present in 6-fold co-ordination, when both minerals are present in the same rock.

In the upper mantle Ga obviously enters the ilmenite structure, either substituting for Fe^3 (6-fold co-ordination) or Ti^4, also in 6-fold co-ordination. The reasons for the substitution are unknown, but may be due to a number of factors: one, most (~ 60%) of the Al in the upper mantle is present in garnet, and Ga is not readily accepted into garnets where it must substitute for Al in 6-fold co-ordination; two, the amount of magnetite in kimberlite in which Ga could reside is very variable, may not be primary and may not always be available as a host mineral; three, the high pressure environment in the upper mantle may cause slight distortion of the ilmenite lattice and allow Ga to substitute more readily for Fe^3 in 6-fold co-ordination than at lower pressures; and, four, the ilmenites possibly crystallized only from metasomatised rocks in which the metasomatic liquids were rich in Ga (see Chapter 14.1). The single spinel sample from kimberlite is also high in Ga (29 ppm), in agreement with data reported by other workers.

The data reported here are included in Table 37 for comparison with those abstracted from the literature for some of the more important rock-forming minerals.

It is clear from Table 37 that there are a number of minerals for which more data are required, especially the pyroxenes, epidote, tourmaline, and the Fe and Ti oxide minerals. In particular, attention should be given to minerals from the upper mantle, some of which have formed at high temperatures and pressures. Data for Ga in clay minerals from the sedimentary environment are very scarce.

In the following chapters frequent reference will be made to the data in Table 37.

CHAPTER 9

ABUNDANCE AND DISTRIBUTION OF GALLIUM IN TERRESTRIAL ROCKS

The general distribution and abundance of Ga in terrestrial materials is well known and has been summarised by Shaw (1957), Burton _et al_. (1959) and Burton and Culkin (1972). Prinz (1967) summarised data on Ga in 219 basaltic rocks. One of the main objects of this work was to define the fine structure of the Ga distribution in rocks and its relationship with Al. A large number of rocks have been analysed to achieve this purpose. Although Ga has been previously determined in many of these rock types by other workers, nevertheless there are a number of instances where the data usefully extend our knowledge. The precision and accuracy of the data presented here is superior to most of that in the literature, which enhances its usefulness.

In Table 38 the Ga data in this work are summarised by rock type or mineral, giving arithmetic mean, median, mode and range of concentrations. Where the Al concentrations are known, data for mean and range of Al and of the Ga/Al ratio are included. The Ga/Al ratio has been multiplied by 10,000. The number of samples in each case is given in brackets after the mean value. As in all works of this nature, mean values for any individual rock type or general type, such as Q + A + P rocks (quartz + alkali feldspar + plagioclase), is bound to be influenced by the relative numbers of samples from individual areas. For example, granites from two or three areas in southern Africa have been analysed, and there is no reason to expect that they should have the same Ga contents as granites from other areas of the world. They might possibly have similar concentration levels, but care must be taken in making detailed comparisons.

A further problem is that many of the samples analysed here were received as powders from overseas. The rock names assigned by the people who sent the samples had, therefore, to be accepted. In many cases workers used different methods of classification, so that often similar rocks have been classified differently. Without having access to the original rock thin sections, samples were allocated to the class or type in the IUGS system according to the rock names given by those workers who originally classified them. In some instances this has led to the rocks being incorrectly placed in groups or classes. Where this is thought to have occurred, it will be pointed out in the text. Generally, the effect on averages for any one class or type will be negligible.

The results summarised in Table 38 are presented in histogram form in Figs 42-72, which give a better idea of the distribution of the Ga data within each rock type and should be read in conjunction with Table 34. Each figure has two parts, giving respectively information for Ga (A) and the Ga/Al ratio (B), the latter always multiplied by 10^4, as elsewhere in this work. The number of samples in each histogram is shown in the top right hand corner.

Fig. 42 shows the Ga and Ga/Al distributions for the five main groups of rock types analysed in this work.

The frequency distribution of Ga for the plutonic and hypabyssal rocks (Fig. 42A) is broad (0-46 ppm) with a prominent mode at 15.7 ppm Ga. The large number of rocks with less than 10 ppm Ga reflects the considerable number of ultramafic rocks analysed in this work (Fig. 44).

The volcanic rocks classified by mineralogy have a bimodal Ga distribution which reflects the distribution of the basaltic rocks (see Fig. 59). The bimodality is caused by the difference in the Ga content of basalts and tholeiite basalts (see Fig. 62). It is noticeable that the Ga content of the volcanic rocks classified by chemistry is much lower than those classified by mineralogy. Most of the chemically classified rocks are from the Barberton Mountain Land, and comprise mainly komatiites with a range of 1.4-15.2 ppm Ga.

The sedimentary rocks have a distribution with no really prominent mode, because most of the samples analysed here represent mixtures of feldspathic and siliceous shales.

The metamorphic rocks have a distribution with a pronounced mode of 22 ppm Ga, which is caused by a relatively large number of rocks from the same area (the Sea Point contact, Cape Town).

In Fig. 42B the Ga/Al distributions of the plutonic and volcanic rocks are positively skewed, reflecting the tendency for Ga to enrich relative to Al during differentiation processes, resulting in Ga/Al ratios that are likely to be high rather than low. It is also noticeable that only in the plutonic and hypabyssal rocks does the Ga/Al ratio exceed 5.0. All the high ratios have been observed in kimberlites, usually in those with a high Fe^3 content. Another interesting feature is that the mean Ga/Al ratios for all groups are essentially constant, ranging from 2.3-2.7. Nevertheless, it will be shown later that variations in the Ga/Al ratio within a group of rocks can be useful in interpreting the geochemistry and history of the group.

Figs 43 and 44 are frequency diagrams for the eight groups of plutonic rocks as classified by the IUGS. The A + P + Q rocks are divided into two separate groups, quartz gabbros and quartz norites, all having Ga values less than 15 ppm, and the other rocks having values greater than 17 ppm (see Fig. 46A). There is a similar division in the Ga/Al ratios, the gabbros and norites having lower ratios than the other rocks (Fig. 46B). In the F + – A + – P rocks (Fig. 44A) the ijolites have a very enriched Ga concentration (31-32 ppm). The distribution of Ga in the ultramafic rocks is positively skewed, whereas the Ga/Al distribution (Fig. 44B) has three modes, the significance of which will be discussed later (Chapter 14).

It is clear that in the group A + P +− Q rocks the spread in the Ga data is essentially that of the gabbroid rocks (see Fig. 47A). The Ga/Al ratios (Fig. 47B) of the anorthosites are lower than those of other rocks.

A large number of gabbroid rocks (230) have been analysed in this work. These can be divided into two main groups: those consisting mainly of plagioclase and pyroxene, and those in which olivine is also a major component (Fig. 48). It might have been expected that those rocks which contain olivine, which does not contain detectable Ga and therefore acts as a diluent, would have had a lower Ga content. The effect is very slight indeed. The difference between the mean Ga values of the two groups is only 0.2 ppm. This is possibly due to the large number of dolerites analysed. These cluster closely about a value of 16 ppm Ga (Fig. 50) and account for the modal peak in the plagioclase + pyroxene rocks. As would be expected, the Ga/Al ratio is similar in the two major groups (Fig. 48B).

The foid-bearing syenites (Fig. 51) analysed here have much higher Ga values and Ga/Al ratios with wider distributions than the foid-bearing gabbros. Most of the foid-bearing syenites are from an igneous complex in the Nejoio area, Angola.

The frequency distributions of Ga and Ga/Al in foid syenites and foid monzodiorites from the Okonjeje Igneous Complex in S.W.A. are given in Fig. 52. The Ga distribution in the syenites again has a greater spread of values than in the monzodiorites and Ga is generally higher in the syenites. The Ga/Al ratio is similar in both rock types.

One of the major contributions in this work to our knowledge of the distribution of Ga is for ultrabasic rock types. Data are presented for 257 samples, about half of which are kimberlites (Figs 53, 54). As would be expected, olivine + pyroxene rocks contain less than 7 ppm Ga, which is low relative to other igneous rock types. The one value higher than 7 ppm Ga is from an amphibolitised websterite, amphiboles having a higher Ga content than pyroxenes (Burton and Culkin, 1972, and Table 37). The Ga content depends on the proportion of olivine to pyroxene. The Ga content is generally highest in those rocks containing the least olivine. The Ga/Al ratio for olivine + pyroxene rocks is usually less than 2.0, again with the exception of the amphiolitised websterite. When plagioclase is present in the rock, the Ga content increases, as does the Ga/Al ratio, although only two values for the ratio in olivine + pyroxene + plagioclase rocks were determined. It is also clear in Figs 53B and 54B that kimberlites have higher Ga/Al ratios than other ultramafic rocks; almost all ratios for kimberlites are greater than 2.0.

For kimberlites (Fig. 54) there are two modes in the Ga/Al ratio distribution which are not so clearly defined in the Ga distribution. Kimberlites will be discussed in detail in Chapter 14.3.

Another group of rocks for which a considerable quantity of new data are presented are the kimberlitic xenoliths. Of 119 samples analysed, 43 were eclogites. Fig. 55 shows that the range for the eclogite xenoliths is essentially the same as that for all xenoliths analysed, with the exception of the ilmenite xenolith which has a high Ga content of 20 ppm. With the exception again of a single value, the Ga/Al ratio is less than 2.0, similar to the ultrabasic rocks other than kimberlites.

The range of Ga values in the volcanic rocks (Fig. 56) analysed here is considerable, from <0.4-67 ppm Ga, which is greater than that found for the plutonic and hypabyssal rocks (Fig. 42). The Ga/Al ratios have a much smaller range of values, 1.1-7.0 in volcanic rocks compared with 0.6-14.7 in plutonic and hypabyssal rocks. As already pointed out, the bimodality of the Ga distribution is due to the large numbers of basaltic rocks analysed, and reflects different Ga contents of basalts and tholeiite basalts (Fig. 62A).

Acidic rocks generally contain more than 20 ppm Ga, while approximately half of the more basic A + P + − Q rocks (Fig. 57) have Ga values less than 20 ppm. It is noticeable that when feldspathoids are present in the rocks, the Ga content increases again. The A + P + − F rocks have the same Ga distribution as the A + P + − Q rocks, but the Ga contents of the A + P + F and F + − A + − P rocks are almost all greater than 20 ppm Ga.

There are too few analyses of Q + A + P rocks (Fig. 58) to make detailed comparisons between the different rock types.

About a quarter of the samples (390) analysed in this work fall into the group A + P + − Q rocks; frequency distributions for the main subdivisions of these rocks are given in Figs 59-62. The range of Ga concentrations in trachytes and alkali trachytes (16-43 ppm) is greater than those found in latites, latite andesites, latite basalts and andesites (Fig. 59A). The range of Ga values reported for the trachybasalts (latite basalts) (19-29 ppm) is much less and they also have a lower mean value of 22.6 ppm Ga compared with ~ 27.5 ppm for the trachytic rocks.

The Ga contents of basaltic rocks (Fig. 60A) range between 7 and 29 ppm with a mean value of 18 ppm Ga. It is for basaltic rocks that differences in methods of classification are most likely to have distorted the distribution patterns. For example, it is clear in Fig. 60A that the plagioclase + pyroxene + olivine rocks have a slightly lower Ga content (16.6 ppm) compared with the plagioclase + pyroxene rocks (18.3 ppm), probably due to the presence of olivine. However, there are probably a number of rocks of low Ga content in the latter group which should have been classified as containing olivine. In Fig. 60B the range in the Ga/Al ratios of the plagioclase + pyroxene rocks covers the values found in all the other groups or subdivisions.

In Fig. 62 the plagioclase + pyroxene rocks (245) have been divided into basalts and tholeiite basalts. The Ga contents and distribution patterns of the two groups are distinctly different. The distribution of Ga in tholeiites approximates that of a normal distribution, with a mean of 15.8 ppm Ga, while the basalts have a strongly negatively skewed distribution and a mean of 19.7 ppm Ga. Prinz (1967) reported a mean of 19 ppm Ga for tholeiite basalts and 20 ppm for basalts. The negatively skewed distribution of the basalts is possibly caused by the inclusion in this group of a number of tholeiite basalts misclassified by various workers. The Ga/Al ratio is also considerably different in the two groups, the tholeiites having a mean value of 1.9 and the basalts a mean of 2.6. It is clear that Ga is depleted in the tholeiites in a manner similar to the alkali elements K and Rb, although not to the same degree.

Histograms for Ga and Ga/Al in the volcanic rocks, classified on the basis of their chemistry, and the two major subdivisions of the subalkaline rocks, the tholeiitic type and the calc-alkaline type, are given in Figs 64-66. Only one sample of the alkaline type was analysed. It contained 23.6 ppm Ga with a Ga/Al ratio of 2.30. All the tholeiitic subalkaline rocks analysed here were komatiites, and for this reason it is unwise to read too much into the marked difference between the Ga contents of the tholeiitic and calc-alkaline types. The Ga/Al ratios of the two types are similar.

96 komatiites, 42 peridotitic and 54 basaltic, have been analysed. The difference in the Ga contents of the two groups is marked (Fig. 65), although the Ga/Al ratios in the peridotitic type are similar to those in the basaltic type. It is clear (Fig. 65) that the Ga contents of the three types of basaltic komatiite are different. The Ga/Al ratios of the three types are similar. The komatiites will be discussed further in Chapter 15.

The distributions for Ga in the sedimentary rocks analysed in this work, which are all shales from the Malmesbury formation in the Cape Province and which can be divided into feldspathic or siliceous shales, are given in Fig. 68. The siliceous type is essentially the feldspathic type diluted with quartz, and it would be expected that, although the Ga content of the siliceous shales should be lower, the Ga/Al ratio should be similar for the two groups, as is the case (Fig. 68B).

In an attempt to remove the effect of quartz dilution, the clay fractions were analysed separately, and the data are included in Fig. 68. The Ga contents and Ga/Al ratios of the clay fractions of the arenaceous shales are similar to those of the feldspathic shales.

Histograms of the Ga and Ga/Al ratio distributions in minerals are given in Figs 69 and 70.

The range of Ga data in the literature for various rock types is so large, whether real or as a result of analytical error, that the data presented here generally fit well within the ranges already reported (Shaw, 1957; Burton and Culkin, 1972). The main contribution of this work has been in filling gaps in our knowledge of the Ga distribution in ultramafic rock types, the komatiites and anorthosites. A comparison of Ga data presented here with that in the literature is given in Table 39 for some major rock types.

As already mentioned, a considerable number of basaltic rocks, both continental and from oceanic islands and the ocean floor, have been analysed. Using the database, it was a simple matter to extract separate sets of data for oceanic and continental basaltic rocks. Data for Ga and Ga/Al ratios in these groups are given in Table 38 and frequency distributions are shown in Fig. 71. There is little difference between the two sets of Ga data with respect to either the range of values or the mean values. The Ga/Al ratios in the oceanic rocks, with the exception of one high value of 4.8, have a more uniform and narrower distribution than in the continental rocks, which are positively skewed.

In Fig. 72 and Table 38 the basaltic rocks have been further divided into basalts and tholeiite basalts for both continental and oceanic types. Slight differences between continental and oceanic rocks are apparent. The ranges of Ga in continental and oceanic tholeiites are identical, i.e. 10 ppm Ga, but the continental tholeiites have a lower mean value of 14 ppm compared with 16.5 ppm Ga for the oceanic rocks. There is considerable overlap between the two groups and it is not possible to distinguish clearly between them. The Ga/Al ratios of the two groups are also similar, with the ratios for the continental rocks, which are all from the Barberton Mountain Land, falling within the range of the oceanic tholeiites.

A similar picture emerges for the basalts, with the ranges of the two groups being almost identical, and the mean value for the continental rocks (19 ppm) just lower than that for the oceanic rocks (20 ppm Ga). The Ga/Al ratios of the continental basalts, in contrast to the tholeiites, have a greater range of values than the oceanic rocks, although the mean values are similar, 2.7 and 2.6 respectively.

In Fig. 73 percent Al has been plotted against ppm Ga for all tholeiite basalts. With the exception of the two ringed samples, it is clear that the Barberton Mountain Land tholeiites can be distinguished from all the oceanic tholeiites. Although the abyssal and Barberton tholeiites have similar ratios, the Barberton rocks have lower Ga concentrations. The two Barberton samples that fall within the oceanic field are a dolerite dyke (13.8 ppm Ga) that is younger than the tholeiites, and a carbonated pillow (16.3 ppm Ga) which may have been contaminated with Ga.

In Fig. 74 Ga and Al data have been plotted for continental and oceanic basalts. There is considerable overlap between the oceanic and continental rocks, but most of the oceanic basalts have a higher Al content than the continental basalts. The six oceanic rocks which plot in the continental field are all from Marion and Prince Edward Islands. The only noticeable feature about these six samples is that they have low differentiation indices (< 30) (see Chapter 12.4, 12.7).

CHAPTER 10

INTER-ELEMENT RATIOS FOR Ga:

Ga/Al, Ga/(Al + Fe^3) AND Ga/(Al + Fe^3 + Na)

It has already been noted that Ga may substitute for Fe^3 as well as for Al, and Taylor (1964) suggested that it should enter the Fe^3 positions more readily than the Al^3. Shaw (1957) suggested that the Ga/(Al + Fe^3) ratio might show more coherence than the Ga/Al ratio. Bowden (1964) suggested that the Ga/(Al + Fe^3) ratio might be more useful in evaluating trends in rock series having variable Fe^3 contents than the Ga/Al ratio. Bowden evaluated both ratios in his discussion of the distribution of Ga in granites from Northern Nigeria, and found that both gave similar information. He was, however, comparing granites from different complexes and it is possible that this tended to blur the picture.

The problem with using the Ga/(Al + Fe^3) ratio can be two-fold. Firstly, if the major element compositions are determined by classical wet chemical techniques, then the Al data are determined by difference and tend to be not only imprecise but also biased towards slightly high values (Ahrens and Fleischer, 1960). The determination of Fe^3 is notoriously difficult if really accurate data are to be obtained, and is also dependent on the degree of grinding the powdered sample has been subjected to before a sub-sample is taken for analysis. The measured Fe^3 concentration may not therefore reflect the true value present in the rock during its crystallization, the value which is of importance when considering Ga substitution for Fe^3. The other problem associated with the use of Fe^3 is that modern instrumental methods of analysis measure only the total Fe content of a sample, and data for Fe^3 are frequently not available.

If, therefore, the Ga/(Al + Fe^3) ratio is to be used, then preferably the Al should have been determined by instrumental methods and the greatest care should have been taken in the determination of the Fe^3, which in the case of routine analyses is often not the case. In addition, to warrant its use the coherence of the Ga/(Al + Fe^3) ratio should be markedly better than that of the Ga/Al ratio.

It is of interest to take a few examples and see whether more information can be obtained from one ratio or the other in those cases where data on both Al and Fe^3 are available.

Pearson's correlation coefficients (r) between Ga-Al and Ga-(Al + Fe^3) for a number of different suites of rocks have been tabulated in Table 40 and the corresponding data have been plotted in Figs 75-83. In some instances the number of data points is too few and the spread of the points too narrow for meaningful conclusions to be reached. The data in Table 40 and Figs 75-83 should be considered together.

For rocks from the Doros igneous complex (Fig. 75) good correlations are obtained for both sets of data, with Ga-(Al + Fe^3) showing a slightly better correlation than Ga-Al. For the Erongo igneous complex (Fig. 76) the spread of the data points for both Ga and Al is small, and no trend is discernible. The Fe^3 values in these rocks vary considerably and accentuate the poor negative correlation found between Ga and Al. For rocks from the Losberg igneous complex (Fig. 76) there is no difference between the two sets of data, both showing very strong correlations. The Kunene anorthosites have a fairly small range in Ga values (Fig. 77) and a high Al/Fe^3 ratio (~ 22), which results in little difference between the two data sets.

The two groups of ultrabasic rock types, the mica-rich kimberlites and the xenoliths from the Matsoku kimberlite pipe (Fig. 78) show very different correlations. For the Matsoku rocks there is excellent correlation for both data sets with little difference between the two, while the kimberlites exhibit a very strong correlation between Ga and Al but an almost random distribution between Ga and (Al + Fe^3). The range of Fe^3 varies very considerably in the kimberlites with apparently no corresponding variation in the Ga content. This is probably due to the fact that much of the Fe^3 was formed during the serpentinisation of olivine. Since olivine contains negligible Ga, there should be no correlation between Ga and olivine-derived Fe^3. If the Fe^3 was present as primary magnetite, then a correlation between Ga and Fe^3 could be expected.

A large number of samples from the Okonjeje igneous complex have been analysed and major element data of the highest quality were made available by Fesq (1978). Rocks from the Okonjeje complex can be divided into two groups, a tholeiitic and an alkalic series. As discussed later (Chapter 13.8), the data points on a Ga-Al plot overlap to a considerable extent for the different rock types in these series, and it was considered preferable to plot each rock type separately to avoid confusion. Data for gabbro-picrites and olivine gabbros have been plotted (Fig. 79), and show opposite features. The Ga-Al data for the gabbro-picrites give the best coherence, while for the olivine gabbros the Ga-(Al + Fe^3) plot shows a better correlation than Ga-Al, although in neither case is the fit as good as that for the gabbro-picrites. In Fig. 80 the olivine ferrogabbros show no correlation at all for either data set. Three different trends are illustrated for hypersthene ferrogabbros, alkali syenites, and pyroxene diorites, monzonites and adamellites. For the hypersthene ferrogabbros the spread of Ga and Al values is small with a much larger spread in the Fe^3 values, resulting in a strong grouping of the points on the Ga-Al plot and a variation in the (Al + Fe^3) values with no variation in the Ga values. The pyroxene diorites, monzonites and adamellites group together for both sets of data points with no discernible trends, while the alkali syenites show a better correlation between Ga and (Al + Fe^3) than between Ga and Al, although the number of points is small.

In the alkali series (Fig. 81) alkali olivine gabbros show a picture similar to that of the olivine gabbros in the tholeiitic series. The granulitised alkali olivine gabbros on the other hand show a better correlation between Ga and Al alone. The nepheline olivine gabbros (Fig. 82) show a better correlation between Ga and Al + Fe^{3}, although only a single sample causes the difference between the two plots. Both the melteigites and the camptonites are plotted together, and here Ga-Al shows the better correlation.

Similar plots and calculations were made for rocks from two oceanic islands, Bouvetoya and Gough (Fig. 83). For Gough Island the Ga-Al data are marginally more coherent ($r = 1.00$) than the Ga-(Al + Fe^{3}) data ($r = 0.98$), while the rocks for Bouvetoya Island, in addition to showing negative correlations for both sets of data, give a better correlation between Ga and (Al + Fe^{3}) than between Ga and Al.

de Albuquerque (1971), in his work on granitic rocks from Portugal, found no significant differences between the two ratios, although the amounts of Fe^{3} were small relative to Al.

Rooke (1964), investigating African acid igneous rocks, reported that Na had an important bearing on the concentration of Ga, and found a good relationship between Ga and Na/(Al + Fe^{3}). This relationship was investigated in the rock suites reported in Table 40, but, with one or two exceptions, correlation coefficients were very low compared with those for the Ga-Al and Ga-(Al + Fe^{3}) relationships. Rooke (1964) was investigating acid rocks in which Fe^{3} would be very low in comparison with Al, and in which Na increases with differentiation. The relationship reported by Rooke probably reflects an increase in Ga with increasing degree of differentiation, with the Na/(Al + Fe^{3}) ratio acting as a crude differentiation index.

In summary it can be concluded that only for the Erongo Igneous Complex, Bouvetoya Island, and the alkali syenites, olivine gabbros and alkali olivine gabbros from the Okonjeje Igneous Complex are there any significant increases in the correlation coefficients between Ga and (Al + Fe^3) as compared with those between Ga and Al. In all other groups examined, either the Ga-Al correlation is better than that of Ga-(Al + Fe^3) or there is little difference between the two.

Therefore, bearing in mind the problems associated with the determination of Fe^3 and in some instances the lack of such data, it was decided to report only the Ga/Al ratio in this work.

CHAPTER 11

GALLIUM IN ABYSSAL ROCKS FROM THE ATLANTIC, PACIFIC AND INDIAN OCEANS

11.1 INTRODUCTION

Gallium has been determined in 60 abyssal rocks from the Atlantic, Pacific and Indian Oceans and in 8 samples from Leg 25 of the Deep Sea Drilling Program in the Indian Ocean (Tables 41-43). The locations from which the samples were collected are shown in Fig. 84, which is adapted from Engel et al. (1965). Of the 60 rocks, all but 6 are tholeiites or dolerites. Data for the tholeiites and dolerites are summarised in Table 44 and illustrated in frequency distribution diagrams in Fig. 85. Seven cross-sections of lava pillows have been analysed.

11.2 COMPARISON WITH OTHER DATA FROM THE LITERATURE

A number of workers have analysed abyssal tholeiites for Ga with very variable results. Muir et al. (1964) reported Ga in DBA 20.0 and 20.2 as 10 ppm compared with the values here of 14 ppm. They also reported the Ga contents of 8 pyroxenes and 2 feldspars from the Rift Zone of the Mid-Atlantic Ridge at 45°N. Their values for the pyroxenes were 6 and 10 ppm Ga and for the plagioclases 30 and 10 ppm, the latter value being exceptionally low and representing the xenocrystal plagioclase. Aumento (1968) reported Ga values ranging from 24 to > 50 ppm for rocks DBA 11-16, compared with the data given here of 15-17 ppm Ga. Cann (1969) reported values of 20 ppm Ga for samples DBI 1 and 2 from the Carlsberg Ridge, and later (Cann, 1970) reported values of 15 ppm Ga in basalts from the Gulf of Aden, which are very close to the average values determined here. Melson et al. (1968)

OL-tholeiites, i.e. those in which olivine crystallized out first, and PL-tholeiites, in which plagioclase crystallized first. There is a third group having both olivine and plagioclase as phenocrysts. Thompson _et al._ (1972) determined Ga in tholeiites from 25°N on the Mid-Atlantic Tidge and found no difference between the Ga contents of OL- and PL-tholeiites, although there was a difference between OL-tholeiites from different stations, i.e. 25° and 30°N. However, the standard deviation of ± 6 ppm (3s) was almost as great as the total range of the Ga data (7 ppm), and his conclusions were probably not statistically valid. Unfortunately, in this work the nature of the phenocrysts in most of the samples was not known, and it was not possible to come to any conclusions as to differences that may be present in the Ga contents of OL- and PL-tholeiites.

11.3.1 Ga and Ga/Al ratio variations in altered pillows

In six instances inside/outside fractions of lava pillows have been analysed, and the data for three of them presented here were reported by Hart _et al._ (1974). For the pillow represented by samples DBP 9-13 (Table 42B), although Ga decreases regularly from core to margin, the variation is within analytical error and the Ga/Al ratio remains constant. DBA 27-28 (Table 41E) shows a slight drop in the Ga content from interior to margin, but again the difference is within analytical error and the Ga/Al ratio is constant. For samples DBA 38-39 the Ga content is higher in the margin, but no Al data are available. DBA 24-26 (Table 41D) shows a higher Ga content in the interior and the Ga/Al ratio is again constant. Ga in DBA 31-32 (Table 41C) is constant. DBA 21-23 is the only pillow to show a significant change in Ga content , with the most weathered or altered fraction, DBA 22, having the lowest Ga value. It is perhaps significant that the Ga/Al ratio remains constant. It is suggested that the variation in Ga content is not due to alteration but rather to variation in composition, as the normative composition of DBA 22 is distinctly different from those of the margin and interior fractions (Hart et al., 1974).

There is no evidence to suggest that in abyssal lava pillows there has been significant alteration of the Ga content or removal of Ga relative to Al, although Hart et al. (1974) suggested that during the initial stages of alteration both Ga and Al are lost from the basalt.

11.3.2 Comparisons between abyssal and island tholeiites

In Fig. 73 Ga is plotted against Al for all tholeiites analysed in this work. For all the abyssal tholeiites, except Station 248, the Ga/Al ratio lies between 1.1 and 2.3, while for tholeiites from the oceanic islands the ratio varies narrowly about a value of 2.7, except for a single olivine tholeiite from Culpepper Island in the Galapagos group which plots with the abyssal tholeiites. The Ga content of island tholeiites ranges between 17.5 and 21.4 ppm Ga, with a mean of 19.1 ppm which is distinctly higher than the abyssal tholeiites. The Ga content of the Hawaiian island tholeiites is, however, similar to that of the highest values of the abyssal tholeiites, but the Al content is lower. The higher Ga content of island tholeiites is consistent with their higher contents of elements such as K, Rb, Ba and Sr (Kable, 1972) relative to abyssal tholeiites, confirming the primitive nature of abyssal tholeiites.

Sample DR 3-1 (Table 41A) is unusual because not only is it a plagioclase-phyric tholeiite, but it has a very low Ga content of 12.9 ppm and a quite exceptionally low Ga/Al ratio of 1.12, relative to the average ratio of 1.9 for abyssal tholeiites. Goodman (1972) determined Ga in plagioclases from two Icelandic tholeiites and in the whole rocks and found Ga/Al ratios of 1.1 and 2.0 respectively. Reference has already been made to Muir et al. (1964) who reported 10 ppm Ga in a plagioclase from a basalt from the Rift Zone of the Mid-Atlantic Ridge 45°N. If this value is correct, the Ga/Al ratio for the plagioclase would be very low indeed, about 0.7. There is evidence to suggest, therefore, that plagioclase which crystallizes at a very early stage in the formation of abyssal tholeiites, and presumably has a high anorthite content, is depleted in Ga relative to those crystallizing at later stages, and that this would account for the low Ga/Al ratio of sample DR 3-1 and possibly DBP 5 (Ga/Al = 1.11).

11.3.3 Indian Ocean

The Ga data on these samples given in Table 43 were originally reported by Erlank and Reid (1974). It has already been pointed out that the three samples, DBI 8, 9 and 12, from Site 248 have distinctly different Ga values from the other sites and also from other abyssal tholeiites. None of the samples from Leg 25 are mid-ocean ridge basalts (Fig. 86), but except for Site 248, both the Ga contents and the Ga/Al ratios fall in the range found for tholeiites from mid-ocean ridges.

Erlank and Reid (1974) reported that the distinctive feature of the basalt from Site 248 is the coarsely porphyritic texture with conspicuous large zoned phenocrysts of plagioclase of composition An_{50-88}. Although Erlank and Reid consider the samples to be considerably altered, so far as Ga is concerned it is difficult to understand how the Ga content could have been increased from about 16 to 22 ppm by alteration, and it is considered that the high Ga content at this site is real and reflects the original composition of the rocks. Erlank and Reid compared the Site 248 basalts with Karroo basalts from the Lebombo region. Ga has been determined in samples from the Lebombo region (Chapter 16) which range from 17 to 24 ppm Ga with Ga/Al ratios between 2.1 and 2.5, ranges which indeed bracket those values found at Site 248. However, Site 249 (Fig. 86) lies on the Lebombo side of the Mozambique Ridge, i.e. between the Lebombo region and site 248, and samples from site 249, DBI 10 and 11, bear no resemblance to the Karroo basalts but are similar to the abyssal basalts.

11.4 COMPARISON BETWEEN DSDP BASALTS AND DREDGED BASALTS

Basalts were collected in many cores drilled during the DSDP project. A number of workers determined Ga in these basalts, which were mostly tholeiitic, and their data for tholeiitic basalts taken from the DSDP reports are summarised in Table 44B.

Most of the analyses were made by optical emission spectroscopy with a precision of ± 15%. Kempe (1976) determined Ga by visual comparison of optical emission spectra (c.o.v. = ± 50%) and reported Ga contents in basalts of 50 ppm. His data have been omitted from this discussion on the basis that they are high by a factor of three when compared with other results.

The marked difference in Ga content and Ga/Al ratio for samples from sites 214 and 216 from the Ninetyeast Ridge (Leg 22) in the Indian Ocean compared with rocks from this and other sites is obvious. Thompson *et al.* (1974) pointed out that the rocks from sites 214 and 216 differ in composition, texture and mineral paragenesis from typical mid-ocean ridge basalts, and suggested that the Ninetyeast Ridge rocks were fractionated lavas that cooled and crystallized in shallow magma chambers before extrusion.

Despite the fact that many samples were altered to a greater or lesser extent, the average DSDP Ga data are in remarkable agreement with those reported here for dredged basalts. The Ga/Al ratios are in equally good agreement. There is no evidence of a change in either the Ga content or the Ga/Al ratio of deep ocean basalts with time.

11.5 CONCLUSION

It has been shown that the variation in Ga content and the Ga/Al ratio of abyssal tholeiites is generally much less than had previously been indicated. The mean value for Ga is 15.7 ppm, with a Ga/Al ratio of 1.9.

Variation of both Ga and Ga/Al ratio between oceans is no greater than that found within a single ocean, and there is no apparent variation with latitude. The data suggest that the Ga content of plagioclase may vary considerably, but more work needs to be done before this can be confirmed.

CHAPTER 12

GALLIUM IN ROCKS FROM OCEANIC ISLANDS

12.1 INTRODUCTION

Ga has been determined in rocks from several oceanic islands whose locations are shown in Fig. 84. Data for islands from the Atlantic Ocean are given in Table 45, for the Pacific Ocean in Table 46, and for the Indian Ocean in Table 47.

Before discussing the data, it is necessary to comment on the rock nomenclature used in the tables. The nomenclature of volcanic rocks from oceanic islands is somewhat confused. Some authors use the general terminology, basalt-trachybasalt-trachyandesite-trachyte, while others used the more specific terminology, basalt-hawaiite-mugearite-benmoreite-trachyte in addition to names such as icelandite and tristanite.

It was not the intention in this work to become embroiled in the contentious field of rock nomenclature, and accordingly in Tables 45-47 the rock names given by the original workers have been used. Where no names were given to the rocks, they have simply been labelled 'basalt', e.g. Table 45A, where sample AZ-2 is almost certainly a picrite basalt or oceanite.

A number of workers (Baker, 1969, for St. Helena Is.; Baker *et al.*, 1974, for Easter Is.; and Verwoerd *et al.*, 1974, for Bouvetoya Is.) have used the Differentiation Index (D.I.) of Thornton and Tuttle (1960) as a guide to the classification of the various rock types. Baker *et al.* (1974) also used the composition of the normative plagioclase as a guide, and where the two criteria did not coincide, gave priority to the normative plagioclase. Verwoerd *et al.* (1974) also deviated slightly from the D.I. classicompared with the values for the trachytes and trachyandesites (25 ppm Ga). Compared with the data reported here, Le Maitre's values for Ga tended to be on the low side by on average 5 ppm, resulting in his calculating too low a Ga/Al ratio, 2.0 as against the 2.5-2.9 found here.

The data of Baker et al. (1964), although substantially correct, when compared with the data given here, were high by about 6 ppm Ga, a relative difference of 25%. Baker et al. reported Tristan de Cunha to be unusual in that the Ga/Al ratio decreases with increasing D.I., thus differing from other alkali provinces but being similar to the trend found by Nockolds and Allen for the Polynesian alkali-basalt province.

In fact the Atlantic Ocean islands as a group are unusual because they exhibit three different trends in Ga and Ga/Al ratio as shown in Table 48 and Fig. 87. In most cases Ga increases with increasing D.I. to the extent of 10-20 ppm Ga as the D.I. increases from 20 to 80, i.e. from ankaramite or picrite basalt to benmoreite. Examples of this trend are Bouvetoya, Iceland and Gough Island. In contrast, Tristan da Cunha and Ascension Island rocks have a constant Ga content with increasing D.I. As a result of the differing trends in Al with D.I., the Ga/Al ratio increases with increasing D.I. for Iceland and Bouvetoya Island, decreases for Tristan da Cunha rocks, and remains constant for Ascension and Gough Islands, although increasing sharply in the trachytes and rhyolites. For Ascension Island rocks the Ga/Al ratio increases from 2.7 for the "benmoreite" to 5.7 for the "rhyolite" or comenditic obsidian (Table 45C). In all cases the "basalts", i.e. D.I. <30, tend to be variable in both Ga and Ga/Al ratio, because they are cumulate rocks, and the data points for this rock group do not always fall on a smooth trend line with those of the other rock groups, which are generally thought to have formed from one another by fractional crystallization, e.g. Gough Island.

12.3 ISLANDS IN THE PACIFIC OCEAN

The Pacific Ocean islands show two trends. Easter Island and the Galapagos Islands exhibit trends similar to Iceland and Bouvetoya Island, but the Hawaiian Island alkali series rocks and the Main series from Tahiti show quite a different trend, i.e. a drop in both Ga and Ga/Al ratio with increasing D.I.

12.4 ISLANDS IN THE INDIAN OCEAN

Of the Indian Ocean islands examined, neither the Comores, Prince Edward nor Marion Islands show a great range in D.I. All show an increase in Ga of approximately the same rate with increase in D.I., and a constant Ga/Al ratio. Mauritius shows a similar trend to Ascension Island, except that there is not a marked increase in Ga/Al ratio for the trachyte group of rocks relative to the other groups, as there is in Ascension.

12.5 GENERAL

Ga has been determined in rocks, for which major element data were not available, from a number of other islands. However, Kable (1972) determined percent SiO_2 in all the samples, and to a first approximation SiO_2 increases with D.I.. Accordingly, in Figs 90-91 ppm Ga has been plotted against percent SiO_2 for all island rocks for which major element data were notavailable.

From comparisons between Figs 87-89 it appears that Madeira is of the same type as Gough and Ascension Islands; the Azores and Tenerife Islands could belong to either the Gough-Ascension type or the Iceland-Bouvetoya type. There are no samples with SiO_2 contents high enough to define the trends conclusively. Jan Mayen Island rocks define a trend different from all other Atlantic Ocean islands, which is similar to the alkali series of Hawaii and the Main series in the Tahiti Islands, i.e. Ga decreases with increase in differentiation.

Although a number of different trends for Ga and Ga/Al ratio have been defined, there does not appear to be any relationship between the type of trend found and the general petrochemistry of each island group. Baker (1973) has grouped Ascension and Bouvetoya Islands as mildly alkaline to transitional, and they both have different trends. He also grouped Gough, Tristan da Cunha and St. Helena Islands as moderately alkaline and Tristan da Cunha shows quite a different trend from the other two. In the Pacific Ocean there appears to be more coherence between trends and petrochemistry since the Galapagos and Easter Islands have similar trends, as do the alkaline series of Hawaii and Tahiti.

12.6 USE OF PARTITION COEFFICIENTS IN DEFINING CRYSTAL FRACTIONATION MODELS TO ACCOUNT FOR OBSERVED TRENDS IN Ga AND Ga/Al RATIOS

Using the Ga data determined in this work, Verwoerd *et al.* (1974), in their discussion on the geochemistry of Bouvetoya Island, concluded that in order for Ga and the Ga/Al ratio to increase with differentiation, some mineral that does not readily accept Ga must have fractionated out together with plagioclase.

Bouvetoya, Tristan da Cunha and Gough Islands show three separate and different trends for Ga and the Ga/Al ratio with increasing D.I. (Fig. 87). Using the sparse partition coefficient data available for Ga, an attempt has been made to define the types and proportions of minerals fractionating from a magma that are necessary to produce the trends found for these three islands. The only partition coefficient data available for Ga (as discussed in Chapter 2) are those presented by Paster *et al.* (1974), and Goodman (1972), who determined partition coefficients in a number of basic volcanic rocks from oceanic islands. The data presented in Goodman's paper have been summarised in Table 49 and Fig. 92.

Pyroxenes showed a range of 6-14.5 ppm Ga and a range of partition coefficients between pyroxene and liquid of 0.30-0.58, with a mean value of 0.41. Plagioclases showed a range in Ga of 17.5-28 ppm and a range in partition coefficients of 0.84-1.27, with a mean of 0.99. Olivines had Ga contents of 1 ppm and partition coefficients of 0.04-0.05.

Other information essential to this discussion is the partition coefficients for magnetite and ilmenite. Magnetite is known to contain about 100 ppm Ga (Vincent and Nightingale, 1974; and Burton and Culkin, 1972), while ilmenite contains about 1 ppm Ga. Paster et al. (1974) determined partition coefficients for trace elements in the Skaergaard complex by calculation and estimated D^{plag}_{Ga} to be 1.7 and D^{Mt}_{Ga} to be 2.0. In view of Goodman's work, the value of 1.7 for plagioclase seems rather high, but the value of 2.0 for magnetite has been accepted here. It has been assumed that ilmenite has approximately the same partition coefficient as olivine, i.e. 0.05. Haslam (1968) investigated the crystallization of magmas at Ben Nevis and determined Ga in biotites, amphiboles and pyroxenes. He reported the mean Ga content of the pyroxenes to be 2 ppm for clinopyroxenes and 7 ppm for orthopyroxenes, with corresponding Ga/Al ratios of 2.2 and 8.6. The mean Ga content of amphiboles was 19 ppm, with a Ga/Al ratio of 6.1. Haslam did not analyse plagioclases, but on the basis of his data and that of Goodman, a partition coefficient of 0.9 has been assumed for amphibole.

12.6.1 Bouvetoya Island

A mean composition was calculated for the hawaiites, and an addition-subtraction plot was used to calculate the composition of the crystal mix that had to be removed from the average hawaiite to give the composition of the rhyolite WJ18B (Table 42D). F, the fraction of liquid remaining, was calculated to be 0.23 and the CIPW NORM calculation of the composition corresponding to the crystal mix gave 63% plagioclase, 18% pyroxene, 6.5% olivine, 5.5% magnetite, and 6.0% ilmenite. A computer program MIXER, written by A.R. Duncan and similar to that of Bryan et al. (1969), using as input the compositions of parent (mean hawaiite), daughter (rhyolite) and minerals plagioclase, pyroxene, magnetite, olivine and ilmenite, calculated the proportions of each mineral which, when removed from the parent, would yield the daughter rock. Results from this calculation for Bouvetoya gave F = 0.24, 62% plagioclase, 17% pyroxene, 6% olivine, 7% magnetite, and 8% ilmenite, a mix very close to that calculated in the CIPW NORM above. Assuming the average hawaiite as parent, the calculation, based on equations from Arth (1976) and using the computer data to estimate the Ga content of the rhyolite, is set out below:

	D^{x}_{Ga}	Weight Fraction
Plagioclase (An_{75})	0.88	0.62
Pyroxene	0.41	0.17
Olivine	0.05	0.06
Magnetite	2.0	0.07
Ilmenite	0.05	0.08
		1.00

$F = 0.24 \qquad D^{mix}_{Ga} = 0.76$

Therefore $C^{l}/C^{o} = F^{D-1} = 1.40$

Ga in hawaiite = 22 ppm

Calculated Ga in rhyolite = 22 x 1.4 = 30.8 ppm

Measured Ga in rhyolite = 31.3 $\pm$ .5 ($2s_c$) ppm

C^{l} = concentration in differentiated liquid

C^{o} = concentration in original (parent) melt

It can therefore be predicted that Ga should increase with D.I. for Bouvetoya Island, and the predicted value agrees with the measured value within 95% confidence limits (counting error).

12.6.2 Gough Island

A similar experiment using the MIXER program was carried out for

Gough Island. G13 (olivine basalt) was chosen as parent to produce sequentially G164 (trachybasalt), G15 (trachyandesite) and G114 (trachyte) (Table 42F), in a similar way to that reported by Zielinski and Frey (1970). The results are given in Table 50. It is shown that it is possible to produce rocks that approximate the measured compositions of those found on Gough Island by crystal fractionation using olivine basalt as parent, and that it is also possible to match calculated and measured Ga concentrations in these rocks for the range olivine basalt to trachyte. It was not possible to produce acceptable results for the late stage aegirine-augite trachytes, probably because the correct mineral compositions were not available.

12.6.3 Tristan da Cunha Island

For Tristan da Cunha an attempt was made to derive the trachybasalt 351 from the olivine basalt 6 by crystal fractionation. In this instance it was necessary to increase the Al content of the rocks from 7.5% Al to 9.1% and at the same time to decrease the Ga content from 22.5 to 21.4 ppm Ga. It was not possible with the mineral compositions used for Bouvetoya and Gough Islands to produce an acceptable major element match by extracting plagioclase, pyroxene, olivine, magnetite and ilmenite. In describing rock 351, Baker et al. (1962) mentioned phenocrysts of partially resorbed amphibole, plagioclase and pyroxene, the plagioclase zoned An_{80-70}, and the amphibole having a thick rim of granular iron ore. Using only plagioclase, pyroxene, amphibole and magnetite, it was possible to obtain the following crystal mix which, when fractionated from rock 6, would yield rock 351:

	D^{x}_{Ga}	Weight Fraction
Plagioclase (An_{70})	1.20	0.17
Pyroxene	0.58	0.41
Amphibole	0.90	0.22
Magnetite	2.00	0.20
		1.00

$F = 0.52$ $D^{mix}_{Ga} = 1.04$

$C^{1}/C^{o} = 0.97$

Ga in 6 = 22.4 ppm

Calculated Ga in 351 = 21.8

Measured Ga in 351 = 21.8

Although it seems possible to derive the measured Ga content in this way, it would be necessary to carry out major element analyses on the appropriate minerals in Tristan rocks to confirm the calculations. A further complication arises because many of the Tristan rocks contain leucite, although never as phenocrysts.

The above calculations were made using the approach of Gast (1968), assuming the simplified case of crystallization of phases in constant proportions with constant distribution coefficients (Arth, 1976).

Attempts were made to model the Kohala Mt. lavas from Hawaii (Table 46I), but without success. However, with the correct mineral compositions and assuming that the rocks are derived from one another by crystal fractionation, a knowledge of the phenocryst phases should make it possible to match measured and calculated data as was done for Tristan da Cunha Island.

12.7 INTER-ISLAND COMPARISONS

12.7.1 Marion and Prince Edward Islands

Kable *et al.* (1971) noted slight but distinct differences between the K/Ba, Ba/Zr and Zr/Nb ratios of the two islands and also between the Zn contents. They concluded that the differences were not established during the differentiation process but were characteristic of the magmas at the time of the formation of the islands.

In Tables 47E, F, G and 48 and Fig. 89 there is clearly no significant difference between the Ga and Ga/Al ratio of younger and older lavas within each island, but there is a difference in the Ga/Al ratios between the two islands, the average ratio for Marion being 2.38 and for Prince Edward 2.74.

Ga has been plotted against Al in Fig. 93, and although there is a slight overlap of points for the trachybasalts, a Student t-test on the Ga/Al ratios indicates that there is a significant difference between the two islands at the 99% confidence level. It is also apparent from Fig. 93 that there is less variation in the Ga/Al ratio for Prince Edward than is the case for Marion Island.

The Ga data presented here therefore confirm the conclusions of Kable et al. (1971), which were based on other trace element data.

12.7.2 General

Inspection of Tables 48 and 51 is helpful in comparing the Ga and Ga/Al ratios for different islands. If the "basalts" are ignored as being cumulative rocks in which the Ga content is strongly dependent on both the proportion and composition of cumulate material, then a number of features become apparent.

Firstly, rocks from Jan Mayen Island are unique in that they exhibit the lowest Ga content of mugearite and benmoreite. The Ga contents of all the rock types in Jan Mayen fall within the range for abyssal tholeiites, despite the range in differentiation. Unfortunately no Al data are available for these rocks. Another island on the Mid-Atlantic Ridge, Flores, in the Azores, also shows very low Ga values, with trachyte having only 20.6 ppm Ga compared with trachytes from other islands which have a minimum of 23 ppm but usually contain about 30 ppm Ga. The unusual distribution of Ga in Tristan da Cunha has already been commented on at length.

In the Pacific Ocean, Pitcairn Island appears to be similar to Easter Island in its Ga content and distribution, while the four samples from Japan show typical abyssal tholeiite levels for Ga.

In the Indian Ocean, the Ga value of 15.8 for hawaiite in Amsterdam Island is very close to the average of 16 ppm Ga found by Gunn et al. (1971). Their data indicate that the mean Ga/Al ratio for Amsterdam Island is 1.7 ± 0.1 (1s). This is a very low ratio, lower even that than found for abyssal tholeiites in this work. It is matched only by that found for Rodriguez Island, which is also located on the mid-ocean ridge. Heard Island is also unusual in that Ga, after increasing with increasing degree of differentiation, finally decreases in the aegirine-augite trachyte.

12.8 GOUGH ISLAND

Gough Island (Table 45F) has the greatest range in Ga concentrations found in oceanic islands studied in this work, with a range from 11.0 to 43.2 ppm Ga and a corresponding range in D.I. of 19.5-87.9. Kable (1972) found that a number of trace elements, i.e. Ba and Sr, after increasing steadily through the differentiation sequence, decreased in the late stage aegirine-augite trachytes as a result of fractionation of plagioclase and alkali feldspar. If the D.I. is taken as the criterion of the degree of differentiation, as has been done in this work, then Ga also decreases in the last liquids, i.e. it decreases in the last three rocks from 43.2 to 41.0 to 30.8 ppm Ga. However, using the crystallization index (C.I.) of Poldervaart and Parker (1964), the reverse is the case. The modified solidification index used by McBirney and Williams (1969) in studying rocks from the Galapagos Islands confirms the C.I. trend, i.e. that Ga continues to increase with increasing differentiation, or at least until the last liquid analysed, and does not pass through a maximum as do Ba and Sr.

12.9 CONCLUSION

In oceanic islands Ga and the Ga/Al ratio follow four different trends against the D.I. Generally, Ga increases with increasing D.I. and the Ga/Al ratio either stays constant until about D.I. 80, when it increases strongly, or it increases steadily and evenly with increasing D.I. For Tristan da Cunha, Ga remains constant with increasing D.I. and the Ga/Al ratio decreases. In alkali series rocks from Hawaii and Tahiti, both Ga and the Ga/Al ratio decrease with increasing D.I. It is possible to model these trends using calculations based on crystal fractionation and the known partition coefficients for the minerals plagioclase, pyroxene, olivine, amphibole, magnetite and ilmenite. Jan Mayen Island, the most northerly island on the Mid-Atlantic Ridge, has exceptionally low Ga concentrations which are similar to those in abyssal tholeiites. Amsterdam and Rodriguez Islands also have similar Ga and Ga/Al ratios to mid-ocean ridge basalts.

CHAPTER 13

GALLIUM IN ROCKS FROM IGNEOUS INTRUSIONS AND COMPLEXES

13.1 THE LOSBERG INTRUSION, FOCHVILLE, TRANSVAAL

The geochemistry of the Losberg Intrusion has been investigated by Danchin and Ferguson (1970). Ga has been determined in the same samples examined by them and the data are reported in Table 52.

The Losberg Intrusion is a flat-lying, layered body about 400 feet thick, intrusive into the shales and quartzites of the Pretoria Series of the Transvaal system. It is underlain by shales and capped by quartzite. The age of the intrusion is 1881 m.y.

The intrusion is of particular interest because it is one of a group of mafic bodies with tholeiitic affinities extending along a north-south line from Rhodesia into the Orange Free State and including the Bushveld Igneous Complex and the Great Dyke (Fig. 94). The rocks of the intrusion represent a differentiation sequence ranging from harzburgite at the exposed base to granophyric quartz gabbro at the roof.

The geologic setting of the intrusion is shown in Fig. 95.

Abbott and Ferguson (1965) subdivided the intrusion into three main units on the basis of the cumulus phases constituting the different rock types, namely harzburgite, quartz norite and quartz gabbro. The variation of the major and trace elements with height, as reported by Danchin and Ferguson (1970), are given in Figs 96 and 97.

Between the 50 and 60 foot levels there is a sharp increase in SiO_2 that marks the cessation of olivine crystallization and the change from harzburgite to quartz norite. However, a similar abrupt change in the concentrations of Al_2O_3, FeO, CaO, Na_2O and K_2O occurs only between the 60 and

70 foot levels, and this change is also reflected in the Ga contents of the rocks. The 60 foot level quartz norite has a similar Ga content to the harzburgites and almost half that of the other two quartz norites. This is due to the large amount of normative hypersthene (51%) present in the sample (LB-4) and the fact that the plagioclase content increases markedly only from the 70 foot level.

Information in Table 52 is plotted in Fig. 98, and, as pointed out by Danchin and Ferguson (1970) for other elements, there is a decrease in the Ga concentration between the 240 and 270 foot levels, which is in contrast to a sudden increase in the MgO content from 5.5% to 12.2%, and a corresponding increase in normative clinopyroxene. This is contrary to Abbott and Ferguson's observations of a decrease in modal clinopyroxene and the constancy of the optically determined Mg contents of clinopyroxene over this range. Danchin and Ferguson suggest that the clinopyroxenes above the 270 foot level are a higher temperature variety of higher MgO content than those lower in the sequence. The increase in normative clinopyroxene results in a decrease of the D.I., which is mirrored by the decrease in the Ga content (Fig. 98).

In the rocks from the Losberg Intrusion Ga increases steadily with increasing D.I., but the Ga/Al ratio stays almost constant, increasing only from 1.7 to 2.0. The four roof rocks from the intrusion have a slight but significantly lower Ga content than those of corresponding D.I's from lower in the sequence.

Danchin and Ferguson state that crystal fractionation was the dominating process operating in the magma chamber, and that the major evidence marking a discontinuity in the differentiation process was that involving the uppermost rocks in the sequence, namely from 270 to 390 feet. All the elements, with the exception of Fe^3, Rb, K, Cs, Cu and Sr, show a marked reversal in concentration beginning at the 270 foot level (Figs 96 and 97), and Danchin and Ferguson suggest that this can be explained either by simultaneous downward crystallization and bottom accumulation or by a sufficiently mafic pulse of new magma. On the basis of symmetry patterns in the concentration versus height plots showing the higher temperature elements aggregating towards the floor and the roof of the intrusion, they suggest the early simultaneous crystallization from both these margins as the most likely process. Abbott and Ferguson, on the basis of petrological data, suggested that a minor influx of magma occurred.

Danchin and Ferguson recognised the following problems which conflicted with the idea of downward crystallization: namely that with increase in height there was no change in concentration of Sr; that the K/Rb ratio tended to decrease steadily; and that the absolute amounts of K and Rb did not show a reversal. They tentatively suggested that a late-stage acid residue resulting from fractionation of the lower members permeated the upper rocks, thereby leaving the K, Rb and Sr contents unchanged.

The Ga data presented here contradict this suggestion. Ga usually increases in late-stage residues, both in absolute amount and also relative to Al. In the Losberg rocks above the 270 foot level, there is an abrupt and marked decrease in the Ga content, but the Ga/Al ratio decreases only slightly. If a late-stage residue had permeated the rocks, it might have been expected that Ga would have remained constant or even have increased and that the Ga/Al ratio would also have increased. The Ga data, therefore, suggest that a second minor intrusion at the 270 foot level is the more likely cause of the observed changes in chemistry and mineralogy.

13.2 THE KOMATIPOORT INTRUSION, N.E. TRANSVAAL

The Komatipoort Intrusion (Fig. 94) is one of three younger basic plutonic masses penetrating, approximately conformably, the basalts of the

Middle Suite of the Drakensberg Lava Stage of the Karroo System on the south-eastern corner of the Kruger National Park (Saggerson and Logan, 1970). The Komatipoort Intrusion consists of a composite body of three separate intrusions, the first of which was a pulse of plagioclase-rich tholeiitic magma. The second was a surge of normal tholeiitic magma emplaced below the first sill, which produced a sub-concordant layered sequence as a consequence of strong differentiation by crystal settling. A final sill of granophyre was intruded along the contact between the two earlier sills.

As indicated in an FMA variation diagram (Fig. 99) for the rocks analysed in this work, the Komatipoort Intrusion shows strong differentiation and considerable iron enrichment during crystallization.

Data for Ga in rocks from the three intrusive phases are given in Table 53 and plotted in Fig. 100.

There is a distinct increase in Ga with increasing D.I. from approximately 18 ppm to a maximum of 29 ppm in the granophyric gabbros and granophyres. Although there is a positive correlation between Ga/Al and D.I., the correlation is not a strong one. This is probably the result of many of the rocks being partial cumulates.

There is no clear distinction between the Ga contents of the three intrusive phases. However, differences in the Ga/Al ratio clearly separate the final phase from the first two. The Ga/Al ratio in the granophyres is extremely high at about 4.7 and demonstrates the strong enrichment of Ga relative to Al in these late-stage rocks.

13.3 THE TROMPSBURG INTRUSION, ORANGE FREE STATE

The Trompsburg Intrusion lies on a southern extension of the line Great Dyke - B.I.C. - Losberg Intrusion (Fig. 94). It is not exposed at the surface (Davies et al. 1970), but its shape and nature have been revealed by drilling and gravity measurements. It is a sheet-like body, roughly circular in outline, about 50 km in diameter, and intrusive into marble which is possibly of Transvaal system age. The body consists mainly of gabbro and anorthosite, with olivine-rich layers in parts, and a roof of granite which was intersected in two of three boreholes. The age of the intrusive is 1372 ± 142 m.y. (Davies et al., 1970).

Unfortunately no major element data are available for the five rocks and there is little that can be said about the Ga content other than that it is constant at about 20 ppm Ga, except for sample TG 1 3970, which presumably represents one of the olivine-rich layers and would have a lower Ga content because of dilution with olivine (Table 54).

13.4 THE BUSHVELD IGNEOUS COMPLEX

Liebenberg (1960, 1961) reported an extensive investigation of the geochemistry of the B.I.C. for both major and trace elements, including Ga. In addition to four of the rocks analysed by him, a number of other samples were analysed in this work and it was considered worthwhile to report the data (Table 55). Unfortunately no Al data were available for these samples.

Liebenberg determined Ga in his samples by optical emission spectroscopy, and it reflects to his credit that nearly 20 years later Ga determined in the same samples by a more precise method gave essentially similar results.

Sample	Liebenberg ppm Ga	This work ppm Ga
LIEB 50	12	12.3
W 4	9	12.3
W 7	13	13.5
LIEB 51	16	16.2

When commenting on the distribution of Ga in the B.I.C. rocks, Liebenberg concluded that in the ultrabasic rocks the Ga contents were controlled by diadochy between Ga^3, Cr^3 and Fe^3, the $Ga^3 - Cr^3$ diadochy being particularly important in chromite-rich pyroxenites. Liebenberg did not determine Ga in chromites. One very unusual and surprising feature of his data, which he did not comment upon, was the very low Ga content of both the upper and lower portions of the magnetite band. Liebenberg reported values of 4 and 5 ppm Ga in the magnetite, much lower than the lowest values reported by Burton <u>et al</u>. (1959) of 20 ppm, and Burton and Culkin (1972) of 10 ppm. Magnetites generally average 60-80 ppm Ga.

Five samples of chromite and five samples of magnetite from the B.I.C. have been analysed for Ga. The locations of the samples are shown in Fig. 101. The chromite samples come from widely dispersed locations, i.e. from the northern, western and eastern Transvaal. Four of the magnetite samples come from the Magnet Heights area in Sekhukhuneland and the other comes from the Pretoria district.

The two chromites from the Swartkop Mines have Ga contents of 36 and 41 ppm (Table 36C), that from Ruighoek, also in the Western Transvaal, 48 ppm, and that from Driekop in the Eastern Transvaal 57 ppm. These values are very much higher than those reported by Shaw (1957) of 4-7 ppm and Burton <u>et al</u>. (1959) of 18 ppm Ga. The single sample from Grasvally has a Ga content of 18 ppm, which is very close to that given by Burton <u>et al</u>. (1959). On a purely semi-quantitative basis (XRF wavelength scans), the Grasvally chromite has the lowest Fe content of the chromites, but it is only slightly lower than that of 6967 (Swartkop) which has twice the Ga content.

From the data in Liebenberg (1960) and Wager and Brown (1968), it is possible to calculate the approximate chromite content of the high-Cr ultrabasic rocks, assuming all the Cr is present as chromite. Assuming an average Ga content in the chromite of 45 ppm, in two pyroxenites the chromite contributes 4 ppm Ga out of a total 7 ppm in the rock, or about 60% of the Ga content. Therefore, as Liebenberg suggested, the high chromite content of some of the ultrabasic rocks does account for the high Ga/Al ratios in these rocks.

All the magnetite samples have high and very similar Ga contents in the range 49-54 ppm. These values are in accord with those found by other workers (Burton and Culkin, 1972), but are an order of magnitude higher than the values reported by Liebenberg (1960). The data confirm that in the B.I.C., as in the Skaergaard Intrusion, magnetite is the major host mineral for Ga, but that in the B.I.C. chromite is also an important Ga host mineral.

Although no Al data are available for the rocks analysed in this work, most of the Ga values reported here fall within the ranges of values reported by Liebenberg (1960). It can, therefore, be assumed that the Ga/Al ratios found by him would be similar to those of the rocks reported here. Liebenberg calculated the altered Larsen function as an index of differentiation, $(1/3SiO_2 + K_2O) - (CaO + MgO)$. The Ga/Al ratio data taken from Liebenberg are plotted against the altered Larsen function in Fig. 102. It is immediately obvious that there are some extremely high values for Ga/Al, mainly in the ultrabasic rocks with high chromite contents. These rocks are indicated separately from the other rock types in Fig. 102.

Apart from the ultrabasic rocks, data for the other rock types tend to plot around a trend line of steadily increasing Ga/Al ratio with increasing differentiation. For comparative purposes, the data presented in this work for rocks from the Skaergaard Intrusion are also plotted in Fig. 102.

The trends of the Ga/Al ratios in the two series are quite different, the enrichment of Ga over Al being distinctly greater in rocks of similar D.I. from the Skaergaard than in those from the B.I.C. The highest Ga value reported by Liebenberg is 28 ppm Ga, compared with 25 ppm in this work, with most of the higher Ga values being less than 25 ppm. By contrast, the Skaergaard has many rocks with Ga contents in excess of 30 ppm with a maximum of 38 ppm (Vincent and Nightingale, 1974).

13.5 THE SKAERGAARD INTRUSION

The geology, petrology and geochemistry of the Skaergaard Intrusion have been discussed at length by Wager and Brown (1968) and others and it is not considered necessary to summarise their work here.

Nine samples from the Skaergaard Intrusion have been analysed for Ga, and the data are reported in Table 56. In a very interesting paper, Vincent and Nightingale (1974) reported the determination of Ga in rocks and minerals from the Skaergaard Intrusion by radiochemical neutron activation analysis. Wager and Mitchell (1951), Paster et al. (1974) and Baedecker et al. (1971) reported Ga in rocks from the Skaergaard Intrusion. The data were determined by emission spectroscopy and neutron activation analysis. Some of their data are summarised in Table 57 for comparative purposes. The different sets of results are, generally, in good agreement. Vincent and Nightingale's data tend to be slightly higher than the values reported in this work for the same samples. They reported 19.6 and 18.3 ppm Ga respectively for G-1 and W-1, values which are higher than those found in this work, and which indicate a systematic bias between the two sets of results. The differences are, however, small and the trends are similar.

Before discussing the distribution of Ga in the Skaergaard complex, two errors in the data reported by Wager and Brown (1968) must be pointed out. Wager and Mitchell (1951) reported 200 ppm Ga in plagioclase from the fayalite ferrogabbro 4142, and 15 ppm Ga in the whole rock. Wager and Brown (1968) reported 28.66% normative plagioclase in this rock. Assuming that none of the ohter minerals present contain any Ga, a simple calculation indicates that the rock should contain 57 ppm Ga, if the plagioclase really contained 200 ppm Ga. The value of 57 ppm Ga is greatly in excess of any other determined in rocks from the Skaergaard, and it must be concluded that the Ga determination on the plagioclase was in error. A value of 40-50 ppm Ga, as found for other Skaergaard plagioclases, appears more reasonable. The error is pointed out because considerable emphasis is placed on the fact that Ga remains constant in plagioclases in the early rocks, and, on the basis of the single determination in plagioclase from 4142, increases in the plagioclases of the last stages of crystallization.

The second error is one of interpretation. It is stated by Wager and Brown (1968) that the low Ga content of the late acid granophyre is due to the abundance of quartz relative to feldspar. This conclusion presumably originated from the modal analysis of the acid granophyre 5259 which is given as 93% modal quartz. The normative calculation gives 31% quartz and the rock contains only 73% SiO_2, which makes the modal value for quartz impossible. In fact, rock 5259 contains 30 ppm Ga (Vincent and Nightingale, 1974) which is no lower than many of the other rocks from the layered series. 3058, the rock sample with the highest D.I., does contain less Ga than the other late differentiates (Table 56), but the lower value, about 50% of the other rocks, cannot be due only to dilution by quartz. The Al_2O_3 content is identical to that of 5259, the quartz content (normative) is only 3% higher than 5259, and yet the Ga content is half that of 5259.

Wager and Brown consider the acid granophyres to have been formed by filter-press action. 3058 presumably represents the very last liquid, from which most of the Ga had already been removed, as was the case for Sr. Evidence that extreme fractionation can perhaps result in a reduced Ga content in the last liquids was discussed earlier for Gough Island rocks.

Vincent and Nightingale (1974) have calculated the Ga content in successive liquid fractions and have shown that the Ga content of the liquid is greater than that of the solid rocks, except for the very last stages (~99.7% solidified) in the crystallization sequence. On this basis, if 3058 represents the liquid squeezed out of the last rocks, it should have a lower Ga content than the last rocks themselves. The Ga data confirm the hypothesis.

Plots of Ga, Ga/Al and Ga/(Al + Fe^3) against D.I. for rocks analysed in this work are shown in Fig. 103. The regular increase of all three variables with increasing D.I., up to a D.I. of 70, is obvious, as is the sudden drop in Ga in the late-stage granophyre. The Ga/Al ratio also decreases for the granophyre and indicates that Ga has been strongly depleted relative to Al in this rock.

In Fig. 104 the data of Vincent and Nightingale have been combined with those reported here. Vincent and Nightingale reported a strong concentration of Ga in magnetite (50-110 ppm) in the Skaergaard rocks. The effect on the Ga/Al ratio of the amount of magnetite in the sample is highlighted in Fig. 104, where rock 5322 has a Ga/Al ratio of 15.7, far in excess of the next highest value of 7.2. When Fe^3 is taken into account in calculating the ratio, the value for this sample drops to a level consistent with those of the other rocks. Although the scatter of points about the trend line is greater than that using the data from this work alone, the steady increase of the ratios with increasing D.I. is confirmed, as is the sudden decrease in the last rocks.

The marked difference between the Skaergaard trend and that found for the B.I.C. has already been discussed.

13.6 THE GREAT DYKE, RHODESIA

The Great Dyke (Fig. 94), extending for a distance of over 320 miles and varying in width from two to seven miles, consists generally of a sequence of rocks, from the base upwards, of dunite, pyroxenite, and harzburgite, capped with gabbroic rocks (Erlank, 1971).

Six samples from the dyke have been analysed for Ga and the data are reported in Table 58. Unfortunately, no Al data are available for these samples. The Ga data for the different rock types are in accord with those reported in this work and elsewhere (Burton and Culkin, 1972). The Ga contents of the gabbros fall within the range of values reported for gabbroic rocks from the B.I.C.

13.7 THE MESSUM IGNEOUS COMPLEX, S.W.A.

The Messum igneous complex is one of a chain of ring complexes of late Karroo age which stretch from Cape Cross in the west to Okurusu in the north-east of S.W.A. (Fig. 105). The complex is about 144 square miles in area and consists of an inner zone and outer ring, both delineated by a system of ring faults. The formation of the complex has been divided into three phases: volcanic, intrusive and alkaline (Mathias, 1956). Rocks from the first two phases have been analysed for Ga and the data are reported in Table 59. No major element data are available for these rocks. Mathias (1956, 1957) reported on the petrology and geochemistry of the complex, and Erlank (1971) determined K, Rb and Cs in the samples analysed in this work.

Mathias (1956, 1957) reported values for Ga in Messum rocks which were determined by Nockolds and Allen by optical emission spectrometry. The concentrations were reported to the nearest 5 ppm Ga and should be regarded as semi-quantitative. Although the samples analysed by Mathias have not been analysed in this work, it is possible to compare results for similar rock types. Mathias (1957) reported Ga values of 25-30 ppm for basalts, while the analyses in this work give values of 15-16 ppm Ga, which are very close to the average for tholeiitic basalts (16 ppm) reported earlier (Table 39). On the basis of the K content reported by Erlank (1971) for the samples analysed here (0.20-0.25% K), the basalts may be of tholeiitic type. For the olivine eucrites Mathias reported Ga contents of 35-40 ppm Ga, while values from this work range between 9 and 13 ppm, differences by factors of three to four. Mathias' data for the gabbros and anorthosites were also high by a factor of two. There was evidently a strong systematic bias in the earlier data reported for these rocks.

Calculated from the normative data of Mathias (1956), the D.I's of the olivine eucrites range from 9-11, from 14-20 for the anorthosites, and the D.I's for the basalts are ~20 and for the gabbros ~ 24. However, as can been seen in Table 59, there is little change in the Ga content of the rocks, except for the olivine eucrite ME 11. Using Al data from Mathias (1956, 1957), it is possible to calculate that the Ga/Al ratio must be relatively constant between 1.2 and 1.8. For the anorthosites the ratio would be about 1.1. It will be shown in the following sections that the relative constancy of the Ga/Al ratio with increasing D.I. seems to be characteristic of some of the igneous complexes of S.W.A.

13.8 THE OKONJEJE IGNEOUS COMPLEX, S.W.A.

13.8.1 Introduction

The Okonjeje Igneous Complex is one of the smallest of the post-Karroo igneous complexes in the Damaraland region of South West Africa and lies approximately halfway between Cape Cross in the west and Okorusu in the east (Fig. 105). The geology and geochemistry of the complex have been described most recently by Simpson (1954). Fesq (1978) has carried out an extensive geochemical study of Okonjeje. Ga has been determined in his samples and the data are reported in Table 60.

The Okonjeje Igneous Complex is exposed over a circular area of about 20 km^2 and consists essentially of a lopolithic complex of tholeiitic olivine gabbros and ferrogabbros, which are associated closely in space and time with a ring-dyke complex of alkali olivine gabbros, essexites and pulaskites (Fig. 106).

The "differentiated group" of the tholeiitic series shows a remarkably regular mineralogical and chemical variation from An_{80-30}, En_{78-27}, Fo_{73-20}, and Fe_{17-32} (augite), but this variation is from top to bottom of the lopolithic stratified series. From this and other evidence Simpson (1954) deduced that the tholeiitic series was formed by the emplacement of successive injections of thin sheets from the top downwards. The core gabbro (alkali series) was emplaced after solidification of the differentiated group and was followed by the intrusion of the marginal acid rock and the ridge syenite dyke. The pulaskites and essexites of Okonjeje Berg were emplaced as a result of the formation of a ring dyke followed by successive slumping of the central block.

Fesq (1978) favours a different mode of formation for the tholeiitic series. He envisages the formation of a ring dyke following the initial intrusion. The sinking of the central block squeezed up the gabbro-picrites, which were crystal cumulates of the initial intrusion. Further sinking of the central block resulted in the intrusion of the first pulse of magma, represented by the ridge gabbros. A second pulse gave rise to the ferrogabbros. Ring fractures resulted in the intrusion of the syenites which represent the last 20% of this pulse. A third and final pulse of magma formed the rocks of the upper and border zone (marginal acid rocks). Fesq's interpretation of the sequence of events and his representation of the tholeiitic series are shown in Fig. 107.

The age of the tholeiitic series is 165 m.y. and that of the alkali series 125-130 m.y.

Because Ga has been reported here for Fesq's samples, reference will be made to his interpretation of events rather than that of Simpson.

Simpson (1954) determined the major and trace element composition, including Ga, of a number of samples from both the tholeiitic and alkali series. Fesq (1978) re-analysed Simpson's samples which were also analysed in this work for Ga (Table 60). Simpson's trace element data were determined by Nockolds and Allen using semi-quantitative (± 30%) optical emission spectrography. The Ga data determined in this work are plotted against those of Simpson in Fig. 108. Although there is a scatter about the 1 : 1 line for the samples from the alkali series, there is no apparent bias. For the tholeiitic samples, Simpson's data are high by an average of 50%, indicating considerable bias in his results.

In Fig. 109 Ga and the Ga/Al ratio are plotted against D.I. for all rocks in the tholeiitic and alkali series, while in Fig. 110 similar plots are given of mean values for individual rock types within each series. The data for the tholeiitic series are presented in Table 60A-G, and for the alkali series in Table 60H-L.

13.8.2 Tholeiitic Series

In the tholeiitic series the mafic cumulates, which according to Fesq are olivine cumulates, may be taken to represent the first liquid composition as far as the Ga/Al ratio is concerned, inasmuch as the proportion of cumulus olivine present will have no effect on the ratio. The average Ga/Al ratio for these rocks is 2.68. The most differentiated rock, which may be taken as the last liquid, of the tholeiitic series is OK 254, an aplite dyke, which has a Ga/Al ratio of 2.70. This ratio is almost exactly the same as that of the intercumulus liquid in the mafic cumulates, indicating that the Ga/Al ratio of the liquid did not change during the formation of the tholeiitic series. Any changes in the ratio which occurred in the rocks were due only to changes in mineralogy. From this aspect the Ga/Al ratio can be very useful as a petrochemical tool.

Rocks formed from the original intrusion comprise the gabbro-picrites and lower "Ridge" gabbros (olivine gabbros) of the Basal Zone, with the remaining gabbros in the lower zone being formed from the first pulse of intruded magma (Fig. 107). The Ga contents of these rocks show a regular increase with D.I. from about 10 ppm to 22 ppm Ga. However, the Ga/Al ratios of the gabbro-picrites and olivine gabbros differ considerably. The ratio for the gabbro-picrites is about 2.7, while the olivine gabbros have a mean ratio of 1.75, ranging between 1.42 and 2.05.

The injection of the second magma pulse initiated the crystallization of the differentiated ferrogabbro series which form the upper zone of the layered series. This series comprises olivine ferrogabbros, hypersthene ferrogabbros, diorites, monzonites and adamellites.

The olivine ferrogabbros continue the increasing trend in Ga and Ga/Al ratio with increasing D.I. shown by the Ridge gabbros, although the Ga/Al ratio varies over a wide range (Fig. 109). The remaining rocks in this series show remarkable constancy in both their Ga content (19.8-22.7 ppm) and in their Ga/Al ratio (2.53-2.90) over a range of D.I. from 31.5-72.2. Fig. 110 indicates these trends very clearly, where the mean values for each rock type have essentially identical Ga/Al ratios and Ga contents. The only two samples having abnormal ratios for this series are OK 229 and 274 (Table 60C), both of which are plagioclase cumulates containing 69% and 78% plagioclase respectively. The particularly low ratio for OK 274 reflects the low Ga/Al ratio for plagioclases found by other workers (Burton and Culkin, 1972, and Table 37).

The same feature of low Ga/Al ratios is exhibited by the alkali syenites (which occur as an arcuate dyke) formed by fractionation of K-feldspar from the last 20% of the second pulse. OK 36 (Table 60F) was contaminated with ferrogabbro and the effect of this contamination on the Ga/Al ratio is clear, OK 36 having a ratio of 2.39 compared with the mean for the other alkali syenites of 1.64.

13.8.3 Alkali Series

Simpson (1954) stated that the intrusive alkali rocks were mostly markedly transgressive to the earlier tholeiitic series, and showed little continuous variation in chemical composition and mineralogy. He did, however, consider that the two basic magmas originated from a common parent. Certainly when the Ga contents and Ga/Al ratios of the olivine (Ridge) gabbros (16.5 ppm Ga and Ga/Al = 1.75) and the alkali olivine (Core) gabbros (18.8 ppm Ga and Ga/Al = 1.91) are compared, there is little difference between the two suites, the later Core gabbros having a slightly higher Ga content and Ga/Al ratio as would be expected if they represent a later differentiate from the same parent. OK 38, an alkali olivine dolerite dyke (Table 60H), is considered by Fesq to represent the liquid composition of the Core gabbros, but this sample has a lower Ga/Al ratio (2.32) than that of the gabbro-picrites (2.68), which was assumed to be the ratio of the original tholeiitic liquid.

The Core gabbros (Table 60H-I) have a fairly restricted range of Ga concentrations (16.6-19.6 ppm), with the exception of two samples, but a wide range of Ga/Al ratios (1.45-2.31) in contrast to the Ridge gabbros (1.45-2.05). Of the two anomalous samples, OK 106 (Table 60H) has a low Ga content but normal Ga/Al ratio for these rocks, as a result of dilution by olivine. This sample contains 25% normative olivine compared with an average of about 8% for the other samples. OK 28 (Table 60I), which has both a high Ga content and high Ga/Al ratio, has been chilled and has twice the magnetite content (6%) of the other Core gabbros, which would account for the high Ga and Ga/Al ratio.

The introduction of nepheline to form the nepheline olivine gabbros has little effect on either the Ga content of the rocks or the Ga/Al ratio, the mean values and ranges for these rocks being very similar to those of the Core gabbros (Fig. 110). The six contaminated alkali olivine gabbros have very high Ga/Al ratios compared to their uncontaminated counterparts and have ratios very similar to the gabbro-picrites and ferrogabbros of the tholeiitic series (Fig. 110).

The essexites and pulaskites continue the tendency for the Ga/Al ratio to decrease with increasing D.I. in the alkali series. If the andesine essexites and pulaskites are considered in detail, the pulaskite dyke and the marginal essexites have distinctly higher Ga/Al ratios than their counterparts. At this stage of crystallization of the alkali magma the liquid probably had a Ga/Al ratio of about 2.2. The higher Ga/Al ratios of the dyke and marginal rocks probably reflect the higher proportion of liquid in these rocks relative to cumulate phases (feldspars), which would have lower Ga/Al ratios.

The last rocks to crystallize in this series were the sodalite tinguaites and a bostonite, which show a considerable increase in Ga, and a correspondingly marked increase in Ga/Al ratio, to the highest values found for the complex.

In this respect the alkali series of rocks differ greatly from the tholeiitic series. Although both series culminate in rocks having approximately the same D.I's, i.e. 91-95, there is no increase in either Ga or Ga/Al for the tholeiitic series with increasing D.I., while the alkali series shows an initial steady but gradual decrease in Ga/Al followed in the last stages by a sharp increase.

Considering the plots shown in Fig. 110, the fact that the Core and Ridge gabbros have essentially the same Ga contents and Ga/Al ratios has already been discussed. The rocks of intermediate D.I. (35-70) are distinctly different in the two series. In the alkali series these rocks have much lower Ga contents than their counterparts in the tholeiitic series, and much lower Ga/Al ratios, 1.7 compared to 2.7 for the tholeiitic series. In this respect the Ga and Ga/Al data can be very useful in deciding for this igneous complex to which series a rock belongs, when there is any doubt. Only for the Core and Ridge gabbros is there any difficulty in separating rocks from the two series on the basis of the Ga content and Ga/Al ratio.

It should be pointed out that sample SOK 36, which Simpson classified as a Core gabbro, has been reclassified by Fesq as a Ridge gabbro (Table 60B). Fesq considers Simpson's sample SOK 36 to be equivalent to OK 236, and certainly the Ga contents and Ga/Al ratios of the two rocks are almost identical. The Ga content confirms Fesq's reclassification of SOK 36 as a Ridge gabbro, because the Ga content of 15.8 ppm is too low for a Core gabbro and would be the lowest of all those analysed, with the exception of OK 106 which has already been shown to have an unusually high olivine content, causing dilution of Ga.

The melteigites or core gabbro fenites represent mixtures of Core gabbros and foyaite liquids (Fesq), and as such their Ga content and Ga/Al ratios might be expected to lie between those of the Core gabbros and foyaites. Three of the melteigites have rather low Ga values, lower than any determined in the Core gabbros, but the Ga/Al ratios do lie on a mixing line between the two end-member rock types.

The lamprophyres occur mainly as dyke rocks, apart from a stock, which consists of differentiated camptonite, at the head of the Auas Valley. The Ga and Ga/Al ratio trends for the lamprophyres follow those of the alkali series as a whole, showing a very slight increase in Ga with increasing differentiation and a slight decrease in Ga/Al.

13.8.4 Olivine Nepheline Melilitite Series

Fesq recognises a third series of rocks at Okonjeje, the olivine nepheline melilitite series and dyke equivalents. Although this series of rocks has fairly low Ga contents, the dyke rocks, nepheline monchiquites, have similar Ga/Al ratios to the dykes of sodalite tinquaite. The high ratios are probably due to the high content of magnetite, clinopyroxene and biotite in these rocks.

Just to the south of Okonjeje is an outlier of Karroo sediments. Three of these rocks have been analysed for Ga and the data reported in

Table 60N.

13.9 THE DOROS IGNEOUS COMPLEX, S.W.A.

The Doros Igneous Complex in S.W.A. (see Fig. 105) is another of the post-Karroo differentiated basic complexes, but lies north of the line joining Cape Cross - Messum - Okonjeje. The complex consists of an elongated funnel-shaped volcanic neck or crater which breaks through baked Karroo sediments resting unconformably on the crystalline basement rocks (Martin et al. 1960). The plug-filling consists of three separate concentric outcrops of olivine gabbro representing multiple intrusions. The core is composed of leucocratic gabbro and is surrounded by two similar rings grading from accumulate picrite to olivine gabbro.

Ga has been determined in a limited number of samples and the data are reported in Table 61 and plotted in Fig. 111.

The Ga data show a very rapid increase with increasing D.I., in sharp contrast to the rocks from Okonjeje, reaching a maximum of 31 ppm in the leucocratic core gabbro. Rocks from both the inner and outer rings follow the same trend line. Ga appears to be strongly enriched in these rocks relative to Okonjeje, the Ga/Al ratios being much higher than for corresponding rock types in that complex.

As was the case for the rocks from the B.I.C. and Okonjeje, there is a sharp decrease in the Ga/Al ratio in moving from the cumulate picrites to the olivine gabbros. The approximate mineral composition of the picrites is known (Fesq, pers. comm.) and it is interesting to relate this information to the Ga contents and Ga/Al ratios.

Sample	Olivine %	Clinopyroxene %	Plagioclase %	Ore %	Ga ppm	Ga/Al $\times 10^4$
D4	45	45	5	5	15.4	4.22
D7	40	40	13	7	12.0	3.31
D2	40	15	30	15	24.9	3.38

The high Ga/Al ratio for D4 is due to the high clinopyroxene content coupled with the low plagioclase content and 5% ore. Both D2 and D7 have the same Ga/Al ratio, but D2 has twice the Ga content of D7. Both rocks have the same olivine content, but D7 has more clinopyroxene than plagioclase and a relatively low ore content, which results in a low Ga content but high Ga/Al ratio. D2 has much less clinopyroxene and much more plagioclase, which would result in a higher Ga content and low Ga/Al ratio. However, the higher ore content, which tends to increase the ratio, compensates for the low ratio of the silicate minerals. These examples stress the important effect which changing mineralogy has on the Ga content and Ga/Al ratio. Conversely, changes in Ga and Ga/Al ratio can alert the geochemist to possible mineralogical changes.

13.10 THE ERONGO IGNEOUS COMPLEX, S.W.A.

The Erongo complex (Fig. 105) is one of predominantly granitic composition (Martin et al., 1960) and, with a mean diameter of 35 km, is the largest of the post-Karroo plutons. The major intrusive rocks are granodiorite and granite, the granodiorite being almost entirely confined to a large central stock which is in turn intruded by the Erongo granite.

Ga data are reported in Table 62 and a single value for the granite in Table 63. The data are plotted in Fig. 111. There is almost no difference in the Ga content of any of the samples. Except for the granite, which has a somewhat higher Ga/Al ratio (3.22) than the other samples, the Ga/Al ratio is also constant.

13.11 GRANITES FROM S.W.A.

Granite samples from four S.W.A. igneous complexes and the Damara Salem granite have been analysed for Ga, and the data are reported in Table 63. The localities are given in Fig. 105. Ga is plotted against Al in

Fig. 112.

It is clear from Table 63 and Fig. 112 that granites from any one area or complex have essentially the same Ga contents and Ga/Al ratios and that it is possible on the basis of the Ga and Al contents to distinguish quite clearly between granites from different areas. It is interesting to note that the Salem granite, which forms concordant syntectonic bodies in the Damara System sediments rather than intrusive plutons, has a lower Ga content than most of the other samples, and a much lower Ga/Al ratio, which perhaps reflects its formation by transformation of sediments rather than by igneous differentiation.

The granites from Okonjeje have higher Ga/Al ratios than any other rocks from that complex. When the Ga/Al ratios are plotted against D.I., the points fall on the same trend line as the late-stage tinquaites and bostonite of the alkali series (Fig. 109), suggesting that the granites may be derived from the same parent magma as the alkali series rocks.

CHAPTER 14

GALLIUM IN UPPER MANTLE ROCKS AND KIMBERLITES

Ga has been determined in both xenoliths from kimberlite and in kimberlite itself, from a number of different pipes in southern Africa and in two pipes from Tanzania.

14.1 MATSOKU KIMBERLITE PIPE, LESOTHO

The location of the Matsoku pipe is given in Fig. 113, and the data for Ga in xenoliths and one sample of kimberlite from this pipe are presented in Table 64. The bulk and mineral chemistry, petrography, mineralogy, and geological history of xenoliths analysed in this work have been extensively described in a number of papers (Cox *et al*., 1973; Harte and Gurney, 1975; Harte *et al*., 1975; Gurney *et al*., 1975; and Harte *et al*., 1977).

Many of the rocks examined by these workers fell within a restricted compositional range in terms of volume percentages of the four minerals olivine, clinopyroxene, orthopyroxene and garnet, which they referred to as common peridotites or CP's and which are indicated as garnet lherzolite (CP) in Table 64. The compositional ranges given by Cox *et al*. (1973) for CP's were olivine 45-75%, orthopyroxene 20-50%, clinopyroxene 0-5% and garnet 0-11%, percent olivine always being greater than percent orthopyroxene. The rocks analysed here may be divided into four main groups; garnet lherzolite (CP), which they interpret as depleted mantle; garnet lherzolites and garnet pyroxenites (which may be banded), interpreted as cumulates (Gurney *et al*., 1975); xenoliths with clinopyroxene-rich garnet lherzolite sheets or veins occurring within a garnet lherzolite (CP) host rock; and other rock types, such as amphibolite, eclogite and kimberlite.

Kramers (1978) determined lead and strontium isotope ratios in separated clinopyroxenes from xenoliths from Matsoku and found that quite a strong Pb isotopic heterogeneity exists within the group of common peridotites (depleted residual mantle material), whereas the cumulates and veined rocks show relatively good homogeneity. He gave an approximate age for the presumed magmatic event that gave rise to the undepleted rocks of 190-360 m.y. Kramers also considered that the lack of any specific Pb or Sr isotopic signature associated with the strong Ti enrichment in one rock (LBM 38B) confirmed the conclusions of Harte et al. (1977) that the Ti enrichment in some Matsoku sheet xenoliths is directly related to the magmatic event giving rise to these samples, rather than being caused by a secondary metasomatic event.

Data for Ga and Al in the CP, cumulate and other rocks from Table 64A,B, i.e. excluding rocks with sheets or veins, are plotted in Fig. 114A. The cumulate rocks, excluding the orthopyroxenite but including the CP LBM 32 which has been metasomatised, fall on a well defined trend line of Ga/Al = 1.45. The CP rocks have a very low Ga content (mean = 0.8 ppm) and a mean Ga/Al ratio of 0.98 which is exceptionally low and is consistent with the hypothesis that these rocks are residual or depleted mantle. LBM 13, which Harte et al. (1975) consider may be slightly metasomatised, has an anomalously high Ga content of 1.6 ppm, twice the mean content for these rocks, which does suggest some degree of metasomatism. It should be noted that the Ga/Al ratio is, however, no higher than that of LBM 16. LBM 26, which Harte and co-workers also consider may be slightly metasomatised, shows no evidence of an increase in either Ga or Ga/Al. LBM 32, which has definitely been metasomatised (Harte et al., 1975), has a very high Ga content, although again the Ga/Al ratio of 1.54 is not much higher than those of LBM 16 or LBM 13.

The cumulate rocks, all pyroxenites, have a much higher Ga content (mean = 3.2 ppm) than the CP rocks, but a Ga/Al ratio of 1.45, only slightly higher than the CP's. The orthopyroxenite LBM 41 has a very high Ga/Al ratio of 3.6, very similar to that of the kimberlite host rock, LBM 100, of 4.1. The effect of orthopyroxene on both the Ga and Ga/Al values in the orthopyroxene-rich band LBM 33B is clear, orthopyroxene having the effect of lowering the Ga content but increasing the Ga/Al ratio.

LBM 100, the host kimberlite, is an example (see section 14.3 on kimberlites) of an uncontaminated kimberlite, with a Ga/Al ratio very close to the mean of all uncontaminated kimberlites analysed in this work of 4.0, as compared with the mean for all South African kimberlites of 2.9.

The Ga/Al ratio for the eclogite and amphibolite rocks averages 2.1, and the eclogite is almost identical in Ga and Al with the Tanzanian eclogites (see section 14.2 and Table 65F).

The rocks with sheets, veins or dykes (Table 64C-E) are extremely interesting. The host rock is usually a CP, and for these host rocks the mean Ga content and Ga/Al ratio is 1.5 ppm and 2.4 respectively (Fig. 114B), both markedly higher than corresponding values for the CP's which are not veined, indicating that Ga has been enriched in these rocks relative to Al which is approximately the same in both sets of samples (0.79% Al for unveined CP's and 0.64% Al in veined CP's). The Ga/Al ratio for veined CP's is variable, but the mean value is similar to that of the amphibolite and eclogite, which may be a coincidence. Most of the other rocks tend to have Ga/Al ratios that fall in the range found for kimberlites (2.1-4.2). Sketches of the veined samples, where the information is available, are given in Figs 115 and 116.

For most of the metasomatised bands or veins in Table 64C-E there has been a very marked increase in Ga relative to the host rocks, and the mean Ga content of the metasomatised CP's is 5.2 ppm. For the metasomatised

CP's there has been no noticeable increase in Ga/Al ratio with accompanying increase in Ga. However, in those cases where the vein or dyke is pyroxene-rich, there is usually a marked increase in Ga/Al, with LBM 172 being an exception.

The minerals associated with metasomatism may be one or more of the following: phlogopite, rutile, ilmenite and sulphides (Harte and Gurney, 1975). Ga is unlikely to be present in significant quantity in rutile, may be present in sulphides, has been shown to be present in ilmenite to the extent of about 20 ppm Ga (Table 36C), and is likely to be present at much higher levels in phlogopite although no reliable analyses are presently available.

The relative proportions of phlogopite, ilmenite, rutile and sulphides differ considerably from xenolith to xenolith (Harte and Gurney, 1975). Ilmenite or rutile may be the dominant primary-metasomatic mineral in any given xenolith, with both minerals being common in LBM 101, while rutile occurs to the virtual exclusion of ilmenite in LBM 22 and ilmenite to the exclusion of rutile in LBM 38B and LBM 108. If the two titanium minerals are the dominant metasomatic minerals and Ga, present only in ilmenite, is introduced into these rocks during the metasomatic process, then the Ga/Al ratio should be sensitive to the presence of ilmenite but not to that of rutile. Indeed, for LBM 22 where rutile is most common, there is no change in Ga/Al between the two samples, although TiO_2 is present in A and B samples at 0.58 and 6.16% respectively. In LBM 38 (and LBM 108) on the other hand, in which ilmenite is the predominant metasomatic mineral, there is a sharp increase in Ga/Al in the B sample, with TiO_2 in LBM 38 at 0.09% in A and 3.60% in B. LBM 108 has TiO_2 contents of 0.20 and 7.82% respectively for A and B samples. LBM 101 shows almost no change in the Ga/Al ratio, although the TiO_2 contents of A and B samples are 0.12 and 18.66%. Both rutile and ilmenite are present in this rock, but the proportions of each are unknown. It appears the metasomatic introduction of Ga may sometimes be associated with the introduction of Ti, but when ilmenite is introduced, the Ga/Al ratio is almost invariably increased.

It should be borne in mind that the Ga content of the primary metasomatic ilmenite in the veined rocks may be different from that measured in the megacrysts, as the metasomatic ilmenites have a lower percentage of Fe_2O_3 and higher Cr_2O_3 than megacrysts and ilmenites occurring as lamellar intergrowths with clinopyroxene.

Harte and Gurney (1975) concluded from a study of the metasomatic minerals that they had been formed as a consequence of infiltration by a hydrous fluid especially enriched in Ti and K, containing also S and probably Fe and minor elements Ni, Cu, Nb and Zr. Ga should now also be added to the list. They considered that the most likely source of the fluid was kimberlite magma prior to eruption. The concentrations of Ga found in kimberlite (next section) are entirely consistent with this hypothesis.

In a recent paper Harte et al. (1977) considered the origin of the clinopyroxene-rich sheets in the veined nodules analysed here and concluded that they were magmatic in origin. The close association of primary-metasomatic minerals with some sheets indicated that the metasomatism was probably related to the magmatic event responsible for the clinopyroxene-rich sheets. They stated that after formation of the veins some transfer of material across vein boundaries had taken place. The Ga data confirm this hypothesis as the CP portions of veined nodules have higher Ga contents and Ga/Al ratios (1.8 ppm and 2.4) than the unveined CP rocks (0.8 ppm and 1.0).

Harte et al. (1977) used the Mg/Fe ratio, expressed as 100MgO / (MgO+FeO*), with FeO* being total Fe expressed as FeO, as an index for distinguishing between cumulate rocks and CP's or depleted rocks, and stated that all sheets and host CP's have Mg/Fe ratios intermediate between those of CP xenoliths, interpreted as being depleted, and cumulate xenoliths. This statement does not hold for all rocks analysed here, as LBM 131 has Mg/Fe ratios less than 80, placing it within the group of cumulate rocks having ratios of similar magnitude. Using the same Mg/Fe ratio, data for Ga, Al, Ga/Al and Cr_2O_3 have been plotted in Fig. 117. Clearly, in Fig. 117, while there appears to be a mixing line for Ga between cumulates and CP's (depleted) and host CP's, all the veins or sheets are enriched in Ga. The CP's in contact with clinopyroxene-rich sheets plot on the mixing line. Al is slightly depleted in the host CP's relative to cumulates and depleted CP's, with the result that the Ga/Al ratio is enriched in all portions of the veined rocks. Harte et al. (1977) state that the high bulk CaO/Al_2O_3 ratio of some of the clinopyroxene-rich margins have a cumulative aspect and suggest that some of the low-melting fraction liquid may have been lost from the sheets. The suggestion is supported by the lower Ga/Al ratio of the marginal zones relative to the inner zones, as Ga could be expected to enter the liquid of the low-melting fraction.

It is interesting to consider the level of Ga required in the mantle in order to be able to obtain a value of 16.5 ppm Ga in MORB tholeiites by partial melting. Le Roex (1978) considers a starting composition of 60% olivine, 25% orthopyroxene, 10% clinopyroxene and 5% garnet, i.e. a garnet lherzolite, would yield a rock of oceanic tholeiite composition by 20% partial melting. Le Roex also considers the parent magma of MORB tholeiites to be a primitive Mg-rich (i.e. olivine-rich) basalt with a Ga content 85% of that of abyssal tholeiites, i.e. $\sim$14 ppm Ga. Assuming values of $D_{Ga}^{ol} = 0.01$, $D_{Ga}^{opx} = 0.3$, $D_{Ga}^{cpx} = 0.4$ and $D_{Ga}^{gt} = 0.01$, the $D_{Ga}^{melt} = 0.122$. Using the formula

$$\frac{C_1}{C_o} = \frac{1}{D + F(1-D)}$$

then for $F = 0.22$, in order to derive 14 ppm Ga in the liquid, Ga in the parent rock must be 4.4 ppm; for $F = 0.20$, Ga must be 4.2 ppm in the parent rock and for $F = 0.18$, it must be 3.9 ppm. For a starting composition of 68% olivine, 26% orthopyroxene, 6% garnet and 0% clinopyroxene for which $D^{Ga}_{melt} = .086$, if $F = 0.18$, Ga = 3.5; if $F = 0.20$, Ga = 3.7; and if $F = 0.22$, Ga = 4.0 ppm. Therefore the Ga content of the source rocks should be between 3.5 and 4.4 ppm. Clearly the only rocks examined here that have sufficient Ga in them are the clinopyroxene-rich bands and metasomatised CP's found in veined rocks. The two cumulate pyroxenites LBM 12 and LBM 18 are also possible source rocks.

The depleted nature of the common peridotites is again emphasised.

The study of Ga has proved useful in confirming that a number of ideas derived from mineralogy and major element chemistry for upper mantle rocks from the Matsoku Pipe hold true also for this incompatible trace element.

14.2 XENOLITHS FROM OTHER KIMBERLITE PIPES

Gallium has been determined in xenoliths from a number of different kimberlite pipes from both South Africa and Tanzania. Most of the rocks are eclogites from Roberts Victor Mine. Data are presented in Table 65 and plotted in Fig. 118.

MacGregor and Carter (1970) reported a wide range in compositions of Roberts Victor eclogites, which have been confirmed by Hatton (1978) who states that they vary in mineralogical composition from almost pure garnet to almost pure clinopyroxene. The Ga and Al data presented here for eclogites and plotted in Fig. 118 indeed show a very large scatter, Ga ranging from 3 to 19 ppm, and the Ga/Al ratio varying from 0.5 to 3.7, within the ranges found for upper mantle garnets and clinopyroxenes. MacGregor and Carter recognised two groups of eclogites, which they considered to be cumulates (Group I) and corresponding liquids (Group II), but Hatton and

Gurney (1977) considered that most, if not all, of the eclogites are cumulates. The Ga data presented here preclude Group II eclogites being corresponding liquids to cumulate Group I eclogites. Liquids resulting from fractional crystallization of Group I eclogites could be expected to be higher in Ga than the cumulates, but the Ga contents of Group II eclogites (possible liquids) reported here (3-8 ppm) are in all cases lower than Group I eclogites (10-18 ppm). The Ga/Al ratios of Group II eclogites (0.5-1.4) are also generally lower than for Group I (1.1-1.9). It should be borne in mind that these results could be slightly affected by secondary alteration by kimberlite along crystal boundaries. Group I eclogites show a more altered appearance than do Group II, and inclusion of kimberlite along grain boundaries would increase both Ga and the Ga/Al ratio in the Group I eclogites.

However, despite possible contamination by kimberlite, the majority of the Roberts Victor eclogites, and indeed of all eclogites reported here, appear to be depleted in terms of Ga, the Ga/Al ratios being mostly lower than the value of 1.42 found for Matsoku garnet lherzolites (CP) and pyroxenites, although this may be entirely due to a high percentage of garnet (Ga/Al $\approx$ 0.8) in these rocks. Hatton (1978) considers partial melting to have dominated the evolution of the melt from which Group II eclogites crystallized, while the Group I eclogites crystallized from a normal melt. The Ga data are not consistent with this hypothesis because the partial melt could be expected to be higher in Ga and Ga/Al ratio than an ordinary melt. Crystal cumulates usually retain some intercumulus liquid which would lead to Group II eclogites having higher Ga and Ga/Al ratios than Group I, but the opposite is true. It is possible that secondary alteration has confused the picture.

There is still uncertainty regarding the formation of Roberts Victor eclogites, but any hypothesis must explain the differences in Ga and

Ga/Al ratio between Groups I and II eclogites.

Eclogites from other pipes fall within the ranges of Ga and the Ga/Al ratios found for Roberts Victor eclogites and exhibit a similar degree of scatter in their values.

Of note is the very low Ga/Al ratio found for the single corundum eclogite analysed, and the very high Ga content (18.9 ppm) found for the clinopyroxene megacryst in HRV 77, although the Ga/Al ratio is similar to some of those found for metasomatised pyroxenite and pyroxene-rich veins in Matsoku xenoliths. Gurney (pers. comm.) considers that the megacryst HRV 77 may have formed at the roof of the magma chamber, i.e. in a volatile-rich (therefore Ga-rich) environment, before falling into the eclogite mush at the base of the chamber. This explanation would account for the very high Ga and Al contents of the megacryst. The Ga/Al ratio of 3.7 is consistent with values found elsewhere in the literature for clinopyroxenes (Table 37 and Burton and Culkin, 1972), although somewhat on the low side.

The megacrysts from Monastery Mine and Kamfersdown Mine are very interesting. Jakob (1977) investigated the compositions of megacrysts from Monastery Mine and reported that olivine + orthopyroxene + clinopyroxene + garnet + – ilmenite co-existed within the temperature interval 1400 to 1150°C at 42.5 kbar pressure. Discrete megacrysts existed in the temperature range 1250 to 1150°C. By matching bulk chemical analyses for the clinopyroxene and garnet megacrysts with Jakob's data, it is possible to estimate crystallization temperatures of 1380°C for the pyroxene (M(A)) and 1340-1380°C for the garnet (M(D)) megacrysts. The crystallization temperature of megacryst M(A) estimated from the pyroxene solvus after the method of Davis and Boyd (1966) was 1395°C, in close agreement with the 1380°C estimated by comparison with Jakob's data. Jakob suggests that the megacrysts formed from a small volume of melt during a magmatic event in the upper mantle, possibly at the end of the Karroo volcanism. The Ga/Al ratio of the garnet confirms the low ratios for this mineral found elsewhere, while the ratio for the clinopyroxene is also on the low side when compared with crustal clinopyroxenes as a whole. The very high crystallization temperatures suggest that these megacrysts crystallized from the melt at an early stage before Ga and other volatile elements had been enriched, which could account for the relatively low Ga/Al ratio in the clinopyroxene.

In contrast, the clinopyroxene from the Kamfersdown Mine (estimated crystallization temperature 1030°C by method of Davis and Boyd (1966)) has a considerably higher Ga content and a very high Ga/Al ratio, one of the highest recorded. The only higher values have been reported by Philpotts (1960) in clinopyroxenes from Quebec norites.

The data for pyroxene megacrysts suggest that the considerable variation in Ga content and the Ga/Al ratio of pyroxenes reported in the literature may be due in part to variations in the temperature at which the minerals crystallized.

Future work should include the determination of the changes in Ga and the Ga/Al ratio occurring in megacrysts which crystallized at different temperatures.

The garnet lherzolites from the Bultfontein Pipe (Table 65E) are almost identical with the CP's from Matsoku, having similar ranges of values for both Ga and the Ga/Al ratio. Chromite harzburgites contain very little Ga, close to the detection limit of 0.3 ppm. The opaque-bearing lherzolite has a very high Ga/Al ratio, which in this rock is not due to the presence of ilmenite as the opaque mineral is spinel. The high Ga/Al ratios of the richterite and phlogopite peridotites confirm the metasomatic nature of these minerals in the rocks.

14.3 GALLIUM IN KIMBERLITES

Ga has been determined in 67 kimberlites from South Africa and

and Lesotho, in 25 kimberlites specially selected by J.B. Dawson (pers. comm.) to be free from crustal contamination, and in 11 kimberlites from Lesotho, also chosen to have low crustal contamination. Kimberlites may belong to either the diatreme or hypabyssal facies and are classified as micaceous or basaltic. All types are represented in the analyses reported here. The data are presented in Table 6 6 and Figs 119 and 120.

The Benfontein rocks have been described by Dawson and Hawthorne (1973) and the kimberlites from Premier, Bellsbank, Mullersvlei, Ebenhaezer and Koffyfontein by Fesq et al. (1975, 1976) and Kable et al. (1975) who reported major and trace element data for all samples.

Dawson (1967, 1972) summarised the geochemistry and modes of origin and formation of kimberlites and concluded that the concept of 'incipient melting' was favoured at that time. The melting of volumetrically small amounts of phlogopite-diopside results in a liquid rich in incompatible elements, and Dawson has pointed out that the high Ga/Al ratio found in kimberlites compared with other ultrabasic rocks is similar to that of late differentiates.

Gurney (1974) put forward a related hypothesis, namely that kimberlite has its origin at least 200 km below the surface and beneath the lithosphere of the continents in a zone of ultrabasic composition with a small amount of interstitial fluid containing dissolved CO_2, H_2O, K, Ti and other elements found in kimberlite, which cannot be readily accommodated as major constituents of the major mantle minerals. Partial melting of mantle peridotite, and especially the degree of partial melting, affects the original magma composition. During its passage upward from the low-velocity zone the kimberlite fluid, already rich in volatiles, incorporates mantle material, predominantly peridotite, some pyroxenite, eclogite and possibly some ilmenite-bearing rock, into the magma. Final emplacement is a complicated and frequently explosive process taking place along tensional structural features, and is accompanied by incorporation of crustal material into the magma.

There have been relatively few reports of Ga in kimberlites; Goldschmidt and Peters′(Shaw, 1957) reported a mean of 4 ppm, Borisenok (1959) found an average of 1 ppm in ten Russian kimberlites with a Ga/Al ratio of 1.0, and Dawson (1962a) reported values of $<$3-30 ppm Ga for 14 Basutoland kimberlites with a mean of approximately 9 ppm Ga, and a Ga/Al ratio of 1.2-4.2 (mean = 2.9) for four samples. The large number of Ga analyses reported here for kimberlite is an important contribution to our knowledge of the Ga content in this volumetrically small but nevertheless important rock type.

The kimberlites analysed here may be divided into six main groups. Premier Mine is basaltic and three types of kimberlite have been analysed. Type 1 contains up to 43% inclusions of which the major component is Waterberg quartzite. Type 2 has approximately 28% inclusions, of which the major component is basic rocks from the B.I.C. Type 3 is similar to Type 1 but has only 20% crustal inclusions (Fesq et al., 1976). Field evidence indicates that the three types are associated with separate intrusive events and that the order of intrusion is Type 2 followed by Types 1 and 3. Ages of 1400 m.y. for Type 2, 1250 m.y. for Type 1, and 1200 m.y. for Type 3 confirm the field evidence. The Bellsbank kimberlites are intruded into sedimentary carbonates. Three dykes have been investigated, and the main crustal contaminant is carbonate. The Bobbejaan and Main fissures are micaceous, while the Water fissure is basaltic. The single rock from Mullersvlei is a micaceous kimberlite. The Koffyfontein-Ebenhaezer group of kimberlites is basaltic and they are characterised by considerable quantities of Karroo shale as crustal contaminant. The rocks from Benfontein are very unusual and only two can be accepted as examples of kimberlite, S8 and S407/3. S8 is a 'normal' kimberlite according to Dawson and Hawthorne

(1973), while S407/3 is a fine-grained contact kimberlite with a lower proportion of olivine megacrysts. It is not certain whether the contact rock for this sample was shale or dolerite. The single sample of kimberlite from Matsoku, described earlier, has been included here for completeness.

Ga data from Table 66A-E have been plotted against Al in Fig. 119, and the Koffyfontein, Premier and Bellsbank kimberlites form distinct groups which lie on a trend line that is not of constant Ga/Al ratio, but which intercepts the Ga axis at about 1 ppm Ga. The two Benfontein kimberlites are distinctly different from all the other samples, while the Monastery kimberlite is enriched in Ga and the Mullersvlei kimberlite is very similar to samples from Ebenhaezer West.

The Premier samples form a very tight group. The Type 3 (black) samples have a distinctly lower Ga content than the other two groups but a significantly higher Ga/Al ratio. The Type 3 kimberlite also has the highest alkali (K, Rb, Cs) and Ba contents, which, together with the higher Ga/Al ratio, may indicate a later stage differentiate than the other two groups in accordance with the youngest age for this group. There is little difference in either the Ga contents or the Ga/Al ratios of the other two types in spite of the considerable difference not only in the degree of crustal contamination but also in the type of contaminant. Fesq et al. (1975) reported loss of volatiles in the relative order $Cs > Rb > K$ for samples JJG 412-414 (Table 66A) near wall-rock contacts and also for JJG 404 near a cross-cutting dyke. No significant loss of Ga or change in Ga/Al ratio is observed in these samples, confirming the results found for oceanic pillow lavas, i.e. that Ga is relatively immobile during thermal alteration, and also that Ga is not lost through association with volatile phases on emplacement of kimberlites.

The Koffyfontein-Ebenhaezer group of kimberlites is characterised by having the highest Ga contents, except for Mullersvlei, and the lowest

Ga/Al ratios of 2.7-3.1. The Ebenhaezer West group has the highest Ga contents of the three, with the exception of sample JJG 454 which has 8.1 ppm Ga, seemingly placing it with the Ebenhaezer East and Koffyfontein samples. However, JJG 454 has 15% more $CaCO_3$ than the other four samples which accounts for the lower Ga and Al contents. Correcting for dilution would give a Ga value of 9.5 ppm placing it with the remaining four western samples.

The effects of crustal contamination on the Ga content and Ga/Al ratio of kimberlite should perhaps be considered at this stage.

Dawson selected a number of kimberlites as being relatively free from crustal contamination, but it is obvious (Table 66F,G and Fig. 120) that there is still considerable variation in both Ga content and Ga/Al ratio. However, mean values are 6.8 ppm Ga and 4.0 for the Ga/Al ratio. Considering the mode of formation of kimberlite, this variation is not surprising. For purposes of examining the effects of crustal contamination, the mean values will be used as a starting point. In the following table data for the Ga and Al contents of various rock types are taken from Horn and Adams (1966) and are used to calculate the resultant values of Ga and Ga/Al for mixtures of 25% crustal rock and 75% kimberlite. Data in brackets are from Mason (1966).

Element or Ratio	Kimberlite	Shale	Carbonate	Igneous rock	Sandstone
Ga (ppm)	6.8	23(19)	2.7(4)	18.5(15)	6(12)
Al (%)	1.7	8.0(8.0)	0.9(0.4)	8.0(8.1)	3.2(2.5)
Ga/Al (x 10^4)	4.0	2.9(2.4)	3.0(10)	2.3(1.9)	1.9(4.8)
Kimberlite with 25% crustal contamination:					
Ga (ppm)		10.9(9.9)	5.8(6.1)	9.7(8.9)	6.6(8.1)
Al (%)		3.3(3.3)	1.5(1.4)	3.3(3.3)	2.1(1.9)
Ga/Al (x 10^4)		3.3(3.0)	3.9(4.4)	3.0(2.7)	3.2(4.3)

The data from Mason (1966) give anomalous Ga/Al ratios for both the carbonates and sandstones, and the data from Horn and Adams (1966) are preferred.

The calculated values for contaminated kimberlite are interesting. Contamination by carbonate results in a lower Ga content with essentially no change in Ga/Al, i.e. a simple dilution of kimberlite. Inclusion of shale in kimberlite results in a higher Ga content but lower Ga/Al ratio, as does the inclusion of igneous rock. Inclusion of sandstone would have the effect of maintaining Ga constant but decreasing the Ga/Al ratio. It is also interesting to note that contamination by 25% of either shale or igneous rock or sandstone all result in similar Ga/Al ratios (3.0-3.3).

Fesq _et al_. (1975) considered that Si/Mg ratios in kimberlites greater than 1.2 indicated excessive crustal contamination, and with the exception of samples from the Main fissure at Bellsbank, all have ratios in excess of 1.1 with those from Ebenhaezer West having the highest ratio of 2.49. The Ebenhaezer West samples are known to be contaminated chiefly by Karroo shale, although the exact proportions are not known. These samples do, however, have the highest Ga contents (~9.5 ppm) and the lowest Ga/Al ratios (~ 2.7), similar in magnitude to the values calculated for shale-contaminated kimberlite in the table above. The Ebenhaezer East samples, being less contaminated than the Ebenhaezer West samples, have lower Ga contents but higher Ga/Al ratios, in accordance with the calculations made above.

When similar considerations are applied to the Premier samples, and if all 40% crustal material is assumed to be sandstone, then the Type 1 kimberlite should have a Ga content of 6.5 ppm Ga and a Ga/Al ratio of 2.8, very close to observed values. For Type 3, which has only 20% contamination, the Ga content should be 6.6 ppm Ga with a Ga/Al ratio of 3.3, compared with measured means of 5.1 ppm and 3.3. These samples are rich in olivine which would reduce the Ga content but not affect the Ga/Al ratio.

It is obvious that the calculation cannot be carried too far because of the presence of many variables, not only within the kimberlite itself, but also within the contaminating material. However, the calculations reported above do indicate that, in general, contamination will result in a decrease in the Ga/Al ratio with either an increase or a decrease in Ga content.

The Bellsbank kimberlites show the greatest range in Ga and Ga/Al ratio of all the groups analysed here, Ga ranging from 2.4 to 6.9 and the Ga/Al ratio ranging from 2.4 to 4.7, with the Main Fissure group being the most variable. Fesq et al. (1975) state that the Bellsbank Main Fissure kimberlites are the rocks least affected by crustal contamination in terms of Si/Mg ratio (0.89), although they do contain up to 60% phlogopite (average 40%). These rocks are intruded into the Campbell Rand dolomitic limestones, which would tend to lower the Si/Mg ratio, but, apart from acting as a diluent, would have little effect on the Ga content or Ga/Al ratio. If the samples are recalculated on a carbonate-free basis, assuming for simplicity that all CO_2 is present as $CaCO_3$, then the mean value for Ga in the Bobbejaan fissure becomes 4.6 ppm (uncorrected 3.3 ppm), for the Main Fissure 5.2 ppm (4.2), and for the Water Fissure 6.2 ppm (3.4). The pattern of distribution remains similar to that described above, namely that maximum dispersion occurs in the Main Fissure kimberlites, and the minimum dispersion in the Water Fissure. The recalculated values would place the Bellsbank group of kimberlites within the range shown by the Premier samples.

The greater range in Ga values found for the Bellsbank kimberlites relative to others is probably due to the high and variable phlogopite contents of this group, but no detailed petrographic descriptions are available for these rocks.

The Benfontein rocks (Table 66E) are most unusual. Dawson and Hawthorne (1973) interpret these kimberlites as being of the hypabyssal type, which, because they consolidated at depth, retained the intercumulus transporting calcium carbonate. S3 is a magnesian calcite (MgO + CaO + CO_2 = 94%, SiO_2 = 0.52%) and it is important to note that Ga was not detectable in this sample ($<$0.4 ppm) and was also not detected in two carbonatites from Oldoinyo Lengai volcano (Chapter 20). Therefore, although calcite represents a potentially volatile fraction of kimberlite, Ga is excluded from it. Samples S5 and S403/2 represent two examples of another extreme reached by pre-injection differentiation in kimberlites, spinel-perovskite cumulates with high Ti, Al and Fe contents and an Fe_2O_3/FeO ratio of 1.6-1.7. The presence of primary magnetite is reflected in the exceptionally high Ga contents of these two samples together with the equally high Ga/Al ratios. The other two rocks, S8 and S407/3, also have anomalous Ga/Al ratios (Fig. 119). The low Ga content of S8 is due to dilution by olivine, but the very low Ga/Al ratio is surprising. Equally unusual is the high Ga content (12.9 ppm) of the fine-grained kimberlite S407/3, a contact rock. The high Ga content is possibly due to the presence of magnetite, which would also account for its unusually high Ga/Al ratio. The Monastery kimberlite, 1870, has a high Ti content, suggesting enrichment in ilmenite which would increase the Ga content and the Ga/Al ratio.

The specially selected kimberlites in Table 66F,G are from a number of different localities. The Ga-Al data are plotted in Fig. 120A. The three carbonatitic kimberlites are all from the Premier Mine and represent the last carbonate-rich dykes, having 42-52% $CaCO_3$. Of the three non-micaceous kimberlites S277 is also a last liquid serpentinised plug which is well oxidised with a high proportion of Fe_2O_3. S30B is another last liquid plug. In both instances Ga has concentrated strongly into the last liquid giving high Ga values and Ga/Al ratios.

Similarly, the three Premier last liquid carbonate-rich dykes have high Ga/Al ratios, although the Ga itself is not as strongly enriched as in the plug kimberlites, even allowing for dilution by $CaCO_3$. The remaining rocks form two groups, those from Star Mine and others. The kimberlites from Star Mine have distinctly lower Ga/Al ratios than the other selected kimberlites and cluster about the trend line found for contaminated kimberlites in Fig. 119, shown as a dotted line in Fig. 120. The remaining selected kimberlites cluster fairly closely about a trend line with a different slope (higher Ga/Al ratio) to that in Fig. 119 but with a similar intercept on the Ga axis of about 1 ppm. This confirms the results and calculations discussed earlier, namely that contamination by crustal materials will tend to lower the Ga/Al ratio of kimberlite. Whether the samples from Star Mine have been contaminated or not is uncertain as only powdered samples were available with no petrographic descriptions.

Fesq _et al_. (1975) reported that kimberlite KN 275/75 from Lemphane in Lesotho was a good example of uncontaminated kimberlite. This and ten other Lesotho kimberlites have been analysed for Ga (Table 66H) and the data plotted in Fig. 120B. The Si/Mg ratios for all except LLT1 and KN278 are < 0.95. Sample KN228 has a high K content, suggesting the presence of phlogopite which would cause an enrichment in Ga. The remaining samples confirm the trend line of Ga/Al = 4.0 found for Dawson's samples, and confirm also that Lesotho kimberlites are generally uncontaminated by crustal material.

14.4 CONCLUSION

Ga is depleted in garnet lherzolites (CP), but has been introduced into veined or banded garnet lherzolites by a metasomatic liquid, together with Ti, Fe, K and Zr. The Ga content of eclogites is very variable indeed and is probably related to the proportion of garnet, which is also very variable, in these nodules. In kimberlite the enrichment of Ga relative to Al is confirmed, and the Ga/Al ratio is dependent on the degree and type of crustal contamination. Uncontaminated kimberlites have a higher Ga/Al ratio

(~ 4.0) than contaminated material. As in other igneous rocks, Ga is strongly enriched in the last stages of fractional crystallization resulting in very high Ga and Ga/Al ratios in last liquids, especially high for an ultrabasic rock type. Both ilmenite and magnetite in the upper mantle contain Ga, its presence in ilmenite possibly being due to the very high pressure regime. A slight possibility existed that Ga might have been present in volcanic carbonates, but its exclusion from igneous as well as sedimentary carbonates is confirmed.

The source of Ga in metasomatic liquids in the mantle is obscure. It is possible that there may originally have been Ga in the earth's core, as in iron meteorites, which could have migrated into the mantle, or which could have remained in the mantle during separation of the core.

CHAPTER 15

GALLIUM IN ROCKS FROM THE BARBERTON MOUNTAIN LAND

Ga has been determined in 139 samples from the Onverwacht Group of the Swaziland Sequence and in 15 intrusive 'granitic' rocks from the Barberton Mountain Land area. The majority of the volcanic samples are from the Lower Ultramafic Unit (Viljoen and Viljoen, 1969). Details of the stratigraphy and distribution of the Swaziland Sequence are given in Fig. 121, locations of granitic samples in Fig. 122, and the data from the analysed rocks in Table 67. Anhaeusser (1973) may be consulted for further references to previous studies of this area, one of the best documented greenstone belts in southern Africa due to its extreme age and exceptional preservation, and one which has been the focus of a number of specialised studies, many of them still in progress. Major and trace element data for most of the samples analysed here may be found in Viljoen and Viljoen (1969) and Smith (1978), who may also be consulted for sample localities.

The Lower Ultramafic Unit is thought to represent a primordial oceanic-type crust (Anhaeusser, 1973) and the age is considered to be well in excess of 3400 Ma old. These represent the oldest rocks in which Ga has been analysed in this work. A comparison between the Ga contents and Ga/Al ratios of these primitive rocks and more recent continental and oceanic basaltic rocks will be made in Chapter 16.

Rocks from Archaean greenstone belts have usually been subjected to a number of alteration processes which may have contributed to changes in the original mineralogy and chemistry of the rocks. This must be borne in mind when comparing data from ancient rocks with modern equivalents. Smith et al. (1978) have discussed in detail the effects of alteration on the geochemistry of some of the pillow lavas analysed here. Ga data were included in their discussion.

Smith (1978) is engaged in a detailed geochemical study of rocks from the Barberton Mountain Land, including many of the samples analysed in this work, and the classification of the various rocks, which in some cases differs from that of Viljoen and Viljoen (1969), is taken from his work.

The Ga and Al data are plotted in Fig. 123. The three types of basaltic komatiite (Barberton, Badplaas and Geluk), together with the peridotitic komatiites, cluster round a trend line that approximates a Ga/Al ratio of 2.2. There is a degree of overlap between the peridotitic komatiites and both the Geluk and Badplaas basaltic komatiites, considerable overlap between the Geluk and Badplaas basaltic komatiites, and again some overlap between the Badplaas and massive Barberton basaltic komatiites. The pillowed Barberton basaltic komatiites form a field of their own due to their higher Al content compared to the massive flow equivalents. The Ga concentrations are similar for the massive and pillow lavas. The difference between the margins and interiors of the pillows should be emphasised, the margins being lower in Ga, except where epidotisation has taken place, and Ga is enriched. If the pillow cores alone are considered, then the pillow lavas have distinctly higher Ga contents than the massive flows, with only one sample in each group overlapping. The effects of alteration on the Ga content will be discussed later.

The Ga-Al plot suggests that fractional crystallization could relate the four types of rock discussed so far, namely the peridotitic komatiites and the three types of basaltic komatiite. Mean values for Ga and Al for the four groups have been plotted in Fig. 124. Smith (1978) has suggested that olivine fractionation can be invoked to account for the formation of the sequence peridotitic komatiite - Geluk - Badplaas basaltic komatiite, followed later by clinopyroxene fractionation to form the Barberton type basaltic komatiites. The Ga data can be used to substantiate these ideas to a certain extent. In Fig. 124 a line with a slope equivalent to a Ga/Al ratio of 2.19 has been plotted through the points representing average peridotitic, Geluk and Badplaas komatiites, together with dotted lines representing three standard deviations (s_c) about the line. Olivine fractionation would cause an increase in Ga and Al, while the ratio would remain constant, and indeed all three points of the peridotitic, Geluk and Badplaas komatiites do lie, within the statistical error limits of the analytical data, on the line of constant Ga/Al ratio. The massive Barberton type basaltic komatiites also fall within the error limits, but the pillows fall outside these limits in the direction of lower Ga/Al ratio. Clinopyroxenes generally have a Ga/Al ratio of about 4-6 (Burton and Culkin, 1972, and Table 37), and clinopyroxene fractionation from a liquid ($D^{cpx/l}_{Ga} \approx 0.4$) would therefore result in the generation of liquids of higher Ga but lower Ga/Al ratio, as is the case for the pillow lavas. On the other hand, it is possible to draw, with an excellent degree of fit, a correlation line of varying Ga/Al ratio between all the points of the rocks discussed, indicating only clinopyroxene fractionation. However, the other major element data preclude the possibility of all the rocks being derived by fractionation of clinopyroxene. In what may be a coincidence, the line representing clinopyroxene fractionation intercepts the Ga axis at almost the exact value (1 ppm) obtained for kimberlites in the previous chapter. Smith (pers. comm.) has calculated, using major element data, that it is necessary to fractionate 26% clinopyroxene from a liquid of massive flow composition to derive pillowed basaltic komatiites. On this basis calculated Ga would be 11.2 (measured 11.4) ppm and the Ga/Al ratio 1.88 (measured 1.85). Other incompatible elements (Nb, Zr, Y, Co, V and Sc) agree equally well, but Ni and especially Cr are in poor agreement, confirming the findings of Herrman et al. (1976), who prefer to derive the basaltic komatiites by a partial melting process.

The decrease in Ga/Al ratio with increase in D.I. is slight, from 2.4 for the peridotitic komatiites (D.I. = 1.5) to 2.0 for the Barberton type pillow basaltic komatiites (D.I. =~27) (see Fig. 124), and although the Ga data do not confirm the concept of olivine fractionation followed by clinopyroxene fractionation with certainty, they do suggest that it is a possible mechanism for the formation of these rocks. A detailed plot of the Ga/Al ratio versus D.I. is given in Fig. 125. Two points are worth consideration. Firstly, although the Ga/Al ratio decreases slightly with increasing D.I. when considering mean values for each group of rocks, inspection of Fig. 125 shows that when intermediate and acidic rocks are also taken into account, the Ga/Al ratio remains fairly constant throughout the sequence, which does not mean that the acid and basic lavas are genetically related. The second point to note is the very considerable variation in the Ga/Al ratio at constant D.I., frequently by a factor of two, and especially for the peridotitic komatiites. The reason for this considerable variation (which for the ultramafic rocks remains unknown at this stage) is to be found possibly in a consideration of the alteration of the rocks.

Condie _et al_. (1977) and Smith _et al_. (1978) have discussed the effects of alteration on major and trace element geochemistry of tholeiitic flows and basaltic komatiites and have pointed out that one of the major problems associated with the interpretation of results from Archaean greenstone volcanics is what effect alteration has had on the composition of the original rocks.

Condie _et al_. (1977) determined Ga, amongst many other trace elements, in three _massive_ lava flows, one which they considered to be unaltered, one which had been carbonated, and another which had been epidotised. Their data are plotted in Fig. 126, together with data from this work for three flows, SD 82-85, SC 6 and HSS 531-536 (Table 67B,C and G). Condie _et al_. (1977) state that the errors in their trace element data are ≤10%, but do not mention precision. However, on three aliquots of the same rock powder they measured a variation in Ga of 25% at the 12 ppm level. The intraflow variation measured for the unaltered massive flow (see Fig. 126) was 54%, measured in six samples collected over a distance of about 1 kilometer. For the pillowed flow SD 82-85, four samples collected over a distance of about half a kilometer, the variation was 7% compared with a $3s_c$ confidence limit of 3-4% calculated from counting statistics. The absolute variation in the Ga data of Condie *et al*. (1977) was 6 ppm (mean = 11.3 ppm) compared with a range of 0.9 ppm and a mean of 12.2 ppm found in this work. It seems likely that much of the variation reported by Condie *et al*. (1977) was due to analytical imprecision. The range of concentrations found by them for Ga in the carbonated flow was 5 ppm and in the epidotised flow 6 ppm, which, as they pointed out, were similar to that found in the unaltered flow. They therefore concluded that Ga was one of the elements which appeared to have been relatively unaffected by the alteration processes and which should be given weight in characterising original magmas and studying their origin. This conclusion seems extraordinary when it is considered that in the epidotised flow the Ga content increased by 55% (see Fig. 126) as the modal epidote content increased from 7% to 59%, and that they stated elsewhere in their paper that increases in Ga appeared to be associated with epidotisation. For Condie's rocks there was, however, no correlation between the increase in Ga content and increase in carbonate content (0-9%). A lack of association of Ga with carbonate has been noted earlier in this work.

When considering variation within massive flows, it is important to remember that variation across flows can be considerable, due either to crystal settling within a flow or fractionation of the lava entering the flow. Ga has been determined in cross-sections of two massive flows, SC 6 and HSS 531-536 (Fig. 124 and Table 67B,C and G). In both instances Ga is lowest at the base of the flow, increases in the middle and decreases again at the top. The variations, expressed as (range/mean) x 100%, are 15% and 29% respectively, greatly in excess of the 7% variation measured along the pillowed flow SD82-85. When considering absolute values of Ga, the effects of variation in H_2O and CO_2 in the rocks must be taken into account. For the rocks mentioned above, recalculation of the analyses on a water and CO_2-free basis makes very little difference, only slightly reducing the variation in Ga. It is better to use Ga/Al ratios rather than absolute Ga values, and when the ratios are considered, the intraflow variation for SD 82-85 is within statistical error ($\pm 3s_c$). The across-flow variation for HSS 531-536 is also within statistical error. That of SC 6 is within $4s_c$, and Smith (1978) reports that olivine and clinopyroxene are important fractionating phases when modelling changes observed in the SC 6 flow. The involvement of clinopyroxene may account for the larger variations in Ga/Al ratio for this flow compared to the HSS 531-536 flow. When considering the variation along flows, it is obviously vital that all the samples are collected from the same level within the flow, as was done in the study carried out by Condie et al. (1977), something that may be difficult to achieve in practice.

Having established that the variation in Ga can be very small along a flow, whereas it may be quite considerable across a flow, and also that the Ga/Al ratio is less sensitive than Ga to changes in composition, the possible effects of alteration, as measured in five pillows in which both margins and cores were analysed, will now be considered. The data are reported in Table 67A,B and plotted in Fig. 126.

For the four pillows SC 3, 5, 8 and 11 the Ga content of the glassy margins is always less than that of the cores, although in the case of SC 8 the difference is not significant. The change in Ga/Al ratio, usually lower in the margins than the cores, is significant only for sample SC 11, but does suggest that Ga has been removed from the margins, or possibly added to the cores, to a relatively greater extent than has Al. Isotopic data suggest that the margins are less altered than the cores (Smith, pers. comm.).

The changes in Ga are sufficiently small to make it difficult to decide whether Ga has been removed during alteration and metamorphism or not. As has been pointed out earlier in a similar discussion on recent submarine pillows, there was no evidence that Ga had been affected by sea water alteration during or after extrusion of lavas on the sea floor. However, Frey _et al_. (1974) have shown that basaltic glasses are subject to larger chemical changes than crystalline basalt during alteration.

Sample SC 2, in contrast to the other four pillows just discussed, shows a very marked increase in both Ga and Ga/Al ratio from core to (glassy) margin. The margin also contains a considerable quantity of epidote compared to the margins of the other pillows (Smith, 1978). Smith _et al_. (1978) have suggested that epidotisation has occurred as a result of the addition of Ca and Fe to the pillow during metamorphism, forming epidote with the Si and Al already present in the rock. In agreement with the data of Condie _et al_. (1977), Ga has also been added to the pillows during epidotisation. From the data presented here and in the literature for Ga in epidote, it is obvious that this mineral generally contains considerably more Ga than most other common rock-forming silicate minerals (see Introduction and Table 37), and its presence in a rock will lead to an increased Ga content. The Ga content and Ga/Al ratio of rocks may be used to differentiate between epidote formed by isochemical alteration of a rock (no change in Ga and Ga/Al) and epidote formed by the metasomatic introduction of elements into a rock (increase in Ga and Ga/Al).

Vallance (1969, 1974) reported Ga determinations in cores and rims of spilitic pillows from various locations, and Naqvi and Hussain (1973) reported Ga in cores and rims of pillows from the Chitaldrug metabasalts in India. Their data are given below.

	ppm Ga	Ga/Al
Vallance (1969)		
Core	10	1.32
Rim	10	1.16
Core	22	2.82
Rim	10	1.28
Core	22	2.33
Rim	28	2.61
Core	15	1.70
Rim	45	4.85
Core	22	2.21
Rim	22	3.25
Vallance (1974)		
Core	18	2.44
Rim	18	2.19

	ppm Ga	Ga/Al
Naqvi and Hussain (1973)		
Core	13	1.34
Rim	5	0.69
Core	5	0.72
Rim	10	1.03
Core	10	1.24
Rim	7	0.96
Core	7	0.93
Rim	15	1.89
Core	15	1.69
Rim	22	2.21

There is some doubt about the quality of the Ga data reported by these authors. Naqvi and Hussain (1972) reported a value for W-1 of 12 ppm Ga with a standard deviation of 2.7 ppm. As the maximum difference between Ga in cores and rims for their pillows was 8 ppm Ga, which is equal to three standard deviations, any variation is within statistical error and cannot be considered significant. In addition, the Ga/Al ratios reported for their pillows are exceptionally low for basaltic rocks, which probably reflects a systematic error in their Ga data, as suggested by their value for W-1 which is low by about 40%.

Vallance did not report details of his analytical method, but the determinations were carried out in collaboration with R. Allen, and presumably the quality of the data was similar to that of Nockolds and Allen (1953, 1954, 1956), i.e. a c.o.v. of about 30%. The six samples analysed by Vallance were each taken from areas as far apart as England, India and Australia, and the difference between pillows is therefore not surprising. Considerable variation probably exists in the mineralogy of some of the core/rim samples analysed by Vallance (1969) in order to account for differences in the reported major element compositions. The sample with 45 ppn Ga has a high CaO and low CO_2 content, possibly indicating a high epidote content, as reflected in the Ga concentration and Ga/Al ratio.

The quality of the data presented above is unfortunately not good enough to allow meaningful comparison between the data reported here and that from other areas in the world.

Aliquots of two samples, SC 2 and SC 5, were leached in cold 3M HCl for three hours, washed and dried, with the object of removing calcite and incorporated trace elements (Smith, 1978). The data in Table 67A,B indicate no significant change in the Ga and Al contents for SC 2 but a significant decrease in Ga for SC 5. The changes in the Ga/Al ratio are not significant. Smith et al. (1978) noted unexpected changes in the concentrations of other trace elements besides Ga, and although unable to offer any acceptable explanation, they considered it possible that some clay minerals dissolved in addition to the calcite. As has been mentioned earlier, it is most unlikely that significant amounts of Ga would be present in the calcite.

A number of samples in Table 67 and Fig. 123 fall outside the regions indicated for the various rock types, e.g. SC 2A and 14J for basaltic komatiites Barberton type, and 87J and 88J for peridotitic komatiites. 14J is known to be epidote-rich (Smith, 1978). 87J and 88J are highly altered and consist of chlorite, serpentine, amphibole and magnetite with ~5 volume % epidote, which is exceptionally high compared to the other peridotitic rocks.

Of the remaining rocks that appear to have anomalously high Ga contents relative to Al, HSS 32 contains abundant huge plagioclase crystals but otherwise appears a normal Badplaas basaltic komatiite, while HSS 27 is exceptionally rich in orthopyroxene phenocrysts. Viljoen and Viljoen (1969) classified sample TS 1 as a metatholeiite, but the Ga content of 9.9 ppm and Al of 6.26% place it in the Barberton type basaltic komatiite field. According to Smith (1978) other trace elements also indicate this sample to be a basaltic komatiite and it has been classified as such in this work. The single basaltic komatiite from the Kromberg formation, M 57, has a high Ga/Al ratio of 2.88 and has been reclassified from a high-Mg basalt (Viljoen and Viljoen, 1969) to a komatiite (Smith, 1978). The high Ga content and Ga/Al ratio may possibly be ascribed to epidotisation.

Smith et al. (1978) consider that, among a number of other elements, Ga is susceptible to alteration and is of limited use for interpreting primary characteristics of lavas from greenschist facies terrains. They also state that excessive development of epidote may be difficult to detect in the altered rocks. The slightly different interpretation presented here indicates that provided the Ga/Al ratio is used in conjunction with the Ga content, then Ga can be useful in those cases where no epidotisation has occurred. Changes in the Ga content and Ga/Al ratio can be used in a positive manner to monitor possible epidotisation, i.e. an increase in both Ga and the Ga/Al ratio would suggest that epidotisation had taken place.

A number of metabasalts and metatholeiites from the Komati, Hoogenoeg and Kromberg formations have been analysed for Ga, and the data plotted in Figs 123, 124 and 125. The Ga values range from 10 to 18 ppm, but the majority of values fall in a more restricted range of 10-13 ppm. Metatholeiites from the Komati formation show the most extreme range in both Ga and Al, sample HSS 34, which contains abundant clinopyroxene phenocrysts, actually plotting within the field of massive Barberton type basaltic komatiites. The carbonated pillow V 13 from the Hoogenoeg formation has a higher Ga content and Ga/Al ratio than all other metatholeiites. As the increased Ga content is unlikely to be associated with the carbonate, epidotisation may also have occurred. In general, as a group, the Barberton metatholeiites have amongst the lowest Ga/Al ratios for any tholeiites analysed in this work (see Fig. 73).

For the metabasalts, as for the metatholeiites, there are two groups, one with a Ga/Al ratio of about 1.6 and another with a ratio of 2.3, similar to that of the ultramafic rocks. The single sample falling outside these two groups, LV 6, is a peculiar rock (Smith, 1978) in terms of the concentration of many trace elements besides Ga. It is noticeable that all samples of metabasalt from the Hoogenoeg and Komati formations fall in the group of lower Ga/Al ratio, while all the Kromberg formation rocks have a higher Ga content and Ga/Al ratio, as did the single basaltic komatiite from this formation. Rocks from the Kromberg formation are the youngest in the Onverwacht group analysed in this work and are possibly more differentiated than those of the other formations, which could result in a higher Ga/Al ratio. Smith (1978) reports that all those metatholeiites and metabasalts with a Ga content greater than 14 ppm are also characterised by having high Ti and Zr contents. The significance of this correlation is not presently understood. However, the fact that the same three elements are enriched in the metasomatised veined nodules from Matsoku Pipe, suggests that the basaltic rocks enriched in these elements may have been derived from mantle containing material similar to that found in the veined nodules.

In spite of variations due to varying degrees and types of alteration, Smith (pers. comm.) has indicated that Ga is among the few trace elements, namely Zr, Y, Sc, Co, Cr, V, Ni and Ga, that have proved to be useful in his study of the Barberton Mountain Land rocks.

In a study of gabbro/amphibole transitions in South Norway, Field and Elliott (1974) reported that Ga seemed to remain immobile during metamorphism, although their data indicated a slight decrease in Ga in the amphibolite.

Herrmann et al. (1976) determined major elements and a number of trace elements, including Ga, in nine ultramafic rocks from the Barberton greenstone belt. Their data were determined by INAA with a 3% counting error ($1s_c$) for Ga and are in excellent agreement with those presented here. They considered, on the basis of very few samples, that a fractional crystallization relationship between the basaltic and peridotitic komatiies was unlikely on the basis of high Ni concentrations in the rocks and variations in the patterns of light and heavy REE, and preferred partial melting of an upper mantle source. Although this is in conflict with the concept of fractional crystallization discussed earlier, the remarkable constancy in the Ga/Al ratio seems to favour the concept of fractional crystallization.

Smith et al. (1978), on the basis of the Zr/Nb ratios found for the Komati formation pillows, suggest that these lavas were derived from a depleted source area with respect to modern oceanic island basalts, but similar to average mid-ocean ridge tholeiites. The low Ga/Al ratio of meta-tholeiites with respect to most oceanic tholeiites has already been pointed out, and the Ga/Al ratio of the metabasalts is significantly lower than oceanic island basalts, 1.6 as against 2.5, which adds support to the suggestion that these lavas have been derived from a source area depleted in Ga as well as other elements. Alternatively, the rocks may have been derived from a primitive mantle that had a different composition with respect to certain elements than present mantle material.

Ga has been determined in a number of the ancient acid intrusive rocks (2.2-3.3 Ma) from the Barberton Mountain Land. The data are presented in Table 67L,K and Figs 123 and 124. Condie and Hunter (1976) and Glikson (1976) reported major and trace element studies on similar rocks, but did not determine Ga. Ga is fairly uniform in the older rocks (3.0-3.3 Ma), between 14.6 and 17 ppm Ga, with the Ga/Al ratio remaining constant, within experimental error, at 2.05. In one sample from the Mpageni pluton, AA 3, Ga is lower (12.5 ppm). Unfortunately no Al data are available for this sample. Although the granitic rocks can be divided into several geochemical groups on the basis of other trace element data, the variation in the Ga data is so slight that the differences are not significant.

CHAPTER 16

GALLIUM IN CONTINENTAL BASALTIC ROCKS, MOSTLY MESOZOIC THOLEIITES

Ga has been determined in a number of continental basaltic rocks (mostly Mesozoic tholeiites), and a few associated acidic rocks, from Antarctica, Tasmania, Greenland, Brazil and southern Africa. The data are given in Tables 68-74 and summarised for dolerites and tholeiite basalts in Table 75. Sample locations for southern African rocks are plotted in Fig. 127 and Ga versus Al in Figs 128-130. Sample locations of the Brazilian rocks are plotted in Fig. 131 and Ga versus Al in Fig. 132.

No Al data or other details are available for the four Greenland and two Californian basalts listed in Table 68, and the data have been used only to widen the spread of localities from which basaltic rocks have been taken. Similar comments apply to the Tasmanian dolerites and granophyres in Table 69, and the Borg dolerites and basaltic dykes from Queen Maud Land, Antarctica, in Table 70. The Queen Maud Land tholeiites (Borg dolerites) and the dolerite dyke cutting the Premier kimberlite pipe are of interest because they are Precambrian rocks which allow a comparison between these ancient rocks and the younger Mesozoic rocks from southern Africa and Brazil. Unfortunately no Al data are available for the Precambrian rocks. A number of Umkondo dolerites (Table 72) from the eastern part of Rhodesia, also of Precambrian age, have been analysed for Ga as well as Al and are therefore of more use for comparative purposes. The Umkondo dolerites are remarkably uniform in Ga content, both Ga and Ga/Al having a c.o.v. of 7-8%. The dolerite dyke J.DY 4A, which Erlank (pers. comm.) considers a possible feeder to the lavas, has a high TiO_2 and total Fe (expressed as Fe_2O_3) content relative to the other rocks, which suggests the probable presence of titanomagnetite;

5% of titanomagnetite could introduce ~4 ppm Ga into the rock, which is sufficient to account for the high Ga and Ga/Al ratio of this sample. Ga is plotted against Al for the Umkondo rocks in Fig. 130. There is a very slight increase in both Ga and Ga/Al ratio with increasing D.I..

A number of workers have studied the Mesozoic Karroo rocks of southern Africa in considerable detail (Cox and Hornung, 1966; Cox et al., 1967; Erlank, 1971; Cox, 1971, 1972; Cox and Jamieson, 1974; Erlank et al., 1977, 1978; and Walker and Poldervaart, 1949) amongst many others. Ga data on rocks from this area have been reported by Nockolds and Allen (1956), Cox and Hornung (1966) and Cox et al. (1967) for Karroo dolerites from the Central area, Lesotho, Swaziland and Nuanetsi (Fig. 127). The coverage has been extended in this work to include samples from the Rhodesian area (Tuli, Featherstone, Nyamandhlovu and Wankie), Botswana, and northern and southern South West Africa. Unfortunately in some instances, e.g. Botswana, only one or two samples were available.

Cox and co-workers divided Karroo basic rocks into two provinces, one in the north (Rhodesia and northern Lebombo) and the other in the south (Swaziland, Lesotho and Karroo dolerites of South Africa). Erlank and co-workers extended this concept of geochemical provinces by including volcanics from Botswana with the northern group. Volcanics from the northern Transvaal and southern S.W.A. showed close mineralogical and geochemical affinities with basalts and dolerites from the central Karroo area and were included with them, while lavas from northern S.W.A. formed a third distinctive geochemical province. The Ga data lend strong support for the division into three provinces.

Data for rocks from the central area are presented in Tables 73A,B (area 1 in Fig. 127) and in Table 73C for the southern Lebombo-Swaziland area (area 2 in Fig. 127). Ga is plotted against Al, and Ga and Ga/Al against D.I., in Fig. 128. There is considerable variation in both Ga and

Ga/Al ratio for these rocks, although the data cluster about a Ga value of 16 ppm and Ga/Al ratio of 2.0. Four samples at 60m intervals from the base to the top of the main dyke in the Spitskopvlei area (Table 73A) show no variation in either Ga or Ga/Al ratio outside analytical error limits and all results are within $2s_c$. Similarly, the feeder dolerite dyke KL37 and basalt KL38 have almost identical values for Ga and Ga/Al ratio. There is no systematic variation in Ga/Al ratio with D.I. for these rocks, nor for Ga if the single sample of picrite is excluded. It should be noted that the highest Ga/Al ratio for a basic rock from the Central area is 2.63. The two acid volcanic rocks from the Swaziland area for which Al data are available show a strong enrichment in Ga and Ga/Al ratio, and all four acid lava rocks from the southern Lebombo area have similar Ga contents (Table 73C). The Ga data differ from the results for other trace elements reported by Erlank (1969) who found similar inter-element ratios (K/Rb, Th/U, U/K, Th/K) on the same samples for both the acid and basic rocks from this area. A feature of some Karroo tholeiitic igneous rocks is the tendency for the Ga/Al ratio to increase with increasing differentiation, according to Nockolds and Allen (1956), in contrast to alkali series rocks in which rhyolites tend to have a lower Ga/Al ratio than more basic rocks. For many other tholeiitic sequences the Ga/Al ratio remains constant or decreases slightly with increasing differentiation (e.g. Okonjeje), which suggests that the acid rocks in the southern Lebombo-Swaziland region are not directly related to the basic rocks. Rocks from the alkali suite (Okonjeje) also differ from other alkali rocks, as both Ga and the Ga/Al ratio increase strongly in late stage rocks. In Fig. 128 the area occupied by Umkondo dolerites has been outlined, and it is interesting to note that the Umkondo dolerites, although Precambrian in age compared with the age of 150-190 m.y. of the Central Karroo rocks, have very similar Ga and Al contents.

Data for rocks from the northern province are given in Tables 73D-F and are plotted in Figs 129 and 130. The localities other than Nuanetsi will be considered first. Ga in the Wankie basalts increases strongly from 19 to 28 ppm with increasing D.I. in a very uniform manner (Fig. 129), as does the Ga/Al ratio, the ratio showing a marked increase from 2.6 to 4.2. The trends are very similar to those found for the Bouvetoya and Easter Island rocks (Figs 87 and 88). The basalts from Nyamandhlovu, the single sample from Tuli and the basalt and dolerite from Botswana all plot on the same trend lines as the Wankie rocks. Of the three rocks from the Featherstone area, KLR 11 plots with those from other areas, while the remaining two indicate possible accumulation of pyroxene which would hardly alter the Ga/Al ratio but would lower the Ga content. The trend line of the Nuanetsi rocks is shown for comparison and falls very close to the trend line followed by the Featherstone rocks.

Data for the Nuanetsi rocks are plotted in Fig. 130 together with those for the Umkondo and other northern province rocks. Sample N 340, an interbedded basalt in rhyolites, is a 'peculiar' rock being deficient in many other trace elements besides Ga (Erlank, pers. comm.). The anomalous nature of this sample is obvious both in Table 73F and Fig. 130 and it is excluded from the following discussion. The remaining basic rocks from Nuanetsi fall on a well defined trend line on the Ga-Al plot. There is, however, no trend of increasing Ga or Ga/Al ratio with increasing D.I. as was found for the other areas. Cox and Jamieson (1974) have suggested that the probable process of formation of the Nuanetsi rocks is one of equilibration of liquids with excess harzburgite wall-rock over a pressure range of 6-12 kbar. An alternative process is one of polybaric crystal fractionation of olivine and orthopyroxene. The Ga data do not make it possible to differentiate between these two processes.

The difference between the Precambrian Umkondo dolerites and the Mesozoic basic rocks of the northern province is clearly evident in Fig. 130.

It should be noted that none of the northern province rocks has a Ga/Al ratio less than 2.60.

The position of the Nuanetsi rhyolites in Fig. 130 is interesting when compared with the acidic rocks from the southern Lebombo. It was noted when discussing the latter samples that Ga was enriched in the acidic rocks resulting in an increased Ga/Al ratio, contrary to the usual trend followed by tholeiitic sequences. In the Nuanetsi rocks the trend is normal, i.e. the rhyolitic rocks do not increase in Ga content and the Ga/Al ratio remains constant or decreases slightly.

The data for rocks from S.W.A. are given in Table 73G and plotted in Fig. 128. There is a marked difference between the rocks from the northern and southern parts of S.W.A., with those from southern S.W.A. having a Ga/Al ratio of about 1.9, while those from northern S.W.A. have a ratio of about 2.5.

The rocks from the northern part all come from the Etendeka Plateau (Fig.127). Samples KLS 22 and 24 were collected from the northern edge of the plateau from the first and third flows above the Damara sediments. The remaining samples were collected at various heights below Tafelberg Peak, between 3750' (KLS 16) and 5075' (KLS 20). Of the two rhyolites, KL 13 was collected between KLS 16 and KLS 19 at 4280', while KL 20 was the highest flow just below Tafelberg Peak at a height of 5575'. There is no significant difference in either the Ga content or Ga/Al ratio of the basalts and dolerites and the corresponding values for the rhyolites are also very similar. Following the trend of the Nuanetsi rocks, the rhyolites have slightly lower Ga contents and Ga/Al ratios than the mean values for the basic rocks.

Data for rocks from the Parana volcanics in Brazil are reported in Table 74 and are plotted in Fig. 132. Sample locations are given in Fig. 131. Sample BRA 10 was not analysed. These rocks also group into northern and southern groups, on the basis of their Ga/Al ratios, with the exception of the northern dolerite BRA 9 which has a ratio similar to those of the dolerites of the southern group. It is noteworthy that although the dolerites from both groups are similar in both Ga and Ga/Al ratio, the Ga contents and Ga/Al ratios of the two groups of basalts are quite different. As was the case for the rhyolites in northern S.W.A. and Nuanetsi, the Ga contents and Ga/Al ratios in the acidic rocks are slightly lower than in the basic rocks. Very few samples from this area have been analysed for Ga, and the analysis of further samples is necessary to confirm the comments and rather arbitrary division into northern and southern groups made above.

For ease of comparison, the data for both dolerites and basalts from various areas have been averaged and the mean values for Ga and the Ga/Al ratio are listed in Table 75. Before discussing these data in detail, it should be pointed out that the early data reported on the Karroo rocks (Central area) by Nockolds and Allen (1956) are higher than those reported here by approximately 50%, which resulted in a change of similar magnitude in the Ga/Al ratio from 2.0 to 3.0. Cox et al. (1967) and Cox and Hornung (1966) reported Ga data for the Lesotho, Swaziland and Nuanetsi rocks which are in good agreement with those given here. They reported no significant differences between the provinces for a number of elements, including Ga, but omitted consideration of the Ga/Al ratio. They were probably mislead to some extent regarding Ga because they included the Nockolds and Allen data which cause the Karroo Central area dolerites to appear very similar to those of the northern province.

In Table 75 it is clear that, except for the northern part of the Parana province and the Botswana samples, for which only one sample each of dolerite and basalt are available, there is no marked difference in either Ga content or Ga/Al ratio for average dolerite and basalt within any one area, and therefore dolerite and basalt can be considered together. The data for Ga and Al from the northern and southern provinces, as postulated by Cox and co-workers, have been plotted in Fig. 133. There is almost no overlap between rocks from each province and a Ga/Al ratio of 2.63 serves as a useful dividing line between the two provinces. Samples from southern S.W.A. plot squarely in the field of the southern province, while rocks from northern S.W.A. straddle between the northern and southern provinces. However, in Table 75, northern S.W.A. forms a definite group of its own.

As reported by Erlank and Duncan (1977) for other elements, the Ga data indicate close similarities between the northern S.W.A. province and the southern Parana Basin in Brazil. The dolerites from the northern Parana Basin appear similar to those from the two areas just described, but the basalts appear more closely related to those of the northern province. There is no apparent correlation of Ga or Ga/Al ratio with the age of the rocks for any group. In fact the constancy of the Ga content of dolerites from Precambrian age to those of 120 m.y. age is remarkable.

Although the acidic rocks are not included in Table 75, when they are considered in a similar way, the rocks from the southern Parana Basin are very close in both Ga and Ga/Al ratio to those from northern S.W.A., but are very different from those of the southern Lebombo (Fig. 133). The rhyolites from Nuanetsi are intermediate between the two previous groups in terms of Ga/Al ratio, but plot in the Ga/Al field of the northern province, i.e. the ratios are greater than 2.63.

Since this work was completed Bristow (1978) has determined Ga in a number of samples from the Central area, southern and northern Lebombo, and the northern province. Frequency distribution diagrams of the Ga/Al ratios for Bristow's samples and those from Tables 73 and 74 are plotted in Fig. 134. The extra data confirm the earlier conclusions, namely that rocks from the southern Lebombo have Ga/Al ratios similar to those of the rocks from the Central area, while the ratios for rocks from the northern Lebombo are similar to those of the northern province. Rocks from the "heel" of the southern Lebombo are intermediate between those of the northern and southern parts in terms of their Ga/Al ratios. The rhyolites from the southern Lebombo have distinctly higher Ga/Al ratios than the basic rocks, and the Ga data confirm the conclusions of Erlank and co-workers that the rhyolites cannot be derived from the basic rocks.

Erlank (1971), in investigating the geochemistry of Karroo-type basic rocks, pointed out, on the basis of variations in K/Rb, Th/K and Sr^{87}/Sr^{86} ratios, the importance of the role of crustal contamination in affecting the chemical composition of these rocks. He pointed out the similarities between the basic lavas from the northern S.W.A. province and those from the southern Parana Basin and concluded that, if they had all been derived from mantle material having the same inter-element and Sr^{87}/Sr^{86} ratios, then the degree of contamination must also have been similar, a remarkable coincidence in terms of the volumes of lava and large areas involved. However, further work by Erlank and co-workers has led them to conclude that the Karroo basic rocks have been derived from inhomogeneous upper mantle and lower crustal sources, and the acid rocks from a relatively homogeneous crustal source region. If the lavas from the Central area are taken as a point of reference (mean D.I. = 27), then it is interesting to note that the lavas from the southern S.W.A. area have a similar mean D.I. (24), while those of the northern S.W.A. area have a mean D.I. of 36 and are more differentiated. The lavas from the Parana Basin have variable D.I's, the numbers of samples are small, and no significant pattern is apparent. The mean D.I. for the northern province is 31, although again there is a wide spread of values. It is possible that the slightly higher Ga content and Ga/Al ratio of the northern S.W.A. lavas, as compared with those from southern S.W.A., simply reflect the more differentiated nature of the northern rocks. This argument cannot be applied to the Brazilian rocks, nor to those of the northern province, and the Ga data presented here emphasise the fact that the rocks from the northern province are enriched in many of the incompatible elements, as reported by Cox and co-workers and Erlank and co-workers. The Ga data also confirm that it is impossible to relate the increased Ga content of these rocks to crustal contamination, as there are no rocks of sufficiently high Ga content that could have caused the measured degree of contamination, i.e. about 6 ppm Ga relative to rocks from the Central area.

Ga and Al data for all continental basalts analysed in this work have been plotted in Fig. 135. The remarkable range of the Ga data is obvious, from about 11 ppm for the Barberton metabasalts of the Lower Ultramafic Unit to 29 ppm for the chilled Botswana basalt. With the exception of three Rhodesian rocks, the spread in Al is relatively small. The 'peculiar' nature of sample LV6 was discussed in Chapter 15.

The depleted nature, in terms of Ga content, of the rocks of the Lower Ultramafic Unit in the Barberton Mountain Land is obvious, as is the relatively low Ga/Al ratio of the rocks from the Central area and southern S.W.A. It is worth noting that Patterson and Swaine (1957) reported a range of Ga for Tertiary dolerite plugs of north-east Ireland of 15-25 ppm with a mean Ga/Al ratio of 2.1, similar to that found for the Central area. The Kromberg metabasalts are similar to those of northern S.W.A., and it is interesting to speculate whether the differences between the two Barberton groups are due to differentiation, leaching of Ga from the Lower Ultramafic Unit rocks, or epidotisation of the Kromberg rocks, or whether the increase in Ga in the Kromberg rocks is the result of these rocks tapping a different source area in the mantle, as has been suggested for the different provinces in the Mesozoic rocks. On the basis of data from a single element, Ga, it is not possible to answer these questions.

CHAPTER 17

GALLIUM DISTRIBUTION DURING THE WEATHERING PROCESS

17.1 GALLIUM IN WEATHERED GRANITES AND MINERALS FROM THE CAPE PENINSULA

Gallium has been determined in the rocks, biotites and feldspars of fresh, partly weathered and weathered granites from three localities in the Cape Peninsula. Sample localities are given in Fig. 136 and the data are reported in Table 76. The Sandy Cove site is about 50m from the sea, while the Kloof Nek site is 300m above sea level.

The Cape granite is a light grey porphyritic rock intrusive into sediments of the Malmesbury Series and has been dated by the Rb/Sr method at 553 ± 8 m.y. (Allsopp and Kolbe, 1965). Kolbe (1966) carried out the first systematic trace element study on the Cape granite plutons, and considered that they formed from a typical high-level fractionated magma with further strongly increasing degrees of differentiation outwards towards the finer grained margins of the granite bodies. During intrusion the granite was contaminated to various degrees by the predominantly argillaceous Malmesbury Series sediments. On the basis of trace element data, Kolbe considered it unlikely that the K-feldspar phenocrysts in the Cape Peninsula granite formed by a general late-stage potash enrichment. He also stated that it appeared possible, but unproven, that the Cape granite was formed by mobilisation of Malmesbury sediments at depth with subsequent differentiation and intrusion.

Brunke (1973) reported no petrographic difference between the Kloof Nek and Sandy Cove granites, but the presence of trace quantities of small crystals of tourmaline in the Miller's Point granite. All three localities were free from xenoliths and at all three sites the zones of fresh, partly weathered and weathered rock were separated by no more than 30m.

Brunke (1973) reported that the biotite separates contained trace amounts of muscovite and that the feldspar separates, which consisted of both plagioclase and microcline perthite, contained some quartz grains ($<5\%$). Brunke also reported that XRD analysis of the rock samples showed the presence of kaolinite in the weathered samples and also in the Kloof Nek and Miller's Point fresh and partly weathered samples, and that the plagioclase was removed at a faster rate than the microcline perthite during the weathering process. He reported that there were no kaolinite reflections in the XRD traces of the feldspar fractions. Pronounced chlorite peaks were present in the fresh biotites, but were absent in the weathered biotite fractions, and Brunke presumed that the 'weathered' chlorite was removed during washing of the powders prior to magnetic separation of the biotite. He also stated that thin section analysis indicated the presence of altered biotite and chlorite in the fresh rocks.

Major element data from Brunke (1973) have been used to calculate Barth Mesonorms, and proportions of selected minerals from these calculations are tabulated in Table 77. In the rock samples from all three sites the plagioclase minerals are the first to weather, accompanied by an increase in the amount of corundum, which in this instance can be taken to represent kaolinite, from fresh to weathered granite. The orthoclase or potash feldspar (microcline perthite) is less susceptible to weathering and actually increases in the Kloof Nek granite, but decreases in the most weathered material at the other two sites. The biotite remains essentially constant, increasing slightly with increase in weathering in the Miller's Point granite. The relatively greater stability of the perthite relative to plagioclase is shown by the initial increase in its concentration in the partly weathered samples from Kloof Nek and Sandy Cove.

The Ga data for biotites given in Table 76B are inconsistent for the three granites. For the Sandy Cove and Miller's Point biotites the Ga content varies in a similar manner, i.e. a decrease of about 15% in the weathered and partly weathered rocks, while the Kloof Nek biotite has a slight increase in Ga. Since Al increases slightly with increasing degree of weathering, the Ga/Al ratio decreases for Sandy Cove and Miller's Point biotites and does not change between the fresh and weathered biotite from Kloof Nek. Kolbe (1966) also analysed biotites from the Cape granites and reported much lower Ga values (mean = 35 ppm). The reasons for the differences are unknown, but perhaps the optical spectrographic method used by Kolbe suffered from matrix effects when comparing biotite micas with the rock standards used to calibrate his data. Kolbe (1966) gave an average modal analysis for 17 coarsely porphyritic granites from the Cape as

Quartz	29%
Microcline perthite	28%
Plagioclase	30%
Biotite	9%
Muscovite	3%
Magnetite	1%

Using mean Ga contents of the fresh biotites and feldspars from Tables 76 and 77 (63 and 15.5 ppm respectively), average Ga values for muscovite and magnetite from Table 37, and combining percentage perthite and plagioclase, it is possible to calculate the expected Ga content of the average coarsely porphyritic Cape granite. The calculated value of 17.7 ppm Ga is very close to the mean of the measured values for the fresh rocks of 17.9 ppm. If Kolbe's value of 35 ppm for the biotite is used in the calculation, the Ga content of the rock works out to be 15.1 ppm Ga. The results indicate that a Ga content of about 60 ppm for the Cape granite biotites is reasonable, although somewhat higher than average for granitic biotites (Burton and Culkin, 1972).

The Ga content of the separated feldspars (Tables 76B and 77) behaves in a similar but opposite manner to that of the biotites, i.e. the Sandy Cove and Miller's Point feldspars increase in Ga with increasing weathering, while those from Kloof Nek show a slight decrease in the partly weathered feldspar followed by an increase in the weathered material. The increase in the Ga content of the feldspar fraction with increasing degree of weathering is at first thought somewhat surprising. Ga is reported to be more mobile than Al during weathering and the Ga/Al ratio tends to decrease rather than increase as it does here.

Mean Ga contents of microcline, microcline perthite and plagioclase are respectively 31, 33 and 31 ppm (Table 37), and corresponding Ga/Al ratios are 2.8, 3.4 and 2.0. If, as Brunke (1973) reports, the plagioclase weathers first from the microcline perthites, then it would be expected that the Ga content of the feldspar should remain fairly constant but that the Ga/Al ratio would increase. The removal of anorthitic plagioclase early in the weathering process would also increase the Ga/Al ratio as albite has a much higher ratio than anorthitic plagioclase (Table 37). In all samples reported here the Ga/Al ratio does increase with weathering, but only to a limited degree.

There are almost no data on Ga in clay minerals. Goldschmidt (1954) reported Ga in kaolinite to vary between 4 and 37 ppm, Wolfenden (1965) reported a mean value of 23 ppm (20-25), Ga/Al = 1.4 (1.3-1.5), for five samples from Malaysia, and McLaughlin (1955, 1959) reported Ga contents for impure kaolinites of 7 ppm Ga and a Ga/Al ratio of 0.4 (0.3-0.5). The Ga data for kaolinites reported by McLaughlin are very low, and a mean value of about 25 is more likely. The formation of some kaolinite, as indicated in the mesonorms, would increase the Ga content of the feldspar fractions but have little effect on the Ga/Al ratios.

The results for the whole rock samples are given in Table 76A. Ga increases with increasing weathering by 15-35% relative to the fresh rocks. There is no significant change in the Ga/Al ratio between fresh and most weathered samples for the Kloof Nek and Sandy Cove granites, but the Miller's Point granite shows a significant increase in the ratio for the weathered rock. There is no immediately apparent reason for the difference in behaviour except that the Miller's Point granite has a much greater initial content of potash feldspar than the other two granites.

The data reported here emphasise the paucity of Ga data in minerals altered during the weathering process, in direct contrast to the abundance of data available for minerals in fresh igneous rocks. The work of Butler (1953) has already been referred to when discussing Ga in tourmaline. He reported that weathering of adamellite resulted in a loss of Ga during alteration, although he compared rock and derived soil. It is possible that further weathering of the Cape granite would result in a loss of Ga relative to Al. Many authors (Burton and Culkin, 1972) report contrasting trends for variation of the Ga/Al ratio during the weathering process. The trend is obviously strongly dependent on the types of mineral present, differences in rate of breakdown in relation to rate of formation of residual minerals, and possibly also on Eh-pH conditions. Without good data on all minerals present in the rocks examined, it can be difficult to draw accurate conclusions as to the changes involved during the process of alteration. The considerable difficulties involved in mineral separation, far greater for weathered material than for fresh, have no doubt mitigated against work being carried out in this field.

17.2 SEDIMENTARY ROCKS FROM THE MALMESBURY SERIES, CAPE PROVINCE

Ga has been determined in argillaceous and arenaceous sediments of the Malmesbury Series which have undergone varying degrees of weathering or alteration, and also in separated clay fractions ($< 2\,\mu m$) from the same samples. The data are reported in Table 78 and sample locations are given in Fig. 137.

Walker and Mathias (1947) described the sediments of the Malmesbury Series in the vicinity of Cape Town as consisting of two main types, arenaceous greywackes and argillaceous shales, commonly interleaved, and of mixtures between the two main types. The apparent age of the Malmesbury Series is given as 595 ± 45 m.y. (Allsopp and Kolbe, 1965).

The fresh argillaceous shales from two different locations reported in Table 78A contain similar concentrations of Ga, 23.4 and 25.4 ppm (Ga/Al = 2.5). In Table 79A Ga data for seven further samples of argillaceous material from widely dispersed locations are reported, with a range of 21.3 to 27.2 ppm Ga (mean = 23.6 ppm) and a mean Ga/Al ratio of 2.5. The fresh arenaceous greywackes contain considerably less Ga, as a result of dilution by quartz, with values in Table 78A of 11.8 and 12.6 ppm Ga and in Table 79A from 11.5 to 13.5 with a mean value of 12.6 ppm Ga and a mean Ga/Al ratio of 2.0, significantly lower than that for the argillaceous samples. The difference between the two types of sediment is clearly defined both in Ga content and the Ga/Al ratio.

Ga and the Ga/Al ratio decrease steadily with increasing degree of weathering for the argillaceous material from the Peninsula Quarry, while there is no change in either Ga content or Ga/Al ratio for the arenaceous samples.

The three argillaceous samples from the Gran Sasso Quarry (ML10, 11 and 13) have similar Ga/Al ratios, although ML13 has considerably higher Ga and Al contents, due to a lower quartz content and the presence of a major quantity of kaolinite (Topping, 1972) which is absent from the other two samples. Although Topping (1972) described ML11 as a fresh rock, the weathering index (Parker, 1970), defined as 100 times the sum of the atomic proportions divided by the respective bond strengths with oxygen of Na, Mg, K and Ca, indicates little difference between the three samples. The application of Parker's weathering index to sediments may be questionable, but it is useful as a guide to the amounts of Na, K, Ca and Mg which remain in the rock after weathering. In this respect it is not possible to place both argillaceous and arenaceous rocks on the same scale, as fresh argillaceous rock will have a much greater weathering index than fresh arenaceous rock.

The Ga results for the separated clay fractions (Table 78B) are interesting. Topping (1972) reported only trace quantities of quartz in a few of the samples and minor feldspar in samples ML11 and 12. As would be expected, the Ga contents of the clay fractions are considerably higher than for the rocks as a result of the removal of quartz and feldspar. Only in the case of the two samples ML4 and ML13 is there no significant change between the rock and clay fractions. ML4 was reported as a clay in Table 78A.

There is a very sharp decrease in Ga/Al ratio for the clay fractions in going from fresh to weathered rock, both for the argillaceous and the arenaceous material. The Ga/Al ratios for three of the four clay fractions from fresh rock are between 3.3 and 3.7, greatly in excess of the average value for the clay fractions from weathered rock of approximately 2.4.

In Fig. 138 Ga shows a very good linear relationship with Al for the rocks, although the Ga/Al ratio is not constant. Sample ML4 is anomalous and falls off the trend line, but should really be plotted as a clay sample. The relationship between Ga and Al for the clay fractions is not so clearly defined, although the plot does suggest a slight negative correlation between the two elements. The Ga/Al ratio has been plotted against Al in Fig. 138 and immediately the striking difference between the clay fractions and the rocks becomes obvious. While for the rocks there is a slight increase in the Ga/Al ratio with increasing Al, in the case of the clay fractions there is a well defined negative correlation between the Ga/Al ratio and Al. Topping (1972) reported that Al increased with increasing degree of weathering, although the relationship is not a strong one (Fig. 138). Topping also reported that illite was the dominant clay mineral in both the fresh argillaceous material and the fresh arenaceous greywacke, kaolinite being absent or present in only trace amounts, while kaolinite became more prominent as the samples became more weathered. There is strong evidence for the separation and removal of Ga from the rocks, relative to Al, during the weathering process, i.e. during the alteration of feldspathic minerals to clay minerals, and during the alteration of illite to kaolinite.

Hirst (1962) reported that in the Gulf of Paria the constancy of Ga/Al ratios in sediments from the river delta and from the Gulf suggested that Ga entered the basin structurally combined within the lattices of the degraded clay minerals, and that the similarity between the Ga/Al ratios for igneous source rocks and the sediments indicated little separation of Ga from Al during weathering and transportation. Hirst also suggested that the greater constancy of the Ga/Al ratio compared with that of the Ga/(Na+K) ratio indicated that the coherence of Ga was better with the total clay content rather than with the illite plus montmorillonite, assuming the bulk of Na and K was sited in these two clay minerals. He therefore suggested that a considerable proportion of the Ga replaced Al in kaolinite, contrary to the view expressed by McLaughlin (1959).

The data reported in Table 78B for the clay fractions provide indirect support for Hirst's suggestion.

On the basis that all the K in the clay fractions was present in illite, and that the illite contained 8.5% K_2O, Topping (1972) calculated the percentage of illite in each sample. The illite content of the fresh samples ranged from 98 to 73%, while for the very weathered samples the illite content dropped to between 25 and 40%. In samples ML4, 9, 15 and 17 the proportion of kaolinite exceeds that of illite. Although ML4 and ML15 have the lowest Ga contents and Ga/Al ratios amongst the clay fractions, the Ga concentration is still fairly high at 26-28 ppm, indicating that Ga must be present to a considerable extent in kaolinite. Calculations involving Topping's estimates of illite content, and assuming the balance of the clay fractions as kaolinite, indicate that the kaolinite has a Ga content of about 20-25 ppm compared with that of about 35 ppm for illite. The Ga/Al ratio for illite is about 3.3, while that for kaolinite is about 1.4, although the ratios are expected to vary considerably. Although the above calculations are not at all accurate, they do give some indication of the Ga content and Ga/Al ratio of kaolinite, and confirm that it has a very low Ga/Al ratio, although the Ga content is about average compared to many rock-forming minerals.

The data for kaolinite is in good agreement with that reported by Wolfenden (1965) on kaolinitic clays from Malaysia (Ga = 23, Ga/Al = 1.4). However, the need for good Ga data for the clay minerals is obvious.

CHAPTER 18

GALLIUM IN ROCKS FROM THE SEA POINT GRANITE-SLATE CONTACT ZONE AT CAPE TOWN

The granite-slate contact zone at Sea Point, Cape Town has been well known to geologists since the early nineteenth century and was visited by Charles Darwin. Few modern chemical analyses of these rocks have been published, the most recent being those of Walker and Mathias (1947), although Kolbe (1966) analysed some of the granites from the area. Erlank (unpubl.) has carried out an extensive geochemical study of these rocks, and Ga has been determined in some of his samples. The general geology and location of the area are given in Fig. 139 and a more detailed map of the contact zone at Sea Point is presented in Fig. 140 together with sample locations in that area. The Ga data are reported in Table 79.

At Sea Point the porphyritic biotite granite of the Cape Peninsula is intrusive into highly inclined, hornfelsed sediments belonging to the Malmesbury Series. The contact is a concordant one with much veining of the sediments and the production of spectacular migmatites in which large porphyroblasts of potash feldspar are conspicuous. In and outside the migmatite zone the contact aureole contains abundant spotted hornfelses and is seamed with veins of aplite, pegmatite and quartz. Xenoliths of Malmesbury sediments are common in the normal granite near the contact, show evidence of plastic deformation, and consist mainly of compact hornfelses. Some of these xenoliths are large, up to 60m long, but smaller rounded xenoliths are more common. Further from the contact zone many of the smaller xenoliths have undergone greater reaction with the magma and have a granitoid texture. They are generally slightly finer in grain size than the granite and are nearly always richer in biotite.

The Malmesbury sediments have already been described as being of two main types, argillaceous and arenaceous. The Sea Point contact is somewhat unusual in that, apart from subordinate argillaceous bands, the Malmesbury beds of the metamorphic aureole have a chemical composition similar to that of the granite, although slightly deficient in alumina and alkalis. Walker and Mathias (1947) pointed out that if the sediments recrystallized without appreciable addition of magma, they would form a similar phasal assemblage to that of the granite, and therefore gains and losses of chemical elements between sediment and magma were difficult to trace.

In Table 79B some samples are labelled WC, and these samples were ground in tungsten carbide vessels. It was pointed out in the chapters on analytical technique and sample preparation that the presence of tungsten in the sample could lead to a systematic error in the Ga determination due to interference by a W line on Zn and one of the background positions. For some of the xenolith samples only material ground in WC vessels was available, while for others material ground in both WC and agate vessels was available, which allowed for an estimate of the degree of error that might be introduced by W contamination. In all cases the difference between contaminated and uncontaminated material is less than $3s_c$ (counting error) and there is no systematic bias. Therefore the data for those samples which were only available with W contamination may be used with confidence.

Erlank (unpubl.) determined Ga in some of the samples analysed here by optical emission spectrography and the two sets of Ga data are compared in Fig. 141. Although there is a tendency for the optical emission results to be slightly lower than those reported here by XRF, the agreement is very good, especially for the hornfelses, xenoliths and granites. The OS data for the sediments in particular seem to be on the high side. The one sample from the Clifton xenolith, M22, is a dark band, consists mainly of biotite, and gives a very low OS result relative to that by XRF. The data for Ga in biotites reported by Kolbe (1966) have been shown to be low, and were also determined by OS.

The Ga data reported in Chapter 17.1 for the fresh Kloof Nek and Sandy Cove granites, which are from the same granite body that forms the contact (see Fig. 139), have been included in the Ga-Al diagrams with those for the coarse-grained granites reported in this chapter. The Ga data for the fresh argillaceous and arenaceous Malmesbury sediments in Chapter 17.2 have also been included with those reported in this chapter. Ga is plotted against Al in Fig. 141 and the majority of samples cluster around a mixing line between the argillaceous and arenaceous Malmesbury sediments. Exceptions are the hornfels xenolith M24, samples from the granitised xenolith from Saunders Rocks, and the Clifton xenolith. Mean values for each group of rocks are also plotted in Fig. 141 and fall very close to a mixing line between the two types of sediment.

It is noteworthy that both the fine-grained aplitic granite and the coarse-grained granite fall on the same mixing line. This may be fortuitous as a result of the similar chemistry of the granites and sediments, or may reflect the fact that the granite, as suggested by Kolbe (1966), was possibly formed by mobilization of the Malmesbury sediments at depth with subsequent differentiation and intrusion. In either case, the plot in Fig. 141 indicates that the arenaceous hornfelses, on the basis of Ga and Al data, can be considered a mixture of arenaceous sediment and coarse-grained granite, while the argillaceous hornfels and hornfels xenoliths together with the granitised xenolith from Bantry Bay can be considered a mixture of argillaceous sediment and either of the granites. The Saunders Rocks xenolith is enriched in Ga relative to Al, but has almost identical Ga contents to the Bantry Bay xenolith samples. Kolbe (1966) reported that the biotite-rich xenoliths from the Peninsula granite, although presumably of sedimentary origin, were slightly enriched in alkali elements. The Ga data would suggest that these two xenoliths, from Clifton and Saunders Rocks, are not relics of Malmesbury sediment but are perhaps relics of an earlier granite not exposed at the present time. It might be expected that other elements, e.g. alkalis, would be enriched together with Ga, but unpublished data (Erlank (pers.comm.) indicate that this is not the case. Sample M24, which is also enriched in Ga, is strongly depleted in K, Rb, Cs and Ba, but is enriched in Fe compared with the other hornfels xenoliths. The enrichment of Fe and Ga suggests the presence of magnetite in this sample. It should be borne in mind that there are considerable difficulties in sampling the xenoliths so as to obtain representative samples, and any sample with too high a proportion of biotite will have a high Ga content relative to other samples and a high Ga/Al ratio, together with high K and Rb.

Walker and Mathias (1947) suggested that feldspathization of the granite and migmatite zone by late potassic solutions gave rise to potash pegmatites and large crystals of perthitic microcline. Kolbe (1966) considered it unlikely that the K-feldspar phenocrysts were formed by a general late-stage potash enrichment. It seems likely that K enrichment would be accompanied by Ga enrichment and, except for two of the xenoliths and one hornfels, there is no evidence of Ga enrichment in the migmatites or granites. The Ga data presented here therefore confirm the conclusion arrived at by Kolbe on the basis of other trace element distributions.

CHAPTER 19

GALLIUM IN ROCKS FROM THE KUNENE BASIC COMPLEX, KAOKOVELD, S.W.A.

The Kunene Basic Complex, situated in northern Kaokoveld, S.W.A., was first mapped in detail by Köstlin (1967) and it forms that part of the Angola anorthosite mass which lies south of the Kunene River in S.W.A. The Complex forms only a very small portion of the anorthosite mass as a whole (Fig. 142). Köstlin (1967) considered the troctolite anorthosite which comprises the bulk of the Complex to have been intruded into older massive anorthosite (Adirondack type), as a result of the formation of ring fractures and subsequent large-scale faulting, which enabled the magma to be intruded in the form of a succession of concentric sheets (see Fig. 142). The troctolitic anorthosite (Bushveld type) is Precambrian in age. Various late- to postkinematic basic and ultrabasic intrusives, consisting of dunite and peridotite and their serpentinised equivalents, norite, troctolite and anorthositic gabbro, also form part of the Complex and are considered to be products of remobilisation of a deep-seated differentiate of the Complex.

Ga has been determined in a number of Köstlin's samples. The data are reported in Table 80 and plotted in Fig. 143.

Köstlin pointed out the homogeneity of the troctolitic anorthosite and the difficulty of establishing differentiation trends due to the lack of variation in the rocks. Although Köstlin reported significant differences in the major element chemistry of the massive and troctolitic anorthosites, he found their lines of descent on a triangular M-F-A diagram to be the same, which suggested a common line of descent for all the anorthosites. Nevertheless, he concluded on other evidence that they were unlikely to be descendants of the same parent magma.

The Ga data show little difference between all three types of anorthosite, namely the troctolitic, noritic and massive anorthosites. The mean Ga contents and Ga/Al ratios are, respectively, 16.7 ppm and 1.24, 19.2 and 1.27, and 17.9 and 1.25. The Ga/Al ratio for all types varies within experimental error, while Ga is slightly enriched in the noritic anorthosite. Only in sample F20 is Ga strongly enriched, and Köstlin considered this sample to be extensively altered. CIPW norm calculations indicate that this sample contains about 8% normative nepheline compared with 2-4% for the other massive anorthosites, and also contains about 4% magnetite (normative), double that of the other samples. Both nepheline and magnetite are minerals strongly enriched in Ga (Table 37), which would increase both the Ga content of the rock and the Ga/Al ratio.

Köstlin reported a slight increase in differentiation of the troctolitic anorthosite from the edge of the Complex to the centre, as indicated by the D.I's in Table 80A. The Ga data show a corresponding increase from about 14 ppm at the edge to 18 ppm at the centre, but no change in Ga/Al ratio (Fig. 143).

There are too few samples of the ultrabasic and basic rocks, peridotite and troctolite, to draw any definite conclusions on the basis of their Ga contents concerning their relationship with the anorthosites. However, they plot to close to a Ga-Al trend line through the anorthosites which would indicate pyroxene fractionation.

The basic dyke, sample F22, is younger than the Complex and the high Ga/Al ratio confirms that it is not genetically related to the rocks of the Complex. The ratio is similar to that found for the dolerites and basalts of the Etendeka plateau in northern S.W.A., namely 2.5.

The importance of the Ga data reported in this chapter lies mainly in the fact that, apart from three Ga values reported for anorthosites from the U.S.A. by Sandell in 1949 (Burton and Culkin, 1972) and a single value by Bell (1953), these are the only data for Ga in anorthosites reported to date. The agreement between the three sets of data is remarkable. Sandell reported a range from 19-21 with a mean value of 20 ppm Ga, Bell reported 20 ppm, and the mean of all determinations in this work is 18 ppm Ga. Sandell's reported Ga/Al ratio was 1.3 and that for this work is also 1.3. Considering the rather restricted mineralogical composition of anorthosites and the very small range found for Ga, the agreement between rocks from the U.S.A. and southern Africa is perhaps not so surprising.

In contrast, three metamafic anorthosites from Namaqualand have a much higher Ga content of 28-29 ppm (Table 81). Unfortunately no major element data are available for these rocks. The single biotite anorthosite has an even higher Ga content, due to the presence of the mica.

CHAPTER 20

GALLIUM IN ROCKS FROM THE ACTIVE CARBONATITE VOLCANO OLDOINYO LENGAI, TANZANIA

The active carbonatite volcano Oldoinyo Lengai, which lies south of Lake Natron in the Eastern Rift Valley of East Africa, is the youngest volcano in the Neogene volcanic province of northern Tanzania (see Fig. 144). It consists of a steep cone composed mainly of ijolitic or nephelinitic pyroclastics containing ejectamenta that indicate the presence of a carbonatite complex at depth. Interbedded with the pyroclastics are minor flows of nephelinite, phonolitic nephelinite and phonolite (Dawson, 1962b, 1966). The extrusive sequence of the volcano has been established as (Dawson, 1962b, 1966):

7. Carbonatite ashes of the 1966-67 eruption (Dawson et al., 1968)
6. Sodium carbonatite flows 1958-66
5. Variegated carbonate ashes of the active crater
4. Minor flows of nephelinite and melanephelinite
3. Black nephelinitic pyroclastics
2. Mica and pyroxene tuffs from parasitic cones
1. Yellow ijolitic pyroclastic rocks with interbedded phonolitic nephelinite and phonolite.

The extruded silicate lavas show a decrease in silica content with decreasing age, the lavas changing from phonolitic nephelinite and phonolite in the earlier stages to nephelinite and melanephelinite in the later extrusions. The trend in silica depletion reached a climax during the period 1958-1966 when sodium carbonate lava containing no silica was extruded. Dawson proposed the name "lengaite" for this lava, but this name has not yet been formally accepted.

Two hypotheses for the formation of the carbonate magma have been proposed: Koster van Groos and Wyllie (1966) suggested that lengaite may be the high-pressure immiscible fraction of a nephelinite, while Milton (1968) proposed that the carbonatite lavas were originally lake trona deposits, and he suggested that the trona was incorporated into an ascending nephelinite melt, with which it was immiscible, and extruded from the volcanic vent in a molten state.

Gallium has been determined in a number of rocks from Oldoinyo Lengai which were supplied by J.B. Dawson. The data are reported in Table 82 and Ga and Al data plotted in Fig. 145. The lavas are listed in their extrusion sequence, starting with the oldest. Plutonic rocks embedded within the yellow and black pyroclastics are included at the end of Table 82B.

Ga has been determined in three rocks from Oldoinyo Lengai by Bowden (Dawson, 1966) who found 50 ppm Ga in each of two phonolites and 30 ppm in a phonolitic nephelinite. The data for the phonolites are very high compared with those reported here.

Characteristic of the Ga contents of the lavas are their relatively high values, 23-35 ppm Ga, and high Ga/Al ratios from 2.5 to 4.6. The phonolites have a lower average Ga value of 27.4 ppm (Ga/Al ratio = 2.7) compared with those from the Nejoio Ring Complex in Angola (Chapter 21) which have a mean Ga content of 39.8 ppm Ga and Ga/Al ratio of 3.8. On the basis of their Ga contents and Ga/Al ratios, the lavas can be divided into three groups: the early phonolites and phonolitic nephelinites, which have a fairly constant Ga content of about 27 ppm increasing suddenly in the last of the phonolitic nephelinites to 34 ppm Ga; the last silicate flows (nephelinite) which have a constant Ga content of 31-35 ppm; and the carbonatite flows in which Ga was not detectable (<0.4 ppm). The Ga/Al ratios follow the same trends: in the early lavas it averages 2.7, increasing to 4.3 in the nephelinites and is not determinable in the carbonatites. Although there is a good positive linear correlation between Al and SiO_2 in the lavas, the correlation between Ga and SiO_2 is negative but poorly defined.

The plutonic rocks show a considerable range in Ga from 11.6 ppm in the ultramafic jacupirangite to 33.8 in the nepheline syenite, but all have a constant Ga/Al ratio between 3.4 and 3.6, which would suggest a common parent. In contrast, the data for the silicate lavas confirm the conclusion reported by Dawson and Gale (1970) on the basis of Th and U contents of these rocks, namely that the lavas are not a straightforward differentiation sequence. The silicate lavas show a negative correlation between Ga/Al and Al and it is possible, as suggested by Dawson and Gale, that they represent a mixture between nephelinite magma and crustal rocks, which would have to have a Ga/Al ratio of less than 2.5 and an Al content greater than 10%.

The Ga data for the carbonatite lavas confirm that Ga is present in igneous carbonates only in minute quantities (<1 ppm), although these carbonates may have been derived from lake trona deposits.

CHAPTER 21

GALLIUM IN ROCKS FROM THE NEJOIO AREA, ANGOLA

21.1 INTRODUCTION

In the Nejoio area, southern Angola (Fig. 146), the Precambrian granitic shield has been intruded by undersaturated alkaline rocks in the form of a ring complex. The intrusion caused fenitisation of the country rocks (Fig. 147). The country rocks are alkaline and subalkaline granites. Tension caused the formation of a ring fault, and the subsidence of the central block into a magma chamber resulted in the injection of the core feldspathoidal syenites. These syenites consist of amphibole-syenites, nepheline-amphibole-pyroxene syenites and nepheline-cancrinite-pyroxene syenites (Rodrigues, 1973). Continued tension resulted in further subsidence and the injection of a second pulse of magma consisting of nepheline syenites, nepheline-cancrinite-hackmanite syenites and cancrinite-hackmanite syenites. Following formation of the coarse-grained rocks of the ring complex, tension changed to compression causing another ring fault and injection of a tinguaitic magma, which carried with it xenoliths of fenitised granites and of the feldspathoidal syenites, and the formation of a cone-sheet breccia. A number of dykes in the area consist of dolerite, phonolite, tinguaite and alkali trachyte. The dolerites are the oldest and predate the ring complex, while the phonolites and tinguaites are thought to be part of the third intrusion. The trachytes are the youngest.

The fenites in the region are of two types, metasomatic and rheomorphic. The metasomatic fenites were classified into three groups by Rodrigues (1973), on the basis of a modal fenitisation index defined as

$$\text{F.I.} = \frac{\text{Biotite} + \text{amphibole} + \text{pyroxene} + \text{ore} + \text{apatite}}{\text{Quartz}} \cdot 10$$

using modal percentages of minerals.

21.2 THE RING COMPLEX

Ga has been determined in rocks from the ring complex and the data are presented in Table 83A-D. The D.I. of Thornton and Tuttle (1960) as used throughout this study did not, for these rocks, act as an efficient index for separating rocks of the three intrusions. Rodrigues (1973) showed that it was possible to correlate the effects of magmatic differentiation with those of endofenitisation, and by means of selected indices he was able to determine the crystallisation sequence of the rocks. The index he used was

$$\text{E.I.} = \frac{SiO_2 + K_2O}{FeO + MnO + MgO + CaO} \quad \text{(weight percentages)}$$

and this index has been used in place of the usual D.I. in Table 83A-D. The Ga, Ga/Al and Al data are plotted in Figs 148-150.

There are a number of interesting points to note in Table 83 and the corresponding figures.

The Ga contents of the rocks are extremely variable, not only between the three intrusions, but within each intrusion, and even within specific rock types. Al on the other hand is relatively constant, with the result that the Ga/Al ratio varies considerably from a minimum of 1.9 to a maximum of 7.0.

The rocks of the first intrusion have very high Ga/Al ratios, 4.0-5.8, higher than most nepheline syenites from the literature (Table 39A). In this intrusion the Ga contents and Ga/Al ratios within each rock type are fairly constant although only a few samples of each rock type were analysed. The second stage of the first intrusion resulted in a sharply increased Ga content which decreased slightly in the third stage rocks (Figs 148-150). The Ga/Al ratios follow a similar pattern, but the decrease in the ratio in the third stage relative to the second is more marked than that of Ga.

Most of the rocks of the second intrusion have much lower Ga contents and very much lower Ga/Al ratios than those of the first intrusion, the ratios being about half those of the first intrusion. Both the Ga contents and the Ga/Al ratios of the nepheline syenites are constant. However, those of the nepheline-cancrinite-hackmanite syenites and the cancrinite-hackmanite syenites are very variable, although the mean values for both groups of rocks are similar. It is not possible in terms of Ga to distinguish between these two rock types. It should perhaps be pointed out that those samples enriched in Ga, e.g. 10-39 and 13-30, are also enriched in other trace elements such as Zr and Zn.

Rodrigues (1973) did not distinguish between individual samples of phonolite and tinguaite, but considered them as a group. These rocks are the most differentiated of the complex and have very variable Ga contents and Ga/Al ratios. The cement of the eruptive breccias was considered by Rodrigues to be tinguaitic magma. The Ga data indicate that this could be the case as all the eruptive breccias have Ga contents and Ga/Al ratios between those of the phonolites and tinguaites and the rocks of the first two intrusions and the fenites (Fig. 148, Table 83).

The dolerites have normal Ga contents and Ga/Al ratios and the ratios are similar to those of dolerites from northern S.W.A. The trachytes are the most differentiated of the rocks reported here and have Ga contents and Ga/Al ratios similar to those of the second intrusion.

Fig. 149 indicates very weak correlations between Ga and Al for both the first and second intrusions. Calculated correlation coefficients (Pearson's r) for Ga-Al are 0.38 and 0.22 for the first and second intrusions respectively. Similar calculations for Ga and ($Al+Fe^3$) give r values of

0.67 and 0.18, and for Ga and $(Al+Fe^{3}+Na)$ r values of 0.79 and 0.04. There is therefore a marked difference between the behaviour of Ga in the two intrusions.

Rodrigues (1973) reported that one of the main differences between the two intrusions was the order of crystallization of hackmanite and pyroxene. In the first intrusion the pyroxenes crystallized first followed by hackmanite, while the reverse occurred in the second intrusion. He also suggested that the second intrusion was the main cause of fenitisation of the country rocks. It would seem, therefore, that in the first intrusion the increase in correlation coefficient between $Ga-(Al+Fe^{3})$ and $Ga-(Al+Fe^{3}+Na)$ relative to that for Ga-Al is a reflection of the early crystallization of pyroxene and the substitution of Ga for Fe^{3} in the pyroxene. The increase in correlation coefficient r when Na is included in the calculation probably reflects the feldspathoid and plagioclase (in perthite) contents of the rocks, these minerals probably containing a considerable proportion of the Ga.

The non-significant, or complete lack of, correlation between Ga and any combination of Al with Fe^{3} or Na for the second intrusion is remarkable. This fact, coupled with the low Ga content of this magma relative to that of the first intrusion, and the conclusion of Rodrigues (1973) that it was the second intrusion which was mainly responsible for the fenitisation process, may be the result of migration of Ga into the country rocks to varying extents during the fenitisation process. This possibility will be discussed in more detail in the next section.

21.3 FENITES

Rodrigues (1973) recognised four groups of fenitic rocks, the fenites 1-3 and the rheomorphic fenites. Data for Ga in these rocks are reported in Table 83E-G and plotted in Figs 150-151. The D.I. in these tables is the modal fenitisation index defined earlier. A single sample of the country rock, an alkaline granite, is included in Table 83E.

Rodrigues reported that the following elements increased throughout the fenitisation process: Al, Fe^3, Fe^2, Mg, Ca, Na, Ti, P, Mn, S, Sr, Cu, Zn, and H_2O+ and CO_2. Si, K, Rb and Pb decreased throughout the fenitisation process, while Cl, Ba, Zr, Y, Nb, Th, Ni and Mo showed irregular changes in concentration. Quartz, orthoclase and perthite decreased with increasing fenitisation, while plagioclase, biotite, hornblende, eckermanite, augite, aegirine-augite, aegirine, apatite and ores showed an increase. The pyroxenes showed a particularly marked increase in the fenites 3.

The Ga content of the feldspathoidal rocks is much greater than that of the granitic country rock (Table 83 and Fig. 150) and the resulting chemical potential or gradient would have resulted in Ga migrating into the country rocks during fenitisation. Figs 150 and 151 indicate on average a steady increase in Ga with increasing degree of fenitisation, although there is some degree of overlap between individual rocks from different groups. This is in agreement with the conclusions of Rodrigues that the metasomatism of the country rocks was not homogeneous. The Ga/Al ratio also increases steadily with increasing fenitisation but with more scatter in the individual rocks.

Rodrigues reported that fenitisation was caused mainly by the first two intrusions, with the third intrusion causing only local effects in the country rock.

In Fig. 150 it is obvious that the rocks of the second intrusion are very depleted in Ga, not only relative to Al but also relative to the rocks of the other two intrusions and to the average values reported for nepheline syenites in Table 39A. It is also clear from Fig. 150 that there is a greater degree of enrichment in both Ga and Al between fenites 2 and fenites 1, 30% and 17% respectively, than between either fenites 1 and granite (15% and 14%) or between fenites 3 and fenites 2 (8% and 5%). The rocks of the second intrusion were richer in volatiles (H_2O+ and CO_2) (3.9%) than those of the first intrusion (2.6%), and during the second intrusion the country rocks were hotter than during the first (Rodrigues, 1973). Assuming the magma of the second intrusion originally had a similar Ga content to that of the first and third intrusions, i.e. ~ 40 ppm Ga, it is interesting to speculate whether, with the higher temperatures and greater volatile content, Ga did not migrate from the second magma into the country rock to a greater extent than during the earlier intrusion, thus causing depletion of Ga in the second magma and a sharp increase of Ga in the fenites 2 and 3. Unfortunately no information is available to allow mass balance calculations to test the hypothesis.

The rheomorphic fenites (Table 83G) have similar Ga contents and Ga/Al ratios to the fenites 3. Rodrigues (1973) considered the rheomorphic fenites to have been formed from the fenites 3 during the second intrusion, although there was no certainty about the composition of the rocks which, by partial fusion, gave rise to the rheomorphic fenites. The Ga data indicate that the fenites 3 could have been those rocks.

Although Ga shows a marked increase as a result of fenitisation of the country rock, this increase (69%) is far smaller than those shown by some other trace elements, e.g. Zn (450%), Cu (200%), Sr (300%). McKie (1966) reported Ga data for fenites from Oldoinyo Dili, Tanzania, resulting from fenitisation of a granitic gneiss. With increasing fenitisation the Ga contents varied slightly but remained essentially constant. The Ga content of the gneiss was 25 ppm, while that of the four most strongly fenitised rocks was 22 ppm Ga. The Ga/Al ratio was very variable, 1.7-5.3, showing no systematic variation.

The data for the Nejoio fenites and those of McKie indicate that, although Ga can be mobile during the fenitisation process, it is less mobile than certain other trace elements.

SYNOPSIS

An analytical technique for the determination of Ga in silicate rocks and stony meteorites using XRF spectrometry has been developed. The method is applicable on a routine basis and has proved capable of producing data that are both precise and accurate, but the need for 2-4g material may be a disadvantage. However, for rock analysis lack of material is seldom a problem. The relatively large quantity of material used does eliminate the problems that may arise due to sampling error when aliquots such as 50mg are used, for example, in spectrochemical analysis.

Data are presented for a large number of stony meteorites and some separated fractions. It is possible using Ga, Al and Fe data to separate the meteorites chemically into the same classes or groups as proposed by various workers on the basis of other criteria. This can be useful when attempting to classify meteorites that are on the borderline between classes using textural, mineralogical and petrological data. The bulk mesosiderites and their separated silicate and non-magnetic fractions, on the basis of their Ga contents, are distinct from all other types of meteorites. The subdivision of the C3 carbonaceous chondrites into C3-V and C3-O classes is confirmed, and the Ga data suggest that the C4 chondrites might be chemically different in terms of Ga and other elements from the C3 chondrites. Evidence has been presented to suggest that a considerable proportion of the Ga in the carbonaceous chondrites is present in the carbonaceous and sulphide fractions.

Ga has been determined in approximately 1500 rocks, and the mean values and ranges for both Ga and the Ga/Al ratio have been summarised by rock type and compared with data from the literature. It was demonstrated that in only a few instances is the correlation between Ga and $(Al+Fe^3)$

better than that between Ga and Al, and that the general use of the $Ga/(Al+Fe^3)$ ratio in preference to the Ga/Al ratio is usually not warranted. The $Ga/(Al+Fe^3)$ ratio can, however, be useful in certain instances. In a number of modern instrumental analytical techniques only total Fe, expressed as Fe_2O_3, is determined and the Fe^3 content of rocks is not reported, which makes the use of the $Ga/(Al+Fe^3)$ ratio impossible.

A number of different minerals were analysed for Ga. Unusually high Ga values (18-58 ppm) were measured for chromites from the B.I.C. These concentrations are two to three times higher than previously reported values. Upper mantle ilmenites contain 16-21 ppm Ga compared with very low ($\sim$1 ppm) levels in crustal ilmenites. However, upper mantle garnets have similar Ga contents and Ga/Al ratios to crustal garnets. The Ga content and Ga/Al ratio of upper mantle clinopyroxenes may be dependent on the temperature at which the mineral crystallized.

The variation in the Ga content and the Ga/Al ratio of abyssal tholeiites is generally much less than had been previously indicated. The mean value for Ga is 16 ppm and for the Ga/Al ratio 1.9. The variation of both Ga and the Ga/Al ratio between tholeiites from three oceans is no greater than that found within a single ocean.

In rocks from oceanic islands four different trends of Ga and Ga/Al ratio against differentiation index were found. It proved possible to model these trends using crystal fractionation and known partition coefficients for plagioclase, pyroxene, olivine, amphibole, magnetite and ilmenite. Exceptionally low Ga concentrations, similar to those of abyssal tholeiites, have been reported for Jan Mayen Island, Amsterdam Island and Rodriquez Island.

The behaviour of Ga in a number of igneous complexes was examined, and it was shown for the Skaergaard, and possibly for rocks from Gough Island, that in the very last stages of extreme fractionation the Ga content of the rocks can decrease markedly, in a fashion similar to trends sometimes found for Ba and Sr. The very high Ga content (200 ppm) in a late-stage Skaergaard plagioclase, so often quoted in the literature as being indicative of enrichment of Ga in plagioclase with increasing differentiation, was shown to be incorrect and probably due to analytical error. Calculations based on the Ga content of the rock and the percentage normative plagioclase indicated a normal Ga content in the plagioclase and that no enrichment had taken place. The results obtained for rocks from various igneous complexes stressed the important effect that changing mineralogy has on the Ga content and the Ga/Al ratio of the rocks. Conversely, changes in the Ga content and Ga/Al ratio can alert the geochemist to possible mineralogical changes that may have taken place.

Granites from five different bodies in S.W.A. were analysed for Ga, and on the basis of their Ga content and Ga/Al ratios, it was possible to distinguish clearly between each body. The data also suggest that the Salem granite has been derived by transformation from sediments rather than by igneous differentiation.

The determination of Ga in a number of upper mantle xenoliths and minerals and kimberlites constitutes an important contribution to our knowledge of the Ga distribution in the earth. The data confirm the depleted nature of common peridotites (CP's), and the presence of considerable quantities of Ga in upper mantle ilmenites. The enrichment of Ga in metasomatised nodules indicates its association with the metasomatic processes and suggests that Ga may have been fairly mobile in the upper mantle. If MORB tholeiites with a mean Ga content of 16.5 ppm Ga have been derived from a 20% partial melt of the upper mantle, then the parent rocks must have contained about 3-5 ppm Ga. The only rocks examined, which had the correct major element composition and which contained this concentration of Ga, were the clinopyroxene-rich bands and the metasomatised CP's found in veined nodules from the Matsoku Pipe.

The Ga data are consistent with a number of ideas which relate to the formation and subsequent history of upper mantle nodules, and which were derived from a study of the nodule mineralogy and major element chemistry. In future, therefore, Ga data could be a help in arriving at similar theories for other materials.

The Ga contents and Ga/Al ratios of eclogites are very low and very variable and are probably related to the varying proportion of garnet in these rocks.

The enrichment of Ga over Al in kimberlites is confirmed, and the Ga/Al ratio is shown to be dependent on the degree and type of crustal contamination. Uncontaminated kimberlites have a high Ga/Al ratio of 4.0.

In rocks from the Barberton Mountain Land, the Ga contents and Ga/Al ratios offer only limited support for a fractional crystallization hypothesis for the origin of basaltic and peridotitic komatiites. As a group, the Barberton metatholeiites have amongst the lowest Ga/Al ratios of any tholeiites analysed in this work, which suggests they were derived from a primitive mantle that was depleted in Ga relative to source areas for modern abyssal basalts. The enrichment of Ga, Ti and Zr in certain of the basaltic rocks indicates that they may have been derived from mantle enriched in the vein material found in veined nodules from Matsoku Pipe, and suggest an inhomogeneous mantle at the time of the formation of the Onverwacht group of rocks.

The Ga content of Karroo dolerites as determined by Nockolds and Allen (1956) has been shown to be about 50% too high. The new mean value reported here is 16.3 ppm Ga with a mean Ga/Al ratio of 2.0, compared with Nockolds and Allen's values of 25 ppm and 3.2. On the basis of major and trace element geochemistry, rocks of Karroo age in southern Africa have previously been divided into three main groups, and the distribution of Ga/Al ratios for these rocks confirms these divisions. The data also suggest that rocks from the Parana volcanics in Brazil may be divided into northern and southern groups in a similar fashion, and that the rocks from the southern part of Brazil closely match those from northern S.W.A. (Etendeka Plateau). The Ga/Al ratio data indicate that rocks from the southern part of the Lebombo monocline are similar to those from the Central area of the Karroo (southern province), while those from the northern Lebombo are close in composition to those from the northern province in Rhodesia. The ratios show further that the rhyolitic rocks of the Lebombo have not been derived from the basaltic rocks by fractional crystallization. Rocks from the "heel" of the Lebombo monocline are shown to be intermediate in composition between the northern and southern groups.

The behaviour of Ga during the weathering process was examined in granites and shales from the western Cape Province, and there was strong evidence for the separation and removal of Ga relative to Al during the alteration of feldspars to clay minerals and during the alteration of illite to kaolinite, with a consequent reduction in the Ga/Al ratio. By inference it was possible to show that kaolinite from this area contained about 20-25 ppm Ga with a Ga/Al ratio of about 1.4, much lower than the ratio for illite (3.3) which contained 35 ppm Ga.

Ga in fenites from the Nejoio area of Angola increased with increasing degree of fenitisation. The Ga/Al ratio also increased, but with less uniformity. Na and Ca increased with increasing fenitisation, and the behaviour of Ga in these rocks is similar to that reported during albitisation. In the Nejoio rocks the increase in Ga content (69%) was much less than that reported for elements such as Zn, Cu and Sr. In the other metamorphic rocks which were examined, from the granite-slate contact at Sea Point, the Ga and Al data indicated that the hornfelses could be considered a simple mix of the intrusive granite and the sedimentary country rock. The

Ga data also suggest that the feldspathization of the granite and migmatite zone is unlikely to be the result of late-stage potash enrichment.

A number of recent papers have suggested that Ga, because of its "immobility" during alteration processes, be used together with other elements to discriminate between different volcanic magma series and their metamorphosed equivalents. Important evidence on the behaviour of Ga during weathering of modern abyssal pillow lavas and of ancient pillows of the Barberton Mountain Land rocks was presented.

Six inside/outside pairs of lava pillows from modern abyssal tholeiites were examined, and in only one case was Ga slightly depleted in the altered sample, while the Ga/Al ratio remained constant for all pairs. In rocks from the Barberton Mountain Land there is little evidence to suggest that Ga and the Ga/Al ratio were affected by alteration of the lavas during or after extrusion on the sea floor. However, the Ga content of the rocks and the Ga/Al ratio were shown to be sensitive to the degree of epidotisation that had taken place, both Ga and the Ga/Al ratio increasing with increasing epidotisation. Ga and the Ga/Al ratio may be used to distinguish between epidote formed by isochemical alteration of the rock (no change in Ga or Ga/Al ratio) and epidote formed by the metasomatic introduction of elements into the rock (increase in Ga and the Ga/Al ratio). Ga in kimberlite was not affected by thermal metamorphism, nor was it lost to the wall-rock during intrusion of kimberlite magma.

Therefore, while Ga may correctly be considered to be an immobile element where limited weathering or alteration of basaltic rocks is concerned, where epidotisation has taken place Ga data should be used with care, and the Ga/Al ratio used to monitor any changes that may have taken place in the Ga content. Ga could also prove useful if it is necessary to decide whether magnetite in altered olivine-bearing rocks is of primary or secondary origin. Primary magnetite is rich in Ga. Secondary magnetite derived from the formation of serpentine from olivine should be low in Ga. The Ga/Al ratio should be greater when primary magnetite is present compared with that when magnetite formed by the alteration of olivine.

The work presented here has naturally suggested a number of fields in which further work on the geochemistry of gallium is desirable and necessary. Probably the single most important fact to emerge from this work is that, in a number of instances, the early data presented in the literature for Ga are unreliable, and this is particularly important in the case of minerals.

The problem always associated with trace element analysis in minerals is that of obtaining adequate quantities of sufficiently pure sample. Unfortunately the analytical technique presented here is not really suitable for the analysis of small quantities of minerals. The two most promising alternative techniques are probably spark source mass spectrometry or mass spectrometric isotope dilution analysis. Small sample capability is essential, coupled with precision and accuracy. Further work is required on the distribution of Ga in minerals, particularly pyroxenes, and especially in minerals from the upper mantle. An extremely interesting study would be the distribution of Ga between minerals that crystallized at different temperatures within the mantle. The relationship between Ga and Ti in the mantle also requires further investigation. More work also needs to be done on crustal ilmenites and chromites. There is still very little data on Ga in sedimentary minerals, such as the clays, and more data are required.

However, perhaps the most important gap in our knowledge of the geochemistry of Ga is the lack of data on partition coefficients for Ga both under different temperature conditions and at different oxygen fugacities.

Finally, it can be stated that this work has presented an analytical technique which may be used in a routine manner in any geochemical laboratory using XRF analysis. In order to establish whether Ga could be a useful element or not, it has been necessary to examine the behaviour of Ga in rock suites whose geochemical history was already known. The results indicate that Ga can be a useful element in distinguishing between different rock groups on a regional basis, and in tracing and interpreting the geochemical history of a rock suite. One of the advantages of using Ga is its relative immobility compared with many other trace elements, and the fact that very low concentrations of the element are present in intercumulus material. It became quite obvious during this investigation that the inter-element ratio, Ga/Al, is usually of more use than the abundance data on Ga alone.

Provided the data are of good quality, Ga can take its place amongst other trace elements that are useful to the geochemist studying igneous, metamorphic and sedimentary processes and the geochemical history of rocks.

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APPENDIX 1

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A Simple Method for Background and Matrix Correction of Spectral Peaks in Trace Element Determination by X-Ray Fluorescence Spectrometry

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Abstract

Between adjacent major element absorption edges, background intensities at differing wavelength positions were found to be related linearly. Also, background intensity at any position is linearly related to the reciprocal of the mass absorption coefficient for any wavelength between the absorption edges.

The method presented here allows for the determination of background, as well as mass absorption coefficient, by a single measurement at an interference-free background position (which can be the Compton scatter 'peak'). If the mass absorption coefficient is already known, backgrounds may be calculated directly.

Tests on geological materials show that, while not as accurate as conventional methods of background determination, relative accuracies of two to five percent are obtainable with a very considerable saving in time, since intensity at only one background position need be measured. Use of low dispersion high reflectivity analysing crystals, e.g. LiF(200), is possible because it is no longer necessary to attain interference-free background positions between peaks.

Furthermore, the method is ideally suited to the determination of background intensities in energy dispersive systems where spectral resolution is a problem and in multi-channel units where only one channel need be used for the determination of both mass absorption coefficient and backgrounds for a group of trace elements.

The method has been used in the low cost determination of trace elements in large numbers of geochemical prospecting samples.

Introduction

The motivation behind this investigation was the need to develop a method for trace element analysis in pressed powder briquettes or uncompacted powders which was more rapid than methods in current use, even if it resulted in slight losses in accuracy. It was desirable that the method should be applicable to a large number of trace elements above atomic number 27 (Co) in a wide range of geological materials and, thus, should include an accepted procedure for correction for matrix variation.

Sample preparation

Tests were carried out using pressed powder briquettes of prepared pure (undiluted) pulverized sample, milled with 10% polyvinyl alcohol binder (e.g. Hoechst Moviol N20-98) and with 10% boric acid. The briquettes prepared with boric acid were found to be the most rigid and can be prepared rapidly by unskilled operators. Tests were also carried out on sample powders poured directly into sample holders with Mylar windows.

It is essential to use sufficient sample to prepare an 'infinitely thick' sample layer for the shortest wavelength under investigation. Tests carried out using pure quartz indicated that for Mo Kα radiation (0.711 Å) a minimum of 8 g was required for a boric acid backed 40 mm diameter briquette. However, at Ba Kα radiation (0.39 Å), more than 20 g of quartz were required for the same diameter backed disc. The tests were carried out on quartz (SiO_2) since it has the lowest mass absorption coefficient of the most common of the geological materials investigated.

Instrumental settings

Instrumental settings were chosen to suit the wavelength regions under investigation. As an example, the following settings were used for the analysis of the commonly required elements which lie in the wavelength region 0.7 to 1.7 Å (Mo Kα to Ni Kα and U Lα to Hf Lα).

The instrument was a Philips PW1220 sequential X-ray spectrometer with X-ray tube, silver target, 1.6 kW; excitation, 70 kV; current, 20 mA; analysing crystals, LiF(220) or LiF(200); detectors, flow plus scintillation with pulse height discrimination; and collimator, fine.

Conventional method

Figure 1 illustrates a typical spectrum obtained using a silver X-ray tube for excitation and a LiF(220) crystal. The characteristic lines of trace elements are superimposed on a background which is most elevated at the Compton peaks of scattered primary radiation. Despite the use of a high dispersion crystal, there are few background positions which are completely interference-free.

In current practice, two or more of the available interference-free background positions are read and the backgrounds beneath spectral peaks are interpolated graphically or mathematically. The method gives reliable results over a limited wavelength range, but tends to be

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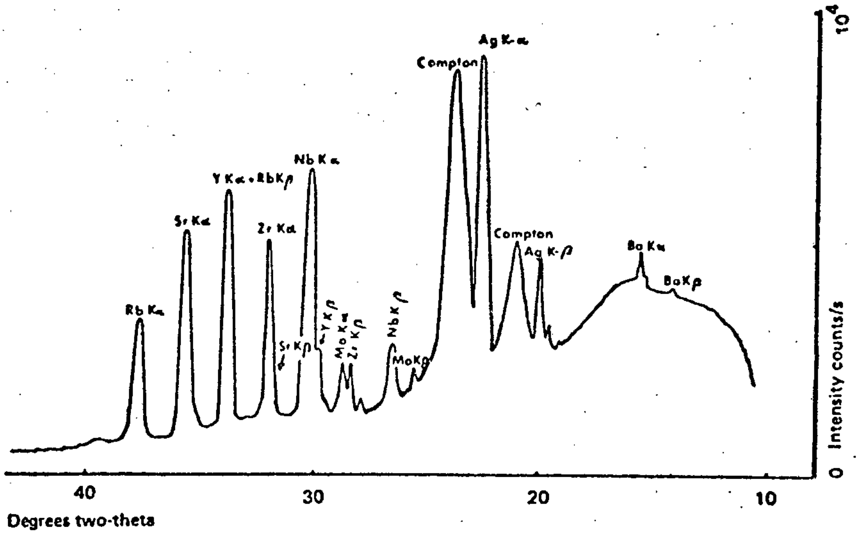

FIG. 1. Typical spectrum obtainable on a rock sample containing a few hundred p.p.m. each of Rb, Sr, Y, Zr, Nb and Ba. In this example a silver target X-ray tube and LiF(220) analysing crystal were used. Compton scattering peaks occur on the longer wavelength sides (higher angles) of the characteristic lines of the X-ray tube.

time consuming. It does not account for irregularities in the background caused by 'spurious' reflections of primary and secondary radiation by the analysing crystal, the so-called ghost peaks[1,2](see Fig. 2). For example, both molybdenum and silver X-ray tubes with a LiF(220) crystal yield 'ghost peaks' in the region between Zr Kα and Pb Lβ, causing considerable difficulties in direct measurement of backgrounds by the current method.

It was necessary that a method be developed which was less time consuming and, which, at the same time, might eliminate some of the difficulties outlined above in determining background.

Relationship of background and mass absorption coefficient (μ)

Background originates essentially from two sources: scattering of primary radiation by the sample and general instrument noise. The scattering is in two forms: coherent or Rayleigh scattering and incoherent or Compton scattering.[3]

Both coherent and incoherent scattering are matrix dependent (e.g. Andermann and Kemp[4]) and Reynolds[5,6] has shown that Compton peak intensity and mass absorption coefficient are inversely related (Fig. 3). It is common practice to generate mass absorp-

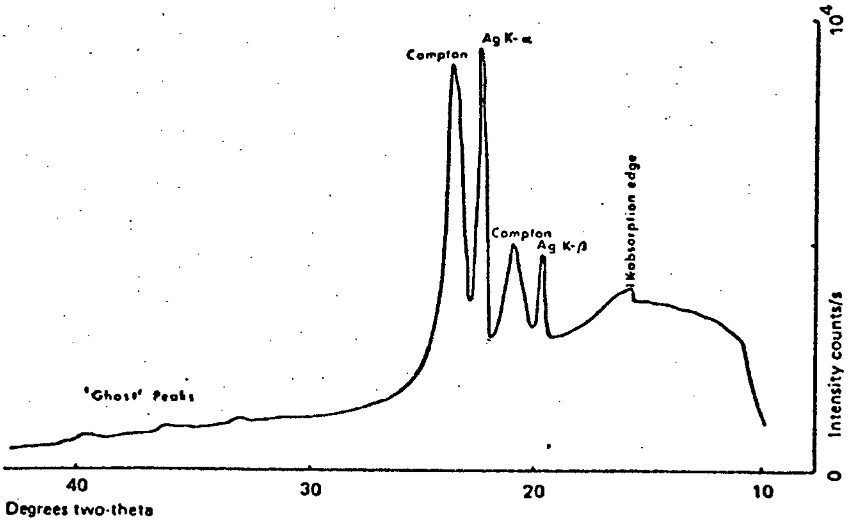

FIG. 2. The spectrum illustrated in Fig. 1 stripped of the lines of the elements present in the sample. Such a spectrum is obtainable using a pure reagent blank. Note the spurious 'ghost peaks' produced by the LiF(220) crystal and the iodine absorption edge due to the thallium doped sodium iodide scintillator in the detector.

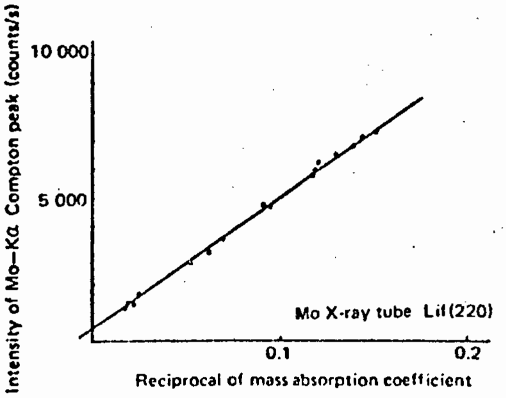

FIG. 3. The relationship of Compton peak intensity and the reciprocal of mass absorption coefficient, as first used by Reynolds.[5,6] (Set of international standards, calculated mass absorption coefficients.)

tion coefficients of samples of unknown major element composition by this method. Willis[7] has shown that the relationship is actually better than 1% relative when Mo Kα Compton intensity and measured mass absorption coefficients (transmission method) are used, provided that a Y_2O_3 filter and LiF(220) analysing crystal are used with a Mo X-ray tube.

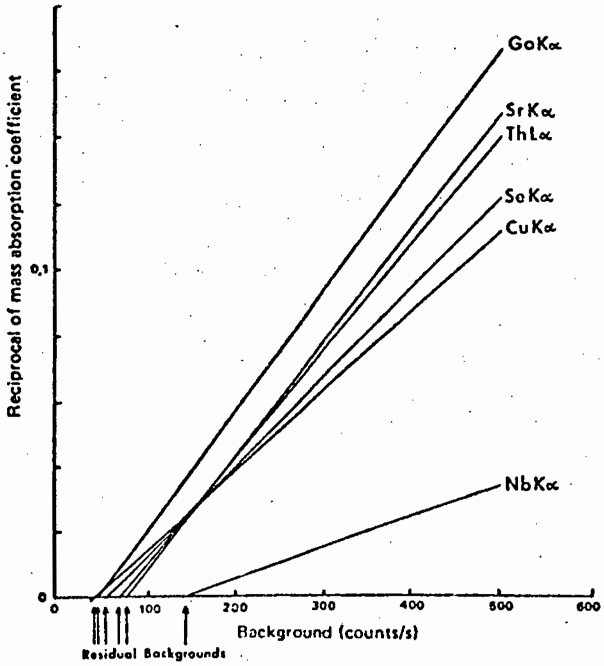

FIG. 4. The relationship of any background wavelength (which may be the Compton peak) and the reciprocal of the mass absorption coefficient is shown to be linear. For each of the wavelengths indicated, the lines were determined separately using blanks, then plotted collectively. Nb Kα is close to the Mo Kα Compton peak (Mo X-ray tube used) and the residual background is somewhat higher than expected, possibly due to excessive scattering within the instrument. Ga Kα radiation is approximately at twice the Mo Kα Compton wavelength, which has displaced the line slightly.

Since not only are the characteristic lines of the X-ray tube target scattered by the sample, but also the continuum, any chosen background may be shown to be similarly inversely related to the mass absorption coefficient (Fig. 4), as demonstrated by Hahn-Weinheimer *et al.*[8] Also, between adjacent major element absorption edges, mass absorption coefficients at all wavelengths are linearly related (Table 1 and Hower[13]). It follows that any two backgrounds in this region are also linearly related.

The relationship was investigated at various wavelengths using briquettes prepared with a number of pure stable reagents, which served as 'blanks' for trace elements under investigation. Linear relationships were obtained (Figs 5 and 6), but in all cases the line did not pass through zero. Particular care was taken to check the blanks previously for contaminants, e.g. Sr in $CaCO_3$, Rb in K salts, Zr in TiO_2, etc.

The intercept which the line makes with the background intensity axis, for convenience, will be referred to as residual background.

It is thought that this nonzero interception of the axes results from background contributed by the actual instrument, e.g. electronic noise and scattering and fluorescence from the analysing crystal, and from the crystal and sample chambers.

Such contributions to background are not matrix dependent, but crystal fluorescence and internal scattering is strongly influenced by the radiation energies which the sample fluoresces. For example, in experiments carried out with the spectrometer set to measure intensity at a wavelength of 0.7 Å, the contribution due to crystal scattering using a sample disc of RbCl (Rb Kα + Kβ radiation (0.93 and 0.87 Å), absorption edge at 0.81 Å), ideally a very heavy absorber of 0.7 Å radiation, was many times in excess of the actual sample scattered radiation diffracted by the crystal.

Ignoring crystal fluorescence and scattering, residual background at a given wavelength is constant for all samples in an analytical run and, if subtracted from the background measured, the difference, here referred to

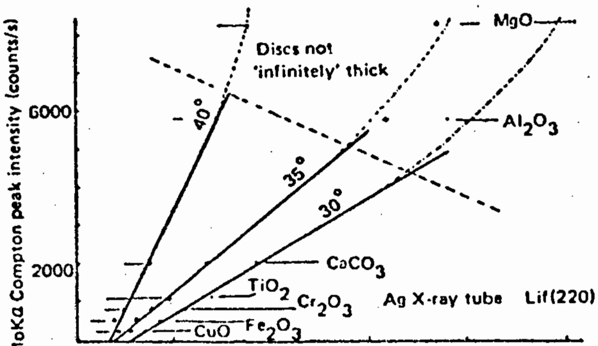

FIG. 5. The linear relationship of two background positions; in this case between Compton peak and background read at 30, 35 and 40°, respectively, using a LiF(220) crystal.

TABLE 1. Between two major element absorption edges, mass absorption coefficients (μ) are linearly related, as tabulated below for measured μ's (transmission method). Sample NIM-L shows deviations (underlined) due to high concentrations of Nb, Zr, Y and Sr present (i.e. absorption edges lie within the wavelength range being examined)

	μ_{Rb}	μ_{Sr}	μ_{Zr}	μ_{Nb}	μ_{Sn}	μ_{Nb}/μ_{Rb}	μ_{Nb}/μ_{Sr}	μ_{Nb}/μ_{Zr}	μ_{Nb}/μ_{Sn}	μ_{Sr}/μ_{Rb}	μ_{Sr}/μ_{Zr}
PG-11	10.04	8.599	6.335	5.493	—	0.547	0.639	0.867	—	0.857	1.357
G-1	10.10	8.662	6.373	5.544	—	0.549	0.640	0.870	—	0.858	1.359
PCC-1	11.28	9.681	7.137	6.194	—	0.549	0.640	0.868	—	0.868	1.356
DTS-1	11.62	9.995	7.368	6.385	—	0.549	0.639	0.867	—	0.860	1.357
OK-272	12.34	10.61	7.825	6.796	—	0.551	0.641	0.869	—	0.860	1.356
M-38	12.45	10.76	7.969	6.940	—	0.557	0.645	0.871	—	0.864	1.350
GSB	12.78	10.97	8.062	6.986	—	0.547	0.636	0.866	—	0.858	1.361
KL-11	15.19	13.11	9.704	8.464	2.560	0.557	0.646	0.872	3.306	0.863	1.351
W-1	15.39	13.22	9.815	8.548	2.564	0.555	0.647	0.871	3.334	0.859	1.347
MRG-1	19.67	17.05	12.64	11.01	3.307	0.560	0.646	0.871	3.329	0.867	1.349
TiO_2	30.09	26.00	19.24	16.71	4.989	0.555	0.643	0.868	3.349	0.864	1.351
NIM-L	14.76	12.71	9.400	8.611	3.002	0.584	0.678	0.916	2.868	0.861	1.352

as 'true' background, is directly proportional to $1/\mu$ and the line passes through zero (Fig. 7).

It follows that the ratio below permits correction for matrix variations within samples:

$$\frac{\text{Total spectral peak intensity} - \text{total background intensity}}{\text{True background}}$$

$$\text{i.e. } \frac{\text{Net peak}}{\text{True background}}$$

Since the μ's at all spectral positions between adjacent major element absorption edges are linearly related (Table 1), the true background used for matrix correction need not necessarily be that of a spectral line under investigation.

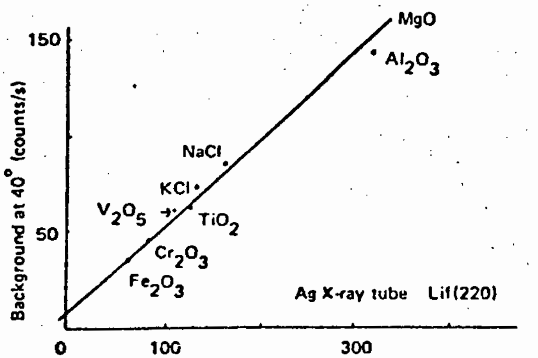

FIG. 6 The linear relationship of two backgrounds; in this case between the background at 35° and the background at 40°, using the LiF(220) crystal.

Significance of the findings

Backgrounds beneath several spectral peaks may be determined by measurement of only one interference-free background position. Also, the true background at this position may be divided into all net spectral peaks under investigation to obtain matrix variation correction. If mass absorption coefficients are known, backgrounds may be calculated directly, obviating the need even to measure an interference-free background position. All calibrations may be set up at the beginning of a run by using blanks, the mass absorption coefficients of which may be calculated easily from tables published in the literature or measured, preferably by a transmission method[9] or by using an X-ray tube Compton peak.[5,6] It is strongly advised that a number of different blanks should be used, which have been checked previously for contaminants.

Correctly speaking, Compton 'peaks' are background regions of elevated intensity and, especially for the silver and molybdenum target X-ray tubes, residual background at these 'peaks' is insignificantly small in comparison with total intensity. Its effect may be ignored when analysing ordinary silicate rocks and soils. However, the method has the advantage of making it no longer necessary to measure Compton peaks where

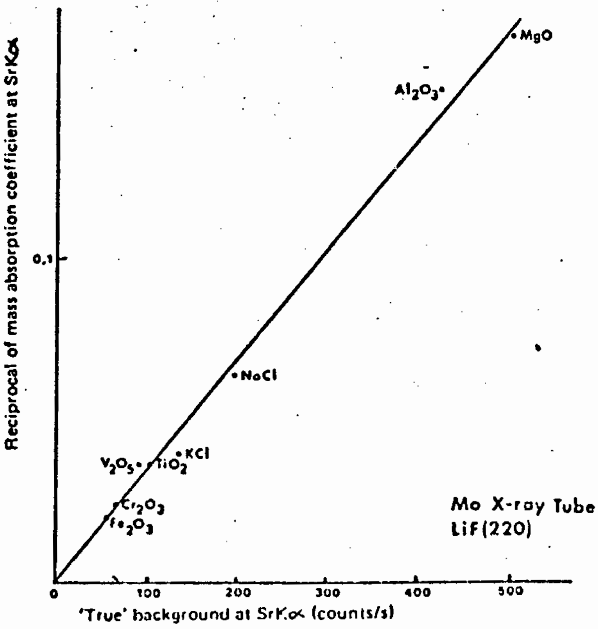

FIG. 7. After removing residual background from readings taken on blanks, the line relating background and reciprocal of mass absorption coefficient plots through zero, as may be expected.

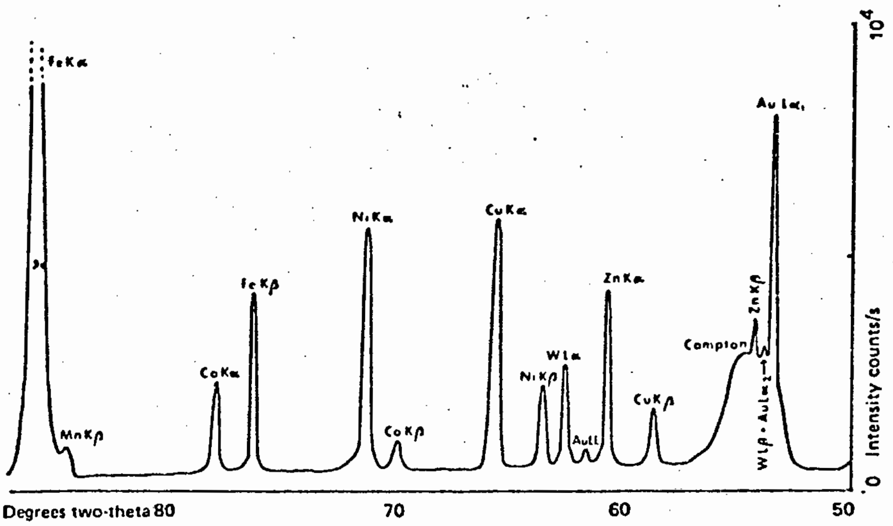

FIG. 8. The spectrum in the region of 1.2 to 2.0 Å, using an Au X-ray tube and a rock sample containing a few hundred p.p.m. each of Mn, Co, Ni, Cu, Zn and W. Note the interferences with the Au Lα Compton peak.

TABLE 2: Comparison of rubidium data obtained using different methods of background determination (W X-ray tube, LiF(220), Rb Kα line measured)

	Concentration of rubidium			
		Method of background determination[b]		
	Recommended		Methods	
Sample	values[10]	Conventional	(1)	(2)
	p.p.m.	p.p.m.	p.p.m.	p.p.m.
G-1[a]	210	210	210	210
W-1	21	21.4	21.5	22.3
GSP-1	254	252	250	253
G-2	168	166	166	169
BCR-1	46.6	46.7	47.0	47.1
AGV-1	67	66.0	67.9	68.2
Knippa	—	28.0	31.2	31.4

[a] G-1 = 210 p.p.m. Rb used as standard.

[b] Methods used: *Conventional* using mathematically interpolated backgrounds from two measured backgrounds on either side of the peaks and mass absorption coefficients determined by the transmission method at Rb Kα, Sr Kα, Nb Kα and Sn Kα wavelengths. (1) Using calculated backgrounds and mass absorption coefficients determined by the transmission method. (2) Using calculated backgrounds and division by 'true' background for matrix correction.

there are numerous interferences (e.g. Ag Kα Compton peak is subject to interference by U Lγ and Ru Kβ, Mo Kα Compton peak by U Lβ, Nb Kα and Y Kβ, and Au Lα Compton peak by W Lβ and Zn Kβ, see Figs 1 and 8).

Data processing

All the relationships described above may be handled mathematically (see Appendix) and thus data processing may be handled rapidly by a small computer.

TABLE 3. Comparison of strontium data obtained using different methods of background determination (W X-ray tube, LiF(220), Sr Kα line measured)

	Concentration of strontium			
		Method of background determination[b]		
	Recommended		Methods	
Sample	values[10]	Conventional	(1)	(2)
	p.p.m.	p.p.m.	p.p.m.	p.p.m.
G-1[a]	249	249	249	249
W-1	190	188	186	190
GSP-1	233	235	236	233
G-2	479	474	471	471
BCR-1	330	328	325	335
AGV-1	657	655	654	656
Knippa	—	1010	1003	1017

[a] G-1 = 249 p.p.m. Sr used as standard.

[b] Methods used as in Table 2.

TABLE 4. Comparison of rubidium and strontium data obtained using different methods of background determination and a Mo X-ray tube, instead of W X-ray tube, as in Tables 2 and 3 (LiF(220), Kα lines measured)

	Rubidium		Strontium	
	Method of background determination[b]			
Sample	Conventional	Method (1)	Conventional	Method (1)
	p.p.m.	p.p.m.	p.p.m.	p.p.m.
G-1[a]	210	210	249	249
W-1	20.7	21.5	186	186
GSP-1	252	250	233	236
G-2	166	166	474	471
BCR-1	46.1	46.9	330	325
AGV-1	66.3	67.9	668	654

[a] G-1 used as standard.

[b] Methods as in Table 2.

TABLE 5. Comparison of thorium and lead data obtained using different methods of background determination. A W X-ray tube was used in the conventional method, as spurious 'ghost peaks' interfere with Th $L\alpha$ and Pb $L\beta$ when a Mo X-ray tube is used [LiF(220)]

	Thorium			Lead		
		Method of background determination[b]			Method of background determination[b]	
Sample	Recommended values[10]	Conventional[a] W X-ray tube	Method (1) Mo X-ray tube	Average values[10]	Conventional[a] W X-ray tube	Method (1) Mo X-ray tube
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
G-1	50	52	45	48	48	47
W-1	2.4	< 3	< 3	7.8	8	7
GSP-1	104	108	—	51.3	55	56
G-2	24.2	23	25	31.2	28	32
BCR-1	6.0	8	7	17.6	15	15
AGV-1	6.4	7	10	35.1	36	37

[a] Data from Cherry *et al.*[11]
[b] Methods as in Table 2.

In a particular application at Anglo American Research Laboratories a Digital Equipment Corporation PDP 11/05 computer was used to process data produced on punched tape from a Philips PW1270 multi-channel X-ray spectrometer, which was equipped with a Philips PW1266 automatic 160 sample changer. In 54 working days, approximately 25 500 samples were analysed for uranium, thorium and rubidium by this method with maximum economy.

Results and conclusions

This method has been widely tested by the authors and Tables 2 to 6 summarize results obtained for a number of elements. Of particular significance are the good results obtained for gallium using a Mo target X-ray tube as the Ga $K\alpha$ peak (1.342 Å) is far removed from the Mo $K\alpha$ Compton peak (0.73 Å) used for background determination and mass absorption correction.

TABLE 6. Comparison of gallium data obtained using different methods of background determination (Mo X-ray tube, LiF(200), Ga $K\alpha$ line)

			Concentration of gallium	
			Method of background determination[b]	
Sample	Recommended values[10]	Values selected from Lit.[a]	Conventional	Method (1)
	p.p.m.	p.p.m.	p.p.m.	p.p.m.
G-1	19.6	18.5	18.7	18.4
W-1	16.0	16.7	16.5	16.5
G-2	22.9	20.9	21.2	21.8
GSP-1	22[c]	19.1	21.0	21.6
AGV-1	20.5	19.3	19.4	19.9
BCR-1	20[c]	22.1	20.9	20.9
PCC-1	0.4[c]	0.6	0.6	< 0.3
DTS-1	0.2[c]	0.4	0.4	< 0.3
GA	16		14.6	14.0
GH	22		21.6	21.0
GR	20		19.3	19.2
BR	20[c]		16.1	17.5
JG-1	20[c]		15.4	15.1
JB-1	17[c]		16.6	17.0
NIM-D	< 3[d]		0.8	1.3
NIM-G	32[d]		26.6	26.0
NIM-L	55[d]		52.0	55.3
NIM-N	19[d]		16.2	16.1
NIM-P	13[d]		6.5	6.9
NIM-S	11[d]		10.8	10.8
MRG-1	—		16.7	17.4

[a] From Willis:[12] Data averaged from at least twenty-five analyses per standard taken from the literature. For PCC-1 and DTS-1 only limited data were available.
[b] Methods as in Table 2.
[c] Magnitudes.
[d] Average.

While not always as accurate as the conventional method described, relative accuracies of 2 to 5% are obtainable with a very considerable saving of time. However, the accuracy of the final result is critically dependent upon the accuracy of μ, or the counting statistics of the measurement of the reference background from which μ and/or all spectral peak backgrounds are being determined, because an error in μ leads to a combined error in background calculation and matrix correction, which is additive.

The main advantage of the method is that for a group of analytical elements only one background reading is used for both background and matrix variation correction of all the spectral peaks being measured, provided that no major or minor element absorption edges occur between the background wavelength and the spectral peaks. Apart from saving time and, in the case of multichannel units, actual spectrometer channels, the method proved to take into account spurious analysing crystal reflections and other irregularities in the background.

The method has the added advantage of once again making possible the use of high reflectivity low dispersion crystals such as the LiF(200), which have previously fallen from favour because of the difficulty in obtaining interference-free backgrounds in the region of 0.5 to 1.5 Å. It is also ideally suited for use with energy dispersive X-ray spectrometry, where the accurate determination of background is very difficult.

Acknowledgements

The authors gratefully acknowledge the cooperation and encouragement received from the Management of the Anglo American Research Laboratories. One of the authors (J.P.W.) wishes to thank the C.S.I.R., Pretoria, for financial support and also Mrs Y. Abrahams for assisting with the analyses.

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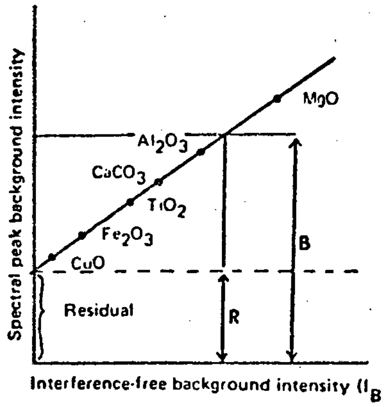

FIG. 9

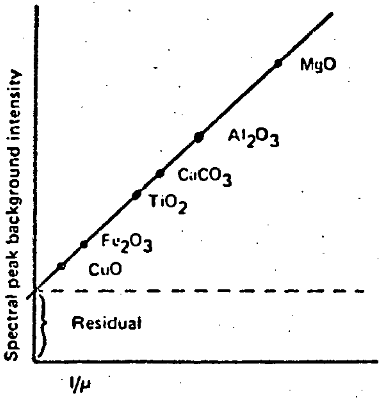

FIG. 10

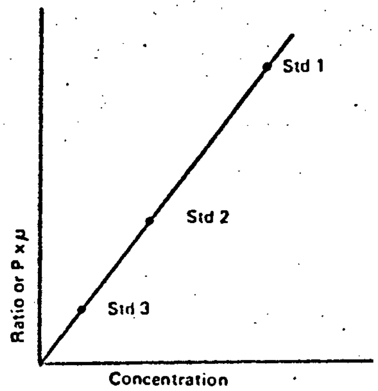

FIG. 11

Appendix: Example of analytical run and calculations

(1) Set up calibration using 'blank' samples relating backgrounds beneath the spectral peaks to a nearby interference-free background (Fig. 9) or to $1/\mu$, if μ is known (Fig. 10).

(2) Using either of the relationships, determine the backgrounds beneath the spectral peaks in both standards and unknowns, and calculate the net spectral peak intensities P.

(3) Divide the net peak intensities P by Compton peak intensity (if read) or by 'true background' (i.e. total background B minus residual background R) (Fig. 9) or multiply by μ, in order to correct for matrix effects.

(4) Plot these matrix corrected ratios, or $P \times \mu$, for the standards against concentration to obtain concentration calibrations (working curves, Fig. 11).

(5) Using the matrix corrected ratios, or $P \times \mu$, obtained for the unknowns, calculate or read off the working curves the concentrations in the unknowns, e.g. the calculations, if μ is not known, may proceed as follows:

In Fig. 9, let m = slope,
R = intercept (i.e. residual background).

For the unknown, measure the intensity of the interference-free background (I_B) and the intensity of the spectral peak (I_P).

It follows that the background beneath the spectral peak is

$$B = mI_B + R$$

and the net peak

$$P = I_P - B$$

Thus, the intensity ratio

$$I_R = \frac{P}{(B-R)} = \frac{P}{mI_B}$$

In Fig. 11, if C = concentration and S = slope, then

$$C = S \times I_R$$

Therefore, for an unknown sample for which only I_B and I_P need be measured, the concentration can be calculated from:

$$C = \frac{S \times [I_P - (mI_B + R)]}{mI_B}$$

where S, m and R are constants.

FORMULATION AND OPERATION OF A GEOCHEMICAL DATABASE

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Many varieties and considerable volumes of geochemical data are being acquired during the search for economic mineralisation. It therefore seems most appropriate to discuss a tool for manipulating and storing such data at a conference whose theme is "Mineralization in Metamorphic Terranes". The primary purpose of the geochemical database that we have established is to provide a tool by which sets and subsets of data may be stored, selected, and manipulated. It has not been our purpose to provide a data repository, although the database system may also be used to this end.

The database (Fig. 1) consists of one record for each variable (e.g. element abundance, age, isotopic ratio, etc.) measured in each sample, thus providing a system which allows the addition of new data for any variable in any sample at any time. Variables may include any parameter which can be represented as a scalar value (i.e. the structure of the database does not restrict its usage to geochemical data). Each database record consists of a sample number (in which locality information is coded), the phase analysed, the variable analysed and its value, the units of measurement, a tag number (to allow association of multiple analyses of single samples), the analytical method, a bibliographic reference, and a rock type code. Supporting files contain additional information on localities (Figs. 2,3), field numbers (Fig. 4), references (Fig. 5) and rock types (Fig. 6).

Figure 2 illustrates the way in which locality information is built into the sample number. Primary classification is by continent, then by country, and locality within a country. For oceanic samples primary classification is by ocean with additional information on the type of sample (e.g. dredge, core, island, grab), then by locality within an ocean. A support file (Fig. 3) lists the number of samples for each locality presently stored in the database.

It is essential to be able to relate database information to sample names or fieldnumbers. Figure 4 illustrates part of the support file matching database number to sample name.

A reference support file (Fig. 5) matches the database reference number to a complete bibliographical reference. The first two digits indicate the year of publication. The third digit is either a 'T' (thesis or other unpublished reference), or a blank (published paper or book). The last three digits allow storage of up to 999 references for each year.

Plutonic hypabyssal rocks are classified according to the IUGS recommendations (Streckeisen, 1973). As no IUGS classifications are yet available for other rock types, we have adopted a similar classification for volcanic rocks, and used modifications of the IGS classification code (Harrison and Sabine, 1970) for sediments, minerals and meteorites. We have adopted a hierarchical classification as illustrated in Fig. 6, showing part of the plutonic rock classification code.

A series of programs provides the means of selecting subsets of data from the database using any combination of criteria selected by the user. Manipulation programs for operation on selected data subsets provide the means of sorting database records on any set of criteria, and of generating a variety of data matrices. Selected subsets may be used for many different forms of data analysis including multivariate statistics, element abundance maps, trend surface analysis, etc.

The database system is currently implemented on a UNIVAC 1106 at the University of Cape Town. However, since all the programs for creating and manipulating routines are written in FORTRAN with only a few machine dependent routines, it should be possible to implement the database on other computer systems with little difficulty.

Streckeisen,A.L. (1973) Plutonic rocks. Classification and nomenclature recommended by the IUGS Subcommission on the Systematics of Igneous Rocks, Geotimes, <u>18</u>, 10, 26-30.

Harrison,R.K. and Sabine,P.A. (1970) A petrological-mineralogical code for computer use. Inst. Geol. Sci. Report 70/6.

FIG. 1

LISTING OF EARTH SCIENCES DATABASE

NUMBER	PHASE	VARIABLE	VALUE	UNITS	TAG	METHOD	REF.	ERRORS	TYPE
1101003063	ALL	GA	.2150+02	PPM	0	XRF	74T001	E	122000
1101003063	ALL	GA/AL	.2380+01		0		74T001		122000
1101003063	ALL	AL	.9050+01	PCT	0	XRF	74T001		122000
1101003064	ALL	GA	.1660+02	PPM	0	XRF	74T001	E	122000
1101003064	ALL	GA/AL	.2060+01		0		74T001		122000
1101003064	ALL	AL	.8060+01	PCT	0	XRF	74T001		122000
1101003065	ALL	GA	.1805+02	PPM	0	XRF	74T001	E	122000
1101003065	ALL	GA/AL	.2220+01		0		74T001		122000
1101003065	ALL	AL	.8140+01	PCT	0	XRF	74T001		122000
1101003066	ALL	GA	.2240+02	PPM	0	XRF	74T001	E	122000
1101003066	ALL	GA/AL	.2660+01		0		74T001		122000
1101003066	ALL	AL	.8410+01	PCT	0	XRF	74T001		122000
1102004001	ALL	GA	.1710+02	PPM	0	XRF	74T001	E	148100
1102004001	ALL	GA/AL	.1440+01		0		74T001		148100
1102004001	ALL	AL	.1190+02	PCT	0	XRF	74T001		148100
1102004001	ALL	FE+++	.9400+00	PCT	0	XRF	67T001		148100
1102004002	ALL	GA	.1615+02	PPM	0	XRF	74T001	E	148100
1102004002	ALL	GA/AL	.1270+01		0		74T001		148100
1102004002	ALL	AL	.1272+02	PCT	0	XRF	74T001		148100
1102004002	ALL	FE+++	.7200+00	PCT	0	XRF	67T001		148100

FIG. 2

BASIC LIST OF LOCALITY NUMBERS FOR EARTH SCIENCES DATABASE

Continental	1000000000	Oceanic	2000000000
Africa	1100000000	Atlantic Ocean	2100000000
Australasia	1200000000	Indian Ocean	2200000000
Antarctica	1300000000	Pacific Ocean	2300000000
North and Central America	1400000000	Antarctic Ocean	2400000000
South America	1500000000		
Greenland	1600000000	Type of Sample = X	21X0000000
India	1700000000	Island Sample	2110000000
Europe	1800000000	Dredge Sample	2120000000
Asia	1900000000	Core Sample	2130000000
		Grab Sample	2140000000
Country = X	11XX000000	Water Sample	2150000000
Locality = Y	11XXYYY000	Locality = Y	211YYY0000
Sample Number = Z	11XXYYYZZZ	Sample Number = Z	211YYYZZZZ
E.g.		E.g.	
South Africa = Country 01 in Africa		Gough Island Sample 1	2110050001
B.I.C. = Locality 014 in South Africa		Gough Island Sample 2	2110050002
S.A., B.I.C., Sample 98	1101014098	Marion Island Sample 63	2210070063

Extra-terrestrial	3000000000
Meteorites	3100000000
Lunar Samples	3200000000

FIG. 3

NUMBER	LOCALITY	LAT.	LONG.
2230010 8	Leg 25, Joides Program	211800 S	514100 E
1101011 6	Namaqualand	300000 S	180000 E
1101900 26	Premier Kimberlite Pipe	254020 S	283100 E
1107007 23	Umkondo Dolerites, Rhodesia	190000 S	300000 E
1600000 4	Greenland	690000 N	400000 W
1401001 2	California, U.S.A.	370000 N	1200000 W
1300001 10	Queen Maud Land, Antarctica	700000 S	420000 E
1202000 10	Tasmania	420000 S	1460000 E
1501001 14	Parana Volcanics, Brazil	120000 S	540000 W
1101015 26	Karroo-Stormberg, Central Area, S.A.		
1104002 10	Karroo-Stormberg, Southern Lebombo Area, Swaziland		
1107003 5	Karroo-Stormberg, Wankie Area, Rhodesia		
1107005 3	Karroo-Stormberg, Nyamandhlovu Area, Rhodesia		
1107004 3	Karroo-Stormberg, Featherstone Area, Rhodesia		
1107002 1	Karroo-Stormberg, Tuli Area, Rhodesia		
1106001 2	Karroo-Stormberg, Botswana Area, Botswana		
1107006 13	Karroo-Stormberg, Northern Lebombo Area, Rhodesia		
1102006 4	Karroo-Stormberg, Southern South West Africa Area, S.W.A.		
1102008 13	Karroo-Stormberg, Northern South West Africa Area, S.W.A.		
1600001 9	Skaergaard Intrusion, East Greenland	682000 N	310000 W
1101012 14	Komatipoort Intrusion, Lebombo Monocline	252500 S	315500 E
1101013 5	Trompsburg Intrusion, S.A.	320200 S	254700 E
1101014 67	Bushveld Igneous Complex, S.A.	250000 S	293000 E

FIG. 4

NUMBER	SAMPLE NAME
1102000001	GR 4 Salem
1102000002	GR 1 Salem
1102000003	GR 2 Salem
1102000004	GR 3 Salem
1102000005	GR 5 Salem
1102000006	GR 7 Brandberg
1102000007	GR 8 Brandberg
1102000008	GR 9 Brandberg
1102000009	GR 6 Erongo
1102000010	OK 190 Okonjeje
1102000011	OK 191 Okonjeje
1102000012	OK 282 Okonjeje

FIG. 5

67T001
E.C. Kostlin, 1967, The geology of part of the Kunene Basic Complex, Kaokoveld, S.W.A., M.Sc. Thesis, Department of Geology, University of Cape Town.

70 001
R.V. Danchin and J. Ferguson, 1970, The geochemistry of the Losberg Intrusion, Fochville, Transvaal, Geol. Soc. South Africa, Spec. Publ. 1, pp 689-714. Symposium on the Bushveld Igneous Complex and other Layered Intrusions.

72T001
Geochemistry Department Honours Project, Student Report, 1972.

73T001
B. Rodrigues, 1973, Processos de Fenitizacao Relacionados com a Estrutura Anelar de Nejoio, Ph.D. Thesis, Department of Geology, University of Luanda.

73 002
K.G. Cox, J.J. Gurney and B. Harte, 1973, Xenoliths from the Matsoku Pipe, in: Lesotho Kimberlites (ed: P.H. Nixon), pp 76-100, publ. Lesotho National Development Corporation.

FIG. 6

- 100000 Plutonic and hypabyssal rocks
  - 140000 A + P ± Q rocks - Q = 0-5% of light coloured minerals
    - 147000 Gabbroid rocks
      - 147200 Gabbroid rocks - plag. + pyx.
        - 147210 Leuco norite
        - 147220 Norite
        - 147230 Mela norite
        - 147240 Leuco gabbronorite
        - 147250 Gabbronorite
        - 147260 Mela gabbronorite
        - 147270 Leuco gabbro
        - 147280 Gabbro
          - 147281 Ferrogabbro
          - 147282 Orthopyroxene ferrogabbro
          - 147283 Biotite orthopyroxene gabbro
          - 147284 Olivine-bearing gabbro
        - 147290 Mela gabbro
        - 1472A0 Dolerite
      - 147300 Gabbroid rocks - plag. + pyx. + amphibole
        - 147310 Leuco amphibole-bearing gabbronorite
          - 147311 Leuco hornblende-bearing gabbronorite

APPENDIX 2

SAMPLE DESCRIPTION AND SOURCES OF Al DATA

In a general work of this kind detailed descriptions of the rocks analysed and of the precise localities from which they were taken are neither feasible nor necessary. Information on rock type has been included in the tables presenting the Ga data, together with information on the general location from which samples were taken, e.g. oceanic island, abyssal basalt, or igneous complex. Where it was deemed necessary, further information regarding localities has been given in the text or in maps and diagrams, e.g. kimberlites, abyssal rocks, Barberton Mountain Land, Sea Point contact, B.I.C. and the Nejoio area in Angola.

Most of the Al data were taken from the references cited in the text. Al was determined in some of the mineral separates and in a few rocks from Gough Island by the author using XRF spectrometry and the fusion technique reported by Norrish and Chappell (1967). Unpublished data for Al in rocks from the Komatipoort Intrusion, the Umkondo dolerites, some Karroo rocks, and the Sea Point contact were kindly made available by A.J. Erlank. E.J.D. Kable made available some unpublished Al data on abyssal rocks and oceanic islands, and J.J. Gurney unpublished data on some of the upper mantle xenoliths. J.B. Dawson supplied Al data for the specially selected kimberlites.

Sources of Al data for abyssal rocks have been included in Tables 41-43, because of the many sources applicable to each table.