A

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entitled

FLUID INCLUSION STUDIES IN APATITE FROM

SOME EAST AFRICAN CARBONATITES AND IJOLITES

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GENERAL INTRODUCTION

A study of inclusions in the apatites from some E.African carbonatites and associated alkaline rocks has been made. The purpose of such a study has been to ascertain the nature, origin and significance of these inclusions and to obtain information concerning the physical and chemical nature of the environment of crystallisation of these rock-types.

An introduction to the study of inclusions in minerals, together with a review of the published accounts of inclusions in minerals from carbonatites and related rocks, are given in the first part of Chapter 1. In the second part of this chapter, the results of a detailed study of inclusions in apatites from rocks of the Wasaki area of W.Kenya are presented. These results are discussed, and inferences drawn concerning the nature of the media responsible for the deposition of apatite from the various rock-types. The reasons for choosing apatite for inclusion studies are also outlined in this chapter.

In Chapter 2 an account is given of the extraction and identification of nahcolite (NaHCO₃) within aqueous inclusions in apatites from carbonatites and ijolites from the Wasaki area and also from ijolites and carbonatites of the Homa, Ruri and Tororo complexes of E.Africa. This is the first reported occurrence of nahcolite in igneous rocks.

Chapter 3 presents the data obtained from homogenisation temperature determinations of aqueous inclusions from the Wasaki carbonatite apatites. These results have been used to determine the minimum formation temperature of the apatites. An account of
the experimental procedure for obtaining the homogenisation temperature together with an assessment of the possible sources of error are also given in this chapter.

The results of a thermometric study of melt inclusions in apatites from Wasaki ijolites are presented in Chapter 4. This study is intended only as a preliminary investigation in order to determine whether melt inclusions can, by analogy with aqueous inclusions, be used as geothermometers. This study was also undertaken to assess and interpret the phase changes which occur within the inclusions as they are heated to high temperatures.

Chapter 5 gives an account of inclusions in apatite from the carbonatites of the Tororo complex of E.Uganda. The results of a detailed thermometric study of the inclusions are presented. The temperature of formation and nature of the "carbonatitic fluid" discussed. The results of similar studies on aqueous inclusions in apatites from carbonatites and ijolites from Homa mountain, Western Kenya are given in Chapter 6.

A method for the determination of the Na\(^+\) : K\(^+\) ratios in aqueous inclusions is outlined in Chapter 7. Results obtained from the analyses of inclusions in apatites from the Wasaki, Homa, Tororo and Ruri complexes are presented and the significance of the data discussed.

Detailed studies of inclusions in apatites from the Ruri carbonatite complex (Dixon, 1963) have not been made. However, the apatites from the carbonatites do contain nahcolite-bearing (Chapter 2) aqueous inclusions, and those from the ijolites contain multisolid inclusions. Na\(^+\) : K\(^+\) ratios have been determined for these inclusions and the results are given in Chapter 7.
(iv)

The usefulness of inclusions in providing information concerning the environment of crystallisation of minerals is well-established. They have been used extensively as indicators of the physical and chemical conditions prevailing during crystallisation of hydrothermal ore deposits (Roedder, 1967a), but unfortunately they have not found wide application in the field of igneous petrology. It is hoped that this present study will show that inclusions in minerals can provide a valuable key to our understanding of magmatic processes, and also point the way for future studies on inclusions in minerals from other igneous rock-types.
CHAPTER 1

THE NATURE, ORIGIN, AND MODE OF ENTRAPMENT OF INCLUSIONS

IN APATITES FROM ROCKS OF THE WASAKI COMPLEX OF EAST AFRICA

1.1. AN INTRODUCTION TO THE STUDY OF INCLUSIONS IN MINERALS

1.1.1. Size of inclusions

A microscopic investigation of the interior of crystalline substances often reveals the presence of small cavities which have trapped a portion of the crystallising medium during the growth of that crystal. These minute inclusions can provide a wealth of information about the conditions prevailing during the formation of rocks and minerals.

Reports of inclusions in a variety of minerals from different geological environments are extensive, and it would appear that these cavities are present in virtually all natural crystalline substances (Roedder, 1972). In many cases they are far too small to be recognised as inclusions, and have generally been dismissed as specks of dust and impurities; such detrimental terms tend to belie their usefulness and importance.

Prior to the development of suitable high-powered microscopes, the study of these cavities was usually restricted to inclusions larger than 100 μ (Brewster, 1826; Sorby, 1858).

Several reports of inclusions greater than 5mm exist in the literature (Davy, 1822; Maslova, 1961; Kvenvolden and Roedder, 1971), but such specimens are exceptionally rare. Inclusions less than about
10 μ are observable under high magnification (x 1000) and in some instances can provide some useful information (Roedder, 1965; Roedder, 1973). Submicroscopic inclusions can be detected by electron microscopy, but because observation is only possible on broken or only polished surfaces/opened inclusions which have lost their contents can be observed. Such studies are thus limited to determinations of the shape, morphology and abundance of these inclusions (Deicha and Sella, 1962; Sella and Deicha, 1962) (see also Plate 1.2 and Plate 1.16).

1.1.2. Classification of inclusions in minerals

Simple classification schemes for inclusions in minerals can be made with reference to the nature of their contents, for instance whether they contain gas, liquid or solid material or combinations of any of these three. Such classifications are purely descriptive and genetic implications cannot be derived. Broad generalisations concerning the environment of deposition of minerals purely on the basis of the contents of inclusions are foolhardy and can lead to serious interpretive errors. To illustrate this point, it might be argued that aqueous saline inclusions present in minerals from granitic rocks imply that the granite has crystallised from an aqueous saline solution, and although this interpretation would no doubt have pleased the early Neptunists, Roedder and Coombs (1967) have shown that such inclusions may merely represent an immiscible aqueous fluid co-existing with the granitic melt.

Elaborate classification schemes are favoured by Russian geologists such as Yermakov (1961) who gives an interesting
classification of inclusions based on the physical nature of their contents at room temperature and at higher temperatures produced during heating-stage studies. In spite of this rather complex classification, once again a genetic significance cannot really be implied. Yermakov's classification leads one to believe that aqueous inclusions indicate a hydrothermal origin for the host mineral, and that monophase aqueous inclusions are characteristic of minerals from cold-water deposits. However, the presence of aqueous inclusions in minerals may simply indicate that a minor aqueous phase was present during crystallisation (Roedder and Coombs, 1967). Likewise, monophase aqueous inclusions are present in many high-temperature minerals (Plate 1.1a, 1.1b), but only represent a necked-down portion of an originally larger, more complex, inclusion (Roedder, 1967a). While it is true to say that inclusions in hydrothermal minerals are generally aqueous saline types and that those present in sublimate minerals are essentially gaseous, it cannot be said that aqueous inclusions always suggest a hydrothermal origin or that gaseous inclusions confirm a sublimation process of crystallisation.

The fact that such a classification scheme assumes trapping of a homogeneous fluid, while in nature this is often not the case, is perhaps its biggest pitfall. Melt inclusions consisting of silicate glass, co-genetic with inclusion composed almost entirely of carbon dioxide, occur in olivine nodules and phenocrysts from basalts (Roedder, 1965). Similarly, aqueous saline inclusions co-existing with glassy inclusions have been found in granitic minerals (Roedder and Coombs, 1967). In these cases where immiscible fractions are present during crystallisation, no single inclusion-type is representative of the
crystallising medium, and all the inclusion-types present must be considered in order to obtain a comprehensive picture of the nature of the fluid from which the host mineral has crystallised.

1.1.3. Morphological features of inclusions

Although most inclusions are observed as irregular cavities, many show a regular and uniform spheroidal or negative crystal morphology. Negative crystal shapes are related to the crystal system of the host mineral. Halite invariably contains cubic or rectangular shaped cavities (Plate 1.1c), while inclusions in apatites show negative crystal shapes which follow the hexagonal symmetry of the host (Plate 1.1e). Tubular inclusions are commonly reported in the literature and appear to be particularly abundant in apatites (Plate 1.1d).

The observed shape of an inclusion is not necessarily its original shape. Constant dissolution and redeposition of the host material from the walls of the cavity by the trapped fluid will, over time, tend to change the cavity shape so that it attains a minimum surface free energy in the form of a negative crystal or sphere. Inclusions which have not undergone this process to any noticeable extent are usually irregular. Negative crystal, spheroidal, and irregular shaped inclusions are all useful for study (Roedder, 1967a), and it does not matter that an inclusion has subsequently changed its shape, provided that it has remained hermetically sealed throughout its history and has not necked-down.
1.1.4. **Necking-down**

One of the most common sources of error in fluid inclusion studies arises from the failure to recognise the extremely common process known as necking-down. Roedder (1962) gives a good pictorial representation of this phenomenon.

In effect, a large primary inclusion can, over time, separate into two or more smaller inclusions. When simple gas/liquid inclusions undergo this process, the vapour bubble is usually isolated in one of the 'necked-down' inclusions. As a result, inclusions containing various proportions of liquid and gas are observed and can ultimately lead to ambiguities when homogenisation temperatures are recorded. The wide range of homogenisation data reported in the literature (for example, Kelly and Turneaure, 1970) is often attributed to necked-down inclusions.

Matters are further complicated when the necking-down of complex inclusions, containing a vapour phase and an aqueous solution together with one or more precipitated daughter minerals, occurs. Any combination of gas, liquid and solids could occur in inclusions resulting from these necking-down processes (Fig. 1.1). It is often very difficult to recognise unaffected co-genetic gas/liquid and solid inclusions when one is constantly aware that such inclusions may have been produced by necking-down.

1.1.5. **Non-hermetic sealing and leakage**

Provided that an inclusion is sealed completely within a crystal, leakage is unlikely from such a closed system. However, microfractures and small, optically unresolvable tubes leading from
the inclusions to the surface of the host crystal sometimes occur, and scanning electron microscopy is able to detect such minute tubular channels (Plate 1.2).

Microfractures and strain from mechanical deformation can be produced during sample preparation, either by sawing or crushing the material (Roedder, 1967a, p.528), and can often cause an inclusion to leak. Evidence for leakage of inclusions under pressure gradients produced in the laboratory has often been cited (Kennedy, 1950; Skinner, 1953), while contrary results which show that most fluid inclusions do not leak have recently been obtained (Roedder and Skinner, 1960). In general, it would appear that inclusions do leak on occasions, but in other instances they do not. Careful scrutiny of dubious inclusions can often reveal minute fractures which traverse the inclusion (Plate 1.1f) but, in general, leakage may be very difficult to recognise.

Choice of suitable host material can reduce the possibility of studying leaked inclusions, for example, calcite, which is easily cleaved, usually contains many leaked specimens. Soft, highly water-soluble minerals such as halite should also be avoided. Leakage from inclusions in halite is renowned (McCulloch, 1959), and leakage from synthetic halite crystals grown from a saturated salt solution at room temperature have been observed by the writer (Plate 1.1c).

1.1.6. Distinction between primary and secondary inclusions

A primary inclusion is one formed by the trapping of fluid during the growth of the host mineral. Subsequent inclusions formed after growth has terminated are known as secondary. These secondary
inclusions are usually located along healed fractures, and, in general, follow curved planes which traverse the crystal. The primary inclusions, which occur in growth zones or in central cavities within a crystal, are usually larger in size than the smaller secondary inclusions (Smith, 1963, p. 54).

In practice, the distinction between primary and secondary inclusions is not always easy. This is particularly so when minerals contain literally thousands of small, closely-spaced inclusions dispersed throughout the crystal.

In recent years a further groups of inclusions has been recognised (Yermakov, 1969; Roedder, 1967a, p. 522). These so-called pseudo-secondary inclusions are formed when a fracture is healed during the actual growth of a crystal. This inclusion-type is only of use when primary inclusions cannot be used, but because it is extremely difficult to distinguish between pseudo-secondary and secondary inclusions they are not really suitable for most inclusion studies. It is obviously essential to choose inclusions which are primary when inclusions are used as indicators of the conditions prevailing during the formation of rocks and minerals.

1.1.7. The trapping of non-representative samples of the crystallising medium

A primary fluid inclusion is a trapped portion of the crystallising medium, but whether or not this portion is representative of the fluid responsible for the growth of the host crystal must be considered before inferences can be drawn from any inclusion study.

Roedder (1967a, pp. 524-523) has dealt with this subject and states that although inclusions are not precisely representative of a
crystallising fluid, the magnitude of the differences between the trapped fluid and the crystallising medium is relatively small. If a crystal grows from a heterogeneous fluid, for example, a magma, portions of gas, aqueous fluid, melt and solid crystalline phases may be trapped independently by a growing crystal as gaseous, aqueous, melt and solid inclusions. Each inclusion so formed is a portion of the environment of crystallisation of the host mineral but is not necessarily a representative sample.

The relative amounts of each phase (for example, aqueous fluid, melt, gas and solids) present in a crystallising medium during the growth of a crystal cannot, in general, be determined from the relative proportion of aqueous, melt, gaseous and solid inclusions trapped by that crystal. This is because certain phases, such as aqueous saline fluid, may preferentially adhere to the growing surface of a crystal, and result in an overwhelming predominance of inclusions of this phase. Roedder and Coombs (1967b) attribute the large numbers of aqueous inclusions in granitic minerals to preferential wetting by an immiscible aqueous fluid phase present in the granitic melt.

Similarly, the presence of large numbers of aqueous inclusions containing globules of hydrocarbon oil in hydrothermal fluorite (Roedder, 1967b) can be explained by preferential wetting of the fluorite crystal during its growth by the oil globules.

In cases where it is probable that a mineral has crystallised from a heterogeneous environment, it is of prime importance to study as many inclusions as possible and not to rely on the data from a few, since it is quite feasible that these may not be truly representative of the nature of the crystallising fluid. Furthermore, if more than
one inclusion-type is present within a crystal, all that can be inferred is that the phases represented by these inclusions were present within the crystallising medium. The actual proportion of each phase present in this medium cannot usually be determined.

1.2. INCLUSIONS IN MINERALS FROM CARBONATITITES AND RELATED ROCKS - A REVIEW

1.2.1. Inclusions in minerals from carbonatites

Reports of inclusions in carbonatite minerals are not uncommon, although, with the exception of a few examples in the Russian literature (Romanchev, 1972; Yezzikova and Moskalyuk, 1964; Penina and Kostyuk, 1971), little more than a brief mention has been made. Apatite and calcite are the minerals which are most often quoted as containing inclusions, although inclusions do exist in other minerals (Table 1.1).

Von Eckermann (1961a) was the first to recognise the significance of inclusions in carbonatite minerals. He was able to show that such inclusions are rich in carbon dioxide and consequently argued that excess CO$_2$ was present during the formation of the Alnösvite. Similarly, Williams (1956, p. 22) found "minute bubbles of carbon dioxide" within the calcite from the Sukulu carbonatite which he cited as evidence for the abundance of CO$_2$ available in the magma, but no evidence was presented to show that the inclusions were primary in origin.

The descriptions of inclusions in carbonatite minerals are varied. Aqueous, gas-bearing inclusions are most often reported, and such inclusions usually contain precipitated daughter minerals.
<table>
<thead>
<tr>
<th>Locality</th>
<th>Minerals Studied</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Napak, Uganda</td>
<td>Calcite</td>
<td>Romanchev, 1972</td>
</tr>
<tr>
<td>Kerimasi, Tanzania</td>
<td>Calcite</td>
<td>Romanchev, 1972</td>
</tr>
<tr>
<td>Fort Portal, Uganda</td>
<td>Calcite, Apatite</td>
<td>Romanchev, 1972</td>
</tr>
<tr>
<td>Amba Dongar, India</td>
<td>Calcite, Apatite</td>
<td>Roedder, 1973</td>
</tr>
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<td>Oka, Canada</td>
<td>Apatite</td>
<td>Girault, 1966</td>
</tr>
<tr>
<td>Kaiserstuhl, Germany</td>
<td>Apatite</td>
<td>Wimmenauer, 1963</td>
</tr>
<tr>
<td>Jacurpiranga, Brazil</td>
<td>Apatite</td>
<td>Melcher, 1966</td>
</tr>
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<td>Alnö, Sweden</td>
<td>Calcite, Apatite</td>
<td>von Eckermann, 1963a</td>
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<td>Mbeya, Tanzania</td>
<td>Calcite, Apatite</td>
<td>van der Veen, 1963</td>
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<tr>
<td>Sukulu, Uganda</td>
<td>Calcite</td>
<td>Williams, 1956</td>
</tr>
<tr>
<td>Bearpaw, U.S.A.</td>
<td>Feldspar</td>
<td>Roedder, 1965</td>
</tr>
<tr>
<td>Lueshe, Zaire</td>
<td>Calcite</td>
<td>Roedder, 1963</td>
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<td>Shawa, Rhodesia</td>
<td>Apatite</td>
<td>Johnson, 1961</td>
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<td>Apatite, Quartz</td>
<td>Kukharenko and Dontsova, 1964</td>
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<td>Gulinskiy, U.S.S.R.</td>
<td>Calcite, Dolomite</td>
<td>Panina and Kostyuk, 1971</td>
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<td>Gula, U.S.S.R.</td>
<td>Calcite, Dolomite</td>
<td>Yevzikova and Moskalyuk, 1964</td>
</tr>
<tr>
<td>Toror, Uganda</td>
<td>Apatite</td>
<td>Prins, 1973</td>
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Wimmenauer (1963) presented sketches of tubular cavities in apatites which contained two cubic phases and a highly birefringent, presumably carbonate, crystal. Evidence was presented to suggest that the cubic phases were halite and sylvite. Similar inclusions were also observed in apatites from the Oka carbonatite (Girault, 1966), and although Girault implied that these inclusions do not contain many solid phases, subsequent work by Roedder (1973) has indicated that quite substantial amounts are present.

Inclusions containing large amounts of solid material, principally carbonates, have been reported on some occasions (Roedder, 1973; Panina and Kostyuk, 1971; Romanchey, 1972). CO₂-liquid is present in apatites from carbonatites from Amba Dongar (Roedder, 1973), Lueshe (Roedder, 1963) and Bearpaw mountains (op.cit., 1963).

Little reference to necking-down of inclusions has been made, even though from the photographs and sketches presented by Girault (1966), Wimmenauer (1963), Yevzikova and Moskalyuk (1954), and from descriptions of inclusions by Johnson (1961), it appears that this process has been extensive. Solid calcite inclusions in apatites, occurring as rounded single crystals are reported from some carbonatites (Girault, 1966; Romanchey, 1972).

1.2.2. **Inclusions in minerals from alkaline silicate rocks associated with carbonatites**

Reports of inclusions from alkaline rock-types associated with carbonatites are even more scarce than reports of their occurrence in carbonatite minerals (Table 1.2). Girault (1966) has noted the presence of inclusions in apatites from rocks genetically related to the Oka carbonatite, but reports that apatites from associated ijolites
<table>
<thead>
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<th>Locality</th>
<th>Rock Types</th>
<th>Minerals Studied</th>
<th>Reference</th>
</tr>
</thead>
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<td>Oka, Canada</td>
<td>Okaites and others</td>
<td>Apatite</td>
<td>Girault 1966</td>
</tr>
<tr>
<td>Napak, Uganda</td>
<td>Ijolites</td>
<td>Nepheline</td>
<td>Romanchev 1972</td>
</tr>
<tr>
<td>Kiwara, Tanzania</td>
<td>Olivine Picrite</td>
<td>Olivine</td>
<td>Romanchev 1972</td>
</tr>
<tr>
<td>Kiwara, Tanzania</td>
<td>Nephelineite</td>
<td>Nepheline</td>
<td>Romanchev 1972</td>
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<tr>
<td>Kiwara, Tanzania</td>
<td>Melanephelineite</td>
<td>Nepheline, Pyroxene</td>
<td>Romanchev 1972</td>
</tr>
<tr>
<td>Khibiny, U.S.S.R.</td>
<td>Khibinite</td>
<td>Nepheline</td>
<td>Bazarova 1965</td>
</tr>
</tbody>
</table>
are devoid of inclusions.

The inclusions studied by Romanchev (1972) were exceedingly complex. The nepheline from the Napak ijolite contained inclusions consisting mainly of numerous solid phases. These included apatite, pyroxene and biotite, in addition to small amounts of gas and liquid. The Kiwaraha rocks contained even more diverse inclusion types; inclusions in olivine from picrite contained up to 90 per cent by volume of solid phases together with some liquid and gas. Similarly, many different inclusion-types such as glass/gas, glass/gas/microcrystals and gas/solids were observed in nepheline from nephelinite. Calcite was tentatively identified within these inclusions (Romanchev, 1972).

The diversity and complexity of inclusions in ijolites and related rocks has been further exemplified by studies on some Russian alkaline complexes (Table 1.2). Gas, gas/liquid and gas/liquid/solid inclusions are reported in apatites from both the Khibiny and Lovozero plutons (Valyashko and Kogarko, 1966), and in nepheline and pyroxene from the same complexes (Bazarova, 1965). However, the work of these authors was limited to thermometric studies, and little mention was made about the origin of these inclusions, even though Zakrzhevskaya (1964) had previously indicated that many inclusions in the Khibiny apatites are secondary.

Besides the inclusion-types described above, inclusions which are essentially composed of solid material are present in the apatites from both complexes. So-called "indurated inclusions", which represent trapped portions of a crystallised melt, occur either as a single crystal plus gas, or more commonly, as two crystal phases plus gas. An
additional type composed of heterogeneous, granular, solid material with or without gas and liquid, and occurring as tubular cavities within apatite has also been described (Valyashko and Kogarko, 1966).

Data from the study of inclusions in minerals from carbonatites and related rocks is rather poor. Many workers have obviously been hampered by the doubtful origin of inclusions studied. The complexity and diversity of inclusion-types present within these minerals underlines the need for a careful and critical study of inclusions in minerals from carbonatite and ijolite complexes if any reliable data is to be obtained. Carbonatites and associated alkaline rocks from the Wasaki area of Western Kenya have been selected for such a study.

1.3. THE WASAKI COMPLEX OF WESTERN KENYA

1.3.1. Geological setting and previous work

The Wasaki peninsula lies to the west of Homa Bay in the western part of Kenya, and includes three main igneous complexes:

(a) The Usaki ijolitic complex
(b) The Nyamaji phonolitic complex
(c) The Sckolo carbonatite complex

LeBas (1966) has briefly described these complexes and a geological sketch map of the area showing the main petrological features has recently been presented (King, LeBas and Sutherland, 1972). These same authors have also described the sequence of events which have taken place in the area.

Pulfrey (1950) presented petrographic and chemical data on the ijolitic rocks at Usaki, and McCall (1958) paid particular attention
to the numerous phonolite plugs present in the area. Ijolites, fenites and urtites, together with phonolite and melanephelinite are common rock-types. Carbonatites and sovites, either in the form of plugs or as agglomerates and breccias, are also exposed (King et al., 1972).

1.4. CHOICE OF MATERIAL FROM THE WASAKI AREA FOR INCLUSION STUDIES

1.4.1. Apatite as a suitable material for study

Apatite is a widespread mineral in most igneous rocks. In carbonatites it is an important accessory and in many cases may be an essential component (Heinrich, 1966, p.159). Apatite is abundant in carbonatites of the Wasaki area, and is similarly present in significant amounts in most of the associated silicate rocks. Reference to Table 1.1 and Table 1.2 is sufficient to show that reports of inclusions in apatites from carbonatites and related rocks are common.

Inclusions are not unknown in apatites from rocks other than the alkaline types previously described. One of the first reports of inclusions in apatites from igneous rocks was made by Groves and Mourant (1929). In his study of the apatite deposits of southeastern Ontario, Currie (1951) referred to long, tubular cavities which run the length of the apatite crystals, and also to globular inclusions which contained gas, liquid and solid phases. Currie (op.cit.) suggested an igneous origin for these deposits on the basis of the acicular and skeletal apatites (those containing tubular inclusions) which he observed.

Experimental work on the system CaO-CaF₂-P₂O₅-H₂O-CO₂ early
in the 1960's revealed that the habit of apatites formed from synthetic melts is dependent upon the environment of crystallisation and history of cooling of the melt. Apatites formed by rapid quenching of the synthetic melt were acicular and often contained a large, central, tubular cavity running the length of the crystal which was filled with quench material identical to the melt which surrounded the apatites (Wyllie, Cox and Biggar, 1962). More recently Kogarko (1971), during a study of the fluorapatite-nepheline system at high temperatures, also produced acicular apatites containing central, tubular inclusions which contained quench material, in this case a silicate glass.

The relationship between the habit of apatites and their mode of origin seems quite acceptable but certain reservations are necessary. A cautious approach was adopted by Wyllie et al. (1962) who "... propose tentatively, that acicular apatite crystals, especially if they exhibit skeletal features or central inclusions, may be used as an additional criterion for the former presence of a liquid phase in a rock". Several authors have subsequently used this criterion to show that granitic apatites were formed from a melt (Capdevilla, 1967; Sabourdy, 1970). Gardner (1972) noted hollow apatites in the Hasvít gabbro from Norway and deduced that they had formed by rapid cooling and had been subjected to some sort of cyclic growth during their history.

The inclusions produced in apatites during experimental runs (Wyllie et al., 1962; Kogarko, 1971) were primary and represented trapped portions of medium responsible for the crystallisation of the apatites. It would therefore seem that since a particular habit of apatite is to form good primary inclusions, this mineral may provide
an excellent means of studying natural inclusions formed by the trapping of the media responsible for the deposition of carbonatites and associated rock-types.

1.4.2. Initial investigation of apatite-bearing rocks from the Wasaki area

During visits to Kenya in 1963 and 1965, Dr M.J. LeBas, of Leicester University, collected rock samples representative of the Wasaki area. These samples are, at present, housed in the departmental collection where locality numbers and sample descriptions are available.

Thin sections were used for an initial investigation of inclusions in the apatites, and it was from these sections that material was selected for further study. The selection of material was limited to a certain extent by the grain size of the apatites; those smaller than about 0.1mm were generally unsuitable. Nineteen apatite-bearing samples were selected for further study, covering nearly all of the rock-types exposed in the area (Table 1.3).

1.4.3. Sample preparation for fluid inclusion studies

Thin sections are inadequate for detailed inclusion studies, and it is preferable to separate the apatite crystals from the bulk rock sample for the following reasons:

(a) So that dispersed apatites can be concentrated, thus eliminating the need for numerous sections in order to obtain a representative sample.

(b) To eliminate the loss of suitable inclusions during preparation of the section, and to avoid the possibility
<table>
<thead>
<tr>
<th>Locality Number</th>
<th>Rock-Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>U705</td>
<td>Sokolo Carbonatite</td>
</tr>
<tr>
<td>U331</td>
<td>Okuge Carbonatite</td>
</tr>
<tr>
<td>U876</td>
<td>Uyi Carbonatite</td>
</tr>
<tr>
<td>U624</td>
<td>Carbonatite in Nyamaji Tuff</td>
</tr>
<tr>
<td>U693</td>
<td>Carbonatite Xenolith in Nyamaji Phonolite</td>
</tr>
<tr>
<td>U488</td>
<td>Ijolite Xenolith in Nyamaji Phonolite</td>
</tr>
<tr>
<td>U271</td>
<td>Usaki Ijolite</td>
</tr>
<tr>
<td>U1256</td>
<td>Usaki Pegmatite Ijolite</td>
</tr>
<tr>
<td>U366</td>
<td>Usaki Pegmatite Ijolite</td>
</tr>
<tr>
<td>U849</td>
<td>Uyi Ijolite invaded by Sovite</td>
</tr>
<tr>
<td>U303</td>
<td>Usaki Wollastonite-Melanite-Ijolite</td>
</tr>
<tr>
<td>U79</td>
<td>Usaki Wollastonite-Urtite</td>
</tr>
<tr>
<td>U1087</td>
<td>Usaki Pyroxenite</td>
</tr>
<tr>
<td>U256</td>
<td>Nyamaji Phonolite with Amygdales</td>
</tr>
<tr>
<td>U1220</td>
<td>Nyamaji Phonolite</td>
</tr>
<tr>
<td>U1223</td>
<td>Nyamaji Phonolite</td>
</tr>
<tr>
<td>U244</td>
<td>Usaki Fenite</td>
</tr>
<tr>
<td>SK10</td>
<td>Usaki Fenite</td>
</tr>
<tr>
<td>U1094</td>
<td>Usaki Micro-Ijolite</td>
</tr>
</tbody>
</table>
that during this preparation, leakage of inclusions has been induced.

(c) So that individual apatite crystals can be studied in three dimensions, thus enabling a composite picture of the shape and contents of the cavity to be gained.

(d) So that the inclusions are readily accessible for crushing-stage studies.

The procedure for separating the apatites varied with rock-type. For the carbonatites, simple digestion of the calcite with dilute acetic acid, buffered with ammonium acetate, followed by magnetic separation, if necessary, was usually adequate. The separation of apatite from harder rocks, such as ijolite and fenite, was more complex. In these cases the jaw-crusher was used to reduce the specimen to a suitable size (about one centimetre chips), and then a steel pestle and mortar of the type described by Smales and Wager (1960, p.12) was used to reduce the sample size still further. The resulting fine-grained fraction was sieved so that it passed 30 mesh bolting cloth and was retained on 120 mesh. Tema milling or grinding are inadvisable since these processes tend to shatter and fracture the apatite crystals. Heavy liquid and magnetic separation, using the Franz isodynamic separator, followed the initial crushing, and relatively pure apatite grains were obtained (Plate 1.3a). When the grain size of the apatite is sufficiently large, as for example in the Usaki pegmatite ijolite (U366, U1256), simple crushing and hand-picking are all that is necessary.
1.4.4. Apatites of the Wasaki area

The X-ray powder diffraction pattern and refractive indices obtained for the apatites from the Wasaki rocks were indicative of relatively pure fluorapatite. Zoned apatites occur in the Okuge carbonatite (U331). The outer zone is considerably lower in refractive index than the inner shell, and the optical discontinuity is sharp (Plate 1.9). Refractive index measurements on the apatites of this sample, together with apatites from other samples, are shown in Table 1.4. The lower refractive indices and the higher birefringence of the outer part of the apatite from U331 indicates that it is a carbonate-rich variety (Heinrich, 1965, p. 81). The inner portion has refractive indices typical of fluorapatite. A diffractometer trace of this specimen showed major peaks typical of fluorapatite and subordinate peaks which could be assigned to carbonate apatite.

The morphology of the apatites differ markedly from sample to sample. Rounded, euhedral crystals are typical of both the Uyi (U785) and Sokolo (U735) carbonatites (Plate 1.3b), whilst well-formed, regular, elongate apatites with pyramidal terminations are typical of ijolitic rocks (U366, U303, U488) (Plate 1.3c). These elongate apatites usually contain long, tubular cavities (Plate 1.3d) filled with solid material. In view of the marked similarity between these apatites and those produced from synthetic melts (Wyllie et al., 1962) it is suggested that these ijolite apatites have crystallised from a melt. The rounded, euhedral apatites from the carbonatites (U785, U876) also show a marked similarity to apatites formed in synthetic systems when an aqueous phase was present, and it is inferred
Table 1.4  REFRACTIVE INDICES OF SOME APATITE FROM ROCKS OF THE WASAKI AREA

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>$\varepsilon$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>U331 (inner zone)</td>
<td>1.634</td>
<td>1.635</td>
</tr>
<tr>
<td>U331 (outer zone)</td>
<td>1.614</td>
<td>1.624</td>
</tr>
<tr>
<td>U076</td>
<td>1.637</td>
<td>1.640</td>
</tr>
<tr>
<td>U795</td>
<td>1.635</td>
<td>1.639</td>
</tr>
<tr>
<td>U693</td>
<td>1.634</td>
<td>1.637</td>
</tr>
<tr>
<td>U430</td>
<td>1.633</td>
<td>1.639</td>
</tr>
<tr>
<td>U849</td>
<td>1.639</td>
<td>1.641</td>
</tr>
<tr>
<td>U1256</td>
<td>1.639</td>
<td>1.641</td>
</tr>
<tr>
<td>U271</td>
<td>1.633</td>
<td>1.639</td>
</tr>
</tbody>
</table>

\[\text{Error in Determination} \pm 0.0027\]

that these crystals have formed in the presence of an aqueous phase.

1.5. **TECHNIQUES EMPLOYED IN THE STUDY OF INCLUSIONS IN APATITES**

1.5.1. **Microscope investigations**

The polarising microscope is the most useful tool for any fluid inclusion study. In order to study inclusions in the minute, separated apatite crystals, the grains were immersed in an oil with a refractive index a little below that of the apatite. A fine-pointed steel probe provided a means of moving small, individual apatite crystals so that better views of their inclusions could be obtained.

The illumination of the specimen is somewhat critical, especially when liquid carbon dioxide is present within the inclusions. Intense illumination at high power is necessary to observe these inclusions, yet the heat produced may be enough to cause the liquid carbon dioxide to become gaseous. In these cases infra-red filters in the form of glass plates have to be used (Roedder, 1965).

1.5.2. **Crushing studies**

A microscope crushing-stage similar to the device described by Roedder (1970) was constructed. The expansion or contraction of a gas phase present within an inclusion is readily observed when the inclusion is opened in oil. An indication of the gas pressure within an inclusion can be obtained in this manner. Estimates of the refractive indices of solid crystalline daughter phases are also possible if the inclusions are opened in oils of known refractive index. Chemical tests on the contents of inclusions by crushing in
various reagents is generally impractical. Besides the problems of manipulating the small quantities of reagents, the extremely small quantities of inclusion material to be analysed (usually no more than $10^{-10} \text{gm}$) require the whole apparatus to be scrupulously clean and the reagents to be exceedingly pure. Only simple tests can therefore, at present, be applied. For example, the action of acid upon solid phases and their behaviour towards various solvents.

1.5.3. Heating studies

Coupled with the polarising microscope the heating-stage is the most widely used method of studying inclusions. Temperatures at which a heterogeneous inclusion becomes homogeneous give an indication of the minimum temperature of formation of the host mineral. Homogenisation temperature data and their significance will be presented in subsequent chapters.

Apart from obtaining homogenisation temperatures, the heating-stage can be used to study the behaviour of various solid phases within an inclusion at various temperatures. In the case of aqueous inclusions containing precipitated daughter phases, estimates of the solubility of these solids can be made.

1.5.4. Cooling studies

Microscope freezing-stages are most useful for studies on dilute aqueous inclusions. Freezing temperatures of such solutions are dependent upon the amount of dissolved salts present, hence estimates of the salinity of these fluids can be made. When dealing with complex inclusions, containing large amounts of solid material,
little can be achieved by cooling studies. Liquid carbon dioxide however, may be observed upon cooling a CO₂-rich inclusion. During this present study only simple cooling-studies down to 0°C have been made.

1.5.5. Methods of manipulation of the apatite grains

Very often, during the course of this study, it has been necessary to transfer single, minute, apatite grains from one place to another (for example from the immersion oil to the crushing-stage). Even the finest tweezers are impractical for this purpose. To remove a grain from an oil it has been found that the best procedure is to use a length of glass tubing drawn out at one end to a very fine capillary. If the fine capillary end is placed in the vicinity of the apatite grain, capillary action due to the surface tension of the oil is sufficient to draw a portion of the oil, together with the grain, up into the glass tube. The size of the capillary can be varied according to the size of the grain to be manipulated. It has been possible to transfer exceedingly small apatite grains using this method, and it has even been possible to manipulate minute (less than 8 μ) daughter minerals which have been released into the oil when an inclusion has been cracked open on the microscope crushing-stage.

A very fine-pointed steel probe or needle can be used to transfer the apatites from one dry slide to another. By slightly wetting the fine point and then placing it near to the grain surface tension again plays its part and the small grain attaches itself to the wetted point. The grain can be subsequently removed by gently tapping the end of the probe so that the grain falls off.
1.6. **INCLUSIONS IN APATITES FROM THE CARBONATITES OF THE WASAKI AREA**

1.6.1. **General considerations**

Inclusions in apatites have been studied from the following samples:

- The Okuge carbonatite U331
- The Uyi carbonatite U876
- The Sokelo carbonatite U785
- Carbonatite Fragment in Tuff U624
- Carbonatite Xenolith in phonolite U693

With the exception of the Okuge apatites (U331), aqueous inclusions are the dominant inclusion-types present, although only minute (less than 10 \( \mu \)) poorly defined, aqueous inclusions are preserved in apatites from U624. Larger inclusions in this sample have lost their contents due to extensive fracturing of the apatite during the history of this fragment. Detailed studies of inclusions from this sample are not possible although many of the features observed in inclusions from samples U693, U876 and U785 are discernible in the minute, unaffected, aqueous inclusions.

The apatites from U331 contain inclusions which are composed almost entirely of solid material. The marked dissimilarity between these inclusions and the aqueous types observed in U876, U785, U693 and U624 is discussed in section 1.6.5.

Inclusions in other minerals from these carbonatites have been observed. Inclusions in calcite occur as planes of minute, aqueous-filled cavities which criss-cross the calcite crystal. These inclusions, besides being far too small for study, are related to healed
fractures, and are therefore undoubtedly secondary in origin (Plate 1.4). Pyrochlore is a common accessory mineral in the carbonatites, and although the presence of inclusions can be demonstrated by an expansion of gas when the mineral is crushed in oil, the high refractive index of the host does not allow details of the nature of these inclusions to be ascertained.

1.6.2. Aqueous inclusions

Aqueous inclusions containing a mobile gas bubble and usually two or more daughter minerals, which have crystallised in situ from the aqueous fluid, are exceedingly common. The inclusions generally occur as spheroidal or tubular cavities in apatites from U876 and U693 (Plate 1.5 and 1.6), although irregular inclusions are characteristic of U785 (Plate 1.7).

In the three main specimens studied (U876, U785 and U693), inclusions are randomly dispersed throughout the apatite crystal. It is not uncommon to find one single, large inclusion (up to 100 μ) in a single apatite crystal (Plate 1.5b). It is, however, more usual to find several smaller cavities (20-50 μ) in a crystal (Plate 1.5a, d), although some apatites may be totally without inclusions (Table 1.5). The reason for this variation in abundance of inclusions in apatites from the same specimen is probably complex, but since inclusions are no more than gross imperfections in a crystal, this variation simply implies that some crystals are more perfect than others.

Necking-down has been extensive, particularly in U785 (Plate 1.7a, g, h). Fortunately, inclusions which show no signs of
Table 1.5  ESTIMATES OF THE ABDUNDANCE OF AQUEOUS INCLUSIONS IN APATITES FROM CARBONATITES OF THE WASAKI AREA.

INCLUSIONS LESS THAN 2 μ IN SIZE HAVE NOT BEEN CONSIDERED

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Number of Inclusions in Apatites (as percentage of total number studied)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>None</td>
</tr>
<tr>
<td>U705</td>
<td>3</td>
</tr>
<tr>
<td>U624</td>
<td>57</td>
</tr>
<tr>
<td>U876</td>
<td>54</td>
</tr>
<tr>
<td>U693</td>
<td>65</td>
</tr>
<tr>
<td>U331</td>
<td></td>
</tr>
</tbody>
</table>

These percentages were determined by counting the number of inclusions in 200 apatite crystals selected at random from each sample.
having undergone this process are available for study (Plate 1.7b).

The primary nature of the aqueous inclusions is readily apparent. Large inclusions, which reduce the host apatite to a mere shell surrounding the aqueous cavity, can only be primary (Plates 1.5b, and 1.6a). Similarly, tubular inclusions, aligned parallel to the c-axis of the apatite, must also be the result of trapping of fluid during the actual growth of the crystal (Plate 1.5b, d, e and f).

1.6.3. Phases present in the aqueous inclusions

(a) The vapour phase

A dark, mobile vapour bubble exists in inclusions in apatites from U876 and U693. In the case of the Sokolo apatites (U785) the bubble consists of either CO₂-liquid or CO₂-liquid plus CO₂-gas (Plate 1.7). The criteria used for the identification of liquid carbon dioxide within the inclusions (in U785) are based upon the characteristic behaviour and large coefficient of thermal expansion of the bubble when the specimen is slightly cooled or heated (Roedder, 1965; Touray and Yajima, 1966). Additional evidence for the existence of high-pressure, high-density carbon dioxide within the inclusions is apparent since only one single homogeneous fluid phase exists above about 31⁰C, the critical temperature of pure carbon dioxide. Only below this temperature can two fluid phases, CO₂-gas and CO₂-liquid, exist.

This high-density CO₂-phase in the aqueous inclusions of the apatites from U785 (Plate 1.7) is in contrast to the relatively low-density vapour bubbles observed in U876 and U693 (Plates 1.5 and 1.6).
Liquified carbon dioxide has been observed at room temperature only on one occasion in U876 and never in U693. However, crushing-stage studies reveal that the gas in U876 is under considerable pressure, and the vapour bubble often expands in diameter by a factor of two or three when the inclusion is opened in oil (Plate 1.8). Cooling of inclusions in U876 does produce a small amount of liquid carbon dioxide. Attempts to cool inclusions in apatite from U693 have failed to show the presence of distinguishable amounts of liquid CO₂, but owing to the poor optical properties of the apatites, a small rim of CO₂ liquid may have been undetected.

(b) The aqueous phase

The dominant phase in all the aqueous inclusions is an aqueous solution which occupies at least 40% of the total volume of the cavity. Its fluid nature is evident from the mobility of the vapour phase within it. Initial investigations of the volatile constituents of these fluids, by mass spectrographic analyses of crushed and heated apatite crystals, have shown that water and carbon dioxide account for over 90% of the volatile content of the inclusions.

Daughter minerals are present in most inclusions. These solids, which have crystallised out from the trapped aqueous fluid, show that this fluid is able to transport large amounts of dissolved material. Results obtained from the analysis of aqueous extracts of crushed apatite samples show that alkalis are present in substantial amounts within these inclusions, and that sodium is always in excess of potassium. Details of the methods and results will be presented in Chapter 7.
(c) **Bicarbonate daughter minerals**

Highly birefringent (up to third order colours) daughter minerals are present in substantial quantities in these aqueous inclusions. In samples U876 and U693 only one crystal of this phase is usually observed, but on occasions two individual, although seemingly identical crystals are present (Plate 1.5b, c, d and e; Plate 1.6b). In sample U785, up to four crystals of this same phase are apparent (Plate 1.7e).

By a variety of optical, chemical and crystallographic methods, the details of which will be presented in Chapter 2, it has been possible to show that these daughter phases consist predominately of NaHCO₃.

(d) **Black opaque daughter minerals**

A marked characteristic of inclusions in apatite from U735, U876 and U693, is the frequent presence of a single, minute, black, opaque speck. These specks occur in almost every inclusion in U735 and U693 but are less common in the inclusions from U876. In most instances these opaque daughter phases appear as little more than a minute speck whose irregularities make its crystallographic form impossible to ascertain. Despite their small size (less than about 0.5 μ), they can sometimes be made to move if a hand magnet is placed near to the specimen. The magnetic properties of these specks are particularly marked in U693 and U785.

Minute, well-formed crystals of the black, opaque, daughter minerals have been observed in some inclusions from U693. They are distinctly plate-like and have a regular hexagonal outline. In view of this distinct habit and marked magnetic properties (Plate 1.6c, d)
they have, in this sample (U693), been identified as pyrrhotite.

In U785 and U876, the magnetic, opaque phase is without any
good crystallographic form. In these inclusions it is possible that
these specks are magnetite, particularly since magnetite is a common
constituent of many carbonatites (Heinrich, 1966).

These opaque mineral phases are most certainly derived from
the aqueous fluid within the inclusion and are considered to be true
daughter minerals, not merely "captured minerals" which were trapped
together with the aqueous fluid as the apatite crystallised. Their
widespread occurrence and constantly small size attest to this.
Perhaps the most important inference to be drawn from the presence of
these phases is the ability of the aqueous fluid within the inclusions
to transport significant amounts of magnetic ore minerals.

(e) Halite

An isotropic daughter phase, with clearly defined cubic faces,
is discernible in about 10% of the aqueous inclusion from U693, although
it has never been observed in aqueous inclusions in the other samples
studied. It dissolves in aqueous glycerol almost immediately it comes
into contact with this medium but is rather sluggish to dissolve in the
inclusion-fluid when the unopened inclusion is heated on the heating-
stage. It has been possible, in one instance, to open an inclusion
in oil with a refractive index of 1.54 and allow the oil to come into
contact with the cube. When this happens, it can be seen that the
cube has a refractive index virtually identical to that of the oil. On
the basis of the predominance of sodium over potassium within the
inclusions, the solubility and approximate value obtained for the
refractive index, this phase has been identified as halite (NaCl).
Small, birefringent (up to second order colours) needles, which are less than 5 μ in length and 0.5 μ wide, occur in about 2% of the aqueous inclusions from U693, although they have never been observed in U624, U076 and U735. These needles react with acidified glycerol and dissolve in aqueous glycerol.

A positive identification has not been possible, although it seems likely that they are alkali carbonates of some sort, and may even represent different habits of the nahcolite crystals also observed within the inclusions.

Besides the phases already described, small amounts of other daughter minerals are often present within the inclusions. They occur as minute, birefringent specks which never exceed 1 μ in size (Plate 1.5e, f). Their marked birefringence, in spite of their exceptionally small size, is indicative of carbonates. They are very sluggish to dissolve in the inclusion fluid upon heating, and only do so at high temperatures (up to ~ 300°C). In view of this, it is unlikely that they are simple alkali carbonates, but their exact nature must remain a matter for speculation.

1.6.4. Summary of phases present in aqueous inclusions in apatite from the carbonatites

Table 1.6 summarises the phases observed within the inclusions in apatite from the three carbonatite samples studied in detail (U705, U076, U693). The amount of each phase present, in terms of the percentage of the total volume of the inclusion which they occupy, is
Table 1.6
SUMMARY OF PHASES PRESENT IN AQUEOUS INCLUSIONS IN APATITE FROM THREE SAMPLES OF CARBONATITE (U705, U376, U693) FROM THE WASAKI AREA

<table>
<thead>
<tr>
<th>Phase Observed</th>
<th>U705</th>
<th>U376</th>
<th>U693</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂-liquid</td>
<td>/</td>
<td>tr.</td>
<td>x</td>
</tr>
<tr>
<td>Bicarbonates</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Black Opaque Specks</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Birefringent Needles</td>
<td>x</td>
<td>x</td>
<td>/</td>
</tr>
<tr>
<td>Halite</td>
<td>x</td>
<td>x</td>
<td>/</td>
</tr>
<tr>
<td>Other Minute Specks of Carbonate</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

/ Present
x Absent
tr. Only observed on a few isolated occasions
* Occurs as black hexagonal platelets and has been identified as pyrrhotite
shown in Table 1.7. These results were obtained by selecting at random ten large primary inclusions, which showed no signs of having necked-down or leaked, and fashioning plasticine models of these inclusions from photomicrographs taken of the cavities in various orientations. This procedure is a seemingly crude but remarkably effective way of attaining a three-dimensional model of the inclusion and its contents, which can then be used for phase percentage calculations (Kelly and Turneaure, 1970). It can be seen that the amount of each of the phases present varies not only between the carbonatites, but also from inclusion to inclusion within the apatites from the same carbonatite. This variation may be due, in part, to nucleation problems (Touray and Sabouraud, 1970), but in most cases it undoubtedly reflects the variable conditions prevailing during crystallisation. Roedder (1973) has also noted a similar variation in the composition of inclusions in apatite from the Anba Dongar carbonatite.

1.6.5. Multisolid inclusions in the apatites from the Okuge carbonatite (U331)

The inclusions in the apatites from the Okuge carbonatite (U331) differ markedly from those present in apatites from other carbonatites of the Wasaki area (U876, U785, U693). While the apatites from the carbonatites described above contain numerous aqueous inclusions, those from the Okuge carbonatite contain inclusions which are composed mainly of solid crystalline material. These solids occupy at least 50% of the total volume of the cavity. Most inclusions contain between 70 and 95% gas and/or an aqueous solution occupy the remainder of the volume.
Table 1.7 ESTIMATES OF PHASES PRESENT IN 10 PRIMARY AQUEOUS INCLUSIONS IN APATITES FROM CARBONATITES OF THE WASAKI AREA

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Percentage of the Total Volume of the Inclusion Occupied by the Phases Indicated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas</td>
</tr>
<tr>
<td>U076</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>47</td>
<td>47</td>
</tr>
<tr>
<td>36</td>
<td>36</td>
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<tr>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>55</td>
<td>55</td>
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<tr>
<td>25</td>
<td>25</td>
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<tr>
<td>53</td>
<td>53</td>
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<tr>
<td>40</td>
<td>40</td>
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<tr>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>56</td>
<td>56</td>
</tr>
<tr>
<td>U705</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>11.5</td>
<td>11.5</td>
</tr>
<tr>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
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<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>6.5</td>
<td>6.5</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>U693</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>6.5</td>
<td>6.5</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>16</td>
<td>16</td>
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<tr>
<td>20</td>
<td>20</td>
</tr>
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<td>15</td>
<td>15</td>
</tr>
<tr>
<td>14.5</td>
<td>14.5</td>
</tr>
<tr>
<td>12.5</td>
<td>12.5</td>
</tr>
</tbody>
</table>

tr. = Less than 0.5% present
nil = No solid phases observed
The inclusions are very small, rarely exceed 10 μ in size (Plate 1.9), and characteristically occur as irregular-shaped cavities. Because of the small size of the inclusions, very little information concerning the nature of the solid phases present could be ascertained. They occur as numerous closely-packed, anisotropic and isotropic crystals. Very highly birefringent crystals, indicative of carbonate minerals, are absent. The absence of such minerals was confirmed by crushing-stage studies in dilute, acidified glycerol. There was a noticeable lack of effervescence when the inclusions were opened in this medium, although many of the solids did, in fact, dissolve completely.

A marked zonation in these apatites has been observed (section 1.4.4.) and it is interesting to note that the inclusions are located entirely within the central core of the apatite, the outer carbonate zone being completely devoid of any inclusion whatsoever (Plate 1.9a, b). The origin of the apatites from this particular carbonatite is questionable. Their occurrence in patches within the rock rather than dispersed throughout the sample, might suggest that they are xenocrysts. The marked zonation further suggests that the apatites were incorporated into the carbonatitic fluid as already precipitated crystals and that only the outer carbonate zone crystallised directly from this fluid. The fact that the central cores of the apatites contain inclusions which are vastly different to those observed in the primary apatites from the other carbonatites (U785, U876, U693), enhance the views held above.

The large amounts of solid crystalline material within the inclusions indicate that the inclusions (in U331) were formed by the
trapping of a melt. This carbonate-poor melt is in contrast to the carbonate-rich aqueous fluid from which the apatites from other carbonatites have crystallised.

1.6.6. Solid calcite inclusions

In addition to the aqueous inclusion in U785, U693 and U876, the apatites also contain large ( > 10 μ ) spheroidal or elongate single crystals of calcite (Plate I.10). These calcite inclusions may occur together with, but not connected to, normal aqueous inclusions (Plate 1.10a). They also occur as solitary inclusions within a single apatite crystal (Plate 1.10b), thus ruling out the possibility that they are necked-down portions of an originally larger, complex inclusions.

These crystals have been identified as calcite on the basis of their exceedingly high order interference colours, marked reaction and effervescence with dilute acid, insolubility in water, and relief relative to the host apatite. This relative relief is particularly diagnostic. An almost perfect match between the refractive index of apatite ( ≈ 1.63 - 1.64) and the highest refractive index of the calcite ( ≈ 1.65 - 1.66) is sometimes observed. In most other orientations the refractive index is substantially lower than apatite (calcite, \( \varepsilon \approx 1.48 \)).

The solid calcite inclusions represent trapped solid phases which were present in the aqueous fluid at the time the apatites crystallised. Occasionally, a portion of aqueous fluid is trapped contemporaneously with a calcite crystal (Plate 1.10f). This confirms that calcite was present within the aqueous fluid as a precipitated phase
prior to the complete growth of the apatites.

In many instances the calcite crystals are not hermetically sealed within the apatite. Consequently, during sample preparation using acetic acid, the calcite has been partially or completely digested. This non-hermetic sealing may indicate that these inclusions have been formed by the infilling of an original aqueous fluid inclusion with calcite, but this hypothesis falls short when one considers the numerous, hermetically sealed, monocrystalline calcite inclusions also present.

During the early part of this study, inclusions resulting from partially digested, non-hermetically sealed calcite inclusions were not recognised, and the complex inclusions that resulted (i.e. calcite plus gas or liquid) caused endless confusion and interpretative errors, which perhaps serves to show the need for a detailed and objective approach to any inclusion study.

1.6.7. Apparent gaseous inclusions

Inclusions composed entirely of a low-pressure gas phase can be easily distinguished from aqueous fluid inclusions because of their black appearance due to total internal reflection of transmitted light within the inclusions. This total internal reflection is a result of the large difference in refractive index between low pressure gases (R.I. \( \sim 1 \)) and apatite (R.I. = 1.63 - 1.64).

The gaseous inclusions (Plate 1.11b, c, e, f) are present in significant numbers (about 1% of all inclusions present) in apatites from U376, U785 and U693, but are only rarely encountered in apatites from U331. Crushing-stage studies have shown that the gas, which
fills the inclusion, did not expand or contract in volume when the inclusions were opened in an inert hydrocarbon oil on the microscope crushing-stage. This confirms that the inclusions contain low-density gas held at approximately atmospheric pressure. CO₂-liquid has never been observed within these inclusions.

Careful examination of the inclusion at very high magnification almost always shows the presence of cracks which lead from the inclusion to the surface of the apatite crystal. Sometimes these fractures are large (Plate 1.1f), but more often they are so small that they are only just discernible (Plate 1.11b). Since these inclusions are associated with fractures which traverse the apatite, and since the 'gas' within the inclusions is not held under a significant positive pressure, it is concluded that these inclusions are secondary in origin. Undoubtedly they result mainly from the complete leakage of aqueous inclusions. However, some may also result from the complete digestion of non-hermetically sealed solid calcite inclusions by acetic acid during the preparation of the apatite concentrates (section 1.4.3.). No evidence whatsoever has been found to indicate that any of these gas-filled inclusions are primary in origin.

1.6.8. Secondary inclusions

The aqueous, solid calcite and multisolid inclusions so far described are primary in origin. Secondary inclusions, that is those formed by the rehealing of a fracture after the growth of the host crystal, are uncommon in the apatite crystals studied here. They can be readily distinguished from true primary inclusions because they
characteristically occur in small planes which traverse the apatite crystal. These inclusions are minute (generally less than 1 μ), and although they probably contain fluid phases, it has been impossible to ascertain, with any degree of certainty, the exact nature of their contents (Plate 1.11a, d).

1.7. INCLUSIONS IN APATITES FROM IJOLITIC ROCKS OF THE WASAKI AREA

1.7.1. Size, shape, abundance and distribution of the inclusions

In contrast to the inclusions observed in primary apatites from the carbonatites, the inclusions present within the apatites from the ijolitic rocks are exceedingly complex. Those composed predominately of solid material are most common, but gaseous, aqueous and even glassy inclusions also occur, together with a variety of inclusions consisting of various proportions of solids, gas, and aqueous solutions.

The size, number and distribution of inclusions in apatites from these rock-types varies greatly from sample to sample. In general, inclusions seldom exceed 150 μ, most being between 10 and 50 μ. Table 1.8 gives an indication of the number of inclusions present in individual apatite crystals from different samples. The results presented in this table were obtained by examining 200 grains selected at random from each sample and counting the number of inclusions greater than 5 μ observed in each grain. The apatites of the Usaki micro-ijolite (U10%) were almost entirely devoid of inclusions. Only on a few occasions have inclusions been observed. However, their small size did not permit any detailed investigations to be made. It is worth noting that the distribution of inclusions in apatite is not
Table 1.8 ESTIMATES OF THE ABUNDANCE OF ALL INCLUSION TYPES IN APATITES FROM IJOLITIC ROCKS OF THE WASAKI AREA.

Inclusions less than 5 \( \mu \) in size were not considered.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>None</th>
<th>1-3</th>
<th>4-10</th>
<th>11 or more</th>
</tr>
</thead>
<tbody>
<tr>
<td>U366</td>
<td>-</td>
<td>6</td>
<td>24</td>
<td>70</td>
</tr>
<tr>
<td>U1256</td>
<td>69</td>
<td>22</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>U499</td>
<td>8</td>
<td>33</td>
<td>37</td>
<td>22</td>
</tr>
<tr>
<td>U271</td>
<td>4</td>
<td>17</td>
<td>34</td>
<td>45</td>
</tr>
<tr>
<td>U79</td>
<td>24</td>
<td>41</td>
<td>29</td>
<td>6</td>
</tr>
<tr>
<td>U303</td>
<td>61</td>
<td>26</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>U849</td>
<td>14</td>
<td>35</td>
<td>37</td>
<td>14</td>
</tr>
<tr>
<td>U1094</td>
<td>99</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
consistent for different samples of the same rock-type. U366 and U1256 are samples of Usaki pegmatite ijolite collected from different localities, and it is immediately evident from Table 1.8 that whilst U366 is particularly rich in inclusions, the apatites in U1256 contain relatively few.

Inclusions in other minerals from these rock-types, such as wollastonite, nepheline and pyroxene, are virtually absent and only occur as small, highly irregular cavities whose primary origin cannot be demonstrated. However, the wollastonite in U79 and U303 does contain inclusions which appear to contain solid material, but because of their minute size and irregularity they are exceedingly difficult to study.

1.7.2. **Multisolid carbonate-rich inclusions**

Apatites from samples U366, U1256, U400 and U303 contain large, tubular cavities which consist almost entirely of masses of solid crystalline material. Several, closely-packed, colourless solids, many of which exhibit high order interference colours, make up the bulk of the inclusion contents (up to 99% by volume), (Plate 1.13). Crushing-stage studies in acidified glycerol have shown that all of these colourless solids react instantly with the acid medium. Complete digestion of these solids, accompanied by rapid effervescence, takes place in a few seconds. From their behaviour in acid solutions and the high order interference colours of many of these solids, it is deduced that they consist mainly of carbonate-bearing minerals. Crushing-stage studies of aqueous glycerol have further shown that although much (\( \sim 70\% \)) of the colourless, predominately carbonate
material remains unaffected, some of these solids did dissolve, but it has not been possible to estimate the amount of water-soluble solids present.

Various proportions of aqueous fluid and/or a vapour phase may also occur within these inclusions (Plate 1.13a, d, f, g), but never in amounts exceeding 25% of the total volume of the cavity. In U306, gas and liquid are only occasionally present, but in U366, U1256 and U303 aqueous fluid phases are common. Liquified, high-density, carbon dioxide, has been observed on occasions in these multisolid, carbonate-rich inclusions in apatite from U366, U1256 and U303.

Besides these colourless, crystalline phases, several other solids are discernible within these inclusions. They are seen as small, black, brown or green crystals and are particularly noticeable after crushing-stage studies in acidified glycerol, since they remain unaffected by the acid and are usually left behind inside part of the inclusion after the bulk of the solids within the inclusions have been digested. Small, isotropic, black specks are most widespread (Plate 1.13) and in some instances a distinct cubic/octahedral form has been observed (U303, U488, U366). When these small, black, opaque minerals, are free to move in a liquid medium, such as acidified glycerol after the bulk of the inclusion contents have been digested by this medium, a hand magnet placed near to the specimen is sufficient to cause movement of these specks. Because of their pronounced magnetism and distinctive form, these phases have been identified as magnetite.

A light brown or straw coloured, pleochroic solid has been observed in multisolid inclusions in U488, and very occasionally in
those from U303. In one instance a particularly well-formed, minute, hexagonal platelet (Plate 1.13h) was observed (U1256) which strongly suggests that this phase is a mica (biotite or phlogopite). Minute, dark-brown, isotropic and green, birefringent solids are present in many of the inclusions in U1256, but in U1256 and U366 they are not apparent, and have only been observed in U303 on a few occasions. Melanite and pyroxene are common minerals in ijolitic rocks and it seems highly probable that these dark-brown and green daughters observed within these inclusions (U1256) are melanite and pyroxene respectively. Their apparent lack of reaction with acid solutions lends additional weight to this identification. Solid phases indicative of nepheline, also a common constituent of these rocks, have not been observed. Finally, a colourless, isotropic, cubic phase, which dissolves rapidly in aqueous solutions and also in acidified glycerol without effervescence, is present in some multisolid inclusions in U1256. This phase is probably either halite (NaCl) or sylvite (KCl).

These carbonate-rich, multisolid inclusions, which often occur as large, central, tubular cavities running the length of the apatite crystal (Plate 1.12), are primary and represent a trapped portion of a melt. Preliminary heating-stage studies have shown that the contents of the inclusions begin to melt at temperatures between about 500 and 600°C, and that at high temperatures (800-1000°C) the contents are completely molten.

1.7.3. Solid silicate melt inclusions
In addition to the multisolid, carbonate-rich inclusions, the
apatites from both samples of ijolite pegmatite (U1256 and U366) also contain silicate melt inclusions.

In U366, they occur as large, central cavities aligned parallel to the c-axis of the apatite, or as small, rounded blebs dispersed throughout the apatite host (Plate 1.14d, e, f). The inclusions are composed of a light brown coloured, optically isotropic glass (Plate 1.15e, b) which has a granular appearance. A single, relatively large, black/brown, isotropic mineral phase (melanite?) is embedded in this glass in all inclusions studied (Plate 1.14d, f; Plate 1.15). Under high magnification, minute birefringent crystals, giving the inclusion a speckled appearance, are also seen embedded in the glassy matrix.

Crushing-stage studies in acidified glycerol showed that the inclusion contents are resistant to acid attack. Occasionally, an inclusion can be removed in toto from its apatite host by carefully cracking open the apatite crystal (Plate 1.15c) on the crushing-stage. The glassy nature of the inclusion could be subsequently confirmed by the irregular fracture shown by the inclusion (Plate 1.15d) and by refractive index measurements on the inclusion contents (n = 1.55 ± 0.01). Scanning electron photomicrographs of these inclusions, which may be exposed on the surface of fractured apatite crystals are shown in Plate 1.16a, b and c.

It is concluded that these inclusions represent trapped portions of a silicate melt, and that the minute crystals embedded in the silicate glass result from the partial devitrification of this glass.

In U1256, similar inclusions (Plate 1.14a, b, c) occur as small, rounded blebs composed mainly of numerous, small, brown, green, black and colourless crystals together with a small amount of silicate
glass ($n = 1.56 \pm 0.02$). Although these inclusions are not so large and widespread as those in U366, they contain larger numbers of crystalline solids. Green, birefringent, pleochroic pyroxene has definitely been observed. The other minerals probably include melanite (brown/black) and nepheline (colourless).

Very often, inclusions intermediate in composition between these glassy silicate inclusions and the multisolid carbonate-rich inclusions described previously, are found in U1256, although they are not apparent in U366. Varying proportions of both carbonate-rich and silicate material are present in these complex, intermediate inclusions (Plate 1.14c), as shown by crushing-stage studies in acidified glycerol. It is inferred that these inclusions represent trapped portions of silicate melt and carbonate-rich melt, which occurred as immiscible fractions within the ijolitic fluid. That these two fractions were immiscible at the time the apatites crystallised is evident from the occurrence of co-genetic silicate melt and carbonate-rich inclusions in the same apatite crystal (U366, U1256).

1.7.4. Other inclusions composed of solid material

Multisolid, carbonate-rich inclusions are sometimes found in apatites from the Usaki wollastonite-urtite (U79) and the Usaki ijolite (U271). However, inclusions consisting of large amounts of solid material occur in the apatites from both of these samples and are the dominant inclusion-type present (Plate 1.17). The absence of significant amounts of carbonate material within these inclusions is shown by crushing-stage studies in acidified glycerol. Little or no
effervescence is observed when the contents of the inclusion are exposed to the acid medium, even though all of the solid crystalline material (which occupies between 60 and 100% of the volume of the inclusion) dissolves completely in this medium in a few minutes. Similar studies in aqueous glycerol have shown that the contents of the inclusion remained insoluble, even when exposed to this medium for 48 hours.

These inclusions consist either of one single crystal of this phase together with minor amounts of liquid and gas, or less commonly as several closely-packed crystals of this same phase sometimes together with small amounts of gas, liquid, and a few minute specks of black, green and brown solids. In tubular inclusions, large, single crystals of this colourless solid are elongate. Such crystals have a straight extinction and are length fast. Birefringence measurements on these crystals gave values ranging from 0.020 to 0.030 (average of 3 samples = 0.026). On one occasion it has been possible to extract a crystal and to align it so that observation down the optic axis was possible. In this position the mineral remained in permanent extinction and must therefore be uniaxial. The basal section was seen to be hexagonal but there is always the possibility that the mineral is a pseudomorph of the tubular negative cavity (hexagonal cross-section) in which it occurs. Refractive index determinations have been possible and values obtained from this minute (∼ 10 µ) extracted crystal were:

\[ \varepsilon_r = 1.515 \pm 0.02 \]
\[ \varepsilon_s = 1.535 \pm 0.02 \]

The crystal is therefore uniaxial negative and probably belongs to the hexagonal crystallographic system.
In spite of the large amount of data accumulated, it has not been possible to positively identify this mineral. Uniaxial minerals found in ijolitic rocks whose refractive indices are anywhere near those obtained above are restricted to nepheline and cancrinite. It is very unlikely that this mineral phase is nepheline, mainly because the birefringence obtained in this study (0.026) is too high. On the other hand, cancrinite would be more feasible but the possibility that this phase is a rare or undocumented mineral cannot be precluded.

Inclusions containing this mineral phase are considered to represent the trapped portion of a carbonate-poor melt. Preliminary heating-stage studies have shown that the contents of the inclusions are completely molten at temperatures between about 730°C and 810°C. Cooling of these inclusions from these high temperatures resulted in complete recrystallisation of this solid phase, and even rapid cooling failed to produce a glass.

1.7.5. **Aqueous inclusions**

Aqueous inclusions are found to some extent in apatites from all the samples studied. In Ul88, Ul255, U303 and U79 they are noticeably scarce (only about one inclusion in every five hundred is an aqueous type). They contain a mobile vapour bubble in an aqueous solution. Daughter minerals are occasionally present but are too small to identify. It is feasible that these inclusion-types have formed from necking-down of larger, complex inclusions, but in specimen U79 a relatively large aqueous inclusion, about 40 μ in size, was observed within a single crystal of apatite devoid of any other inclusions. In this case, the inclusion must be primary and unaffected
by necking-down processes. The small numbers of primary aqueous inclusions present in these samples indicate that aqueous fluids were present during crystallisation.

In samples U271 (Plate 1.17) and U366 (Plate 2.2) aqueous inclusions are found in quite large numbers (about 50% of the total number of inclusions present). These inclusions contain a large amount of aqueous fluid, a CO$_2$-rich gas bubble, which occupies up to about 50% of the total volume of the inclusion, and one or more highly birefringent, water-soluble, alkali carbonate daughter minerals which consist predominately of nahcolite (Chapter 2). The amount of nahcolite present in the inclusions varies from a few per cent. up to approximately 60% of the volume of the cavity. This large variation in the amounts of both nahcolite and vapour present indicates that necking-down processes have been extensive. Many inclusion do in fact show positive evidence of having necked, but not all. Apart from these water-soluble alkali carbonates, other daughter minerals are notably absent, except for a minute, black, anhedral, magnetic, crystalline speck sometimes present in the aqueous inclusions from U271, but only very occasionally in those from U366. These specks are probably either magnetite or pyrrhotite.

The aqueous, nahcolite-bearing inclusions differ from the multisolid, carbonate-rich inclusions also present in these two samples. This difference is evident not only from the large amounts of aqueous fluid within the aqueous inclusions but also from the differences in the composition of the solid phases present in these two inclusion-types. Whereas the solids (daughter minerals) in the aqueous inclusions are almost entirely water-soluble alkali carbonates, those in
the multisolid inclusions are, in the main, water-insoluble and therefore not simple alkali carbonates. Furthermore, heating-studies on the multisolid-carbonate rich inclusions (Chapter 4) have shown that the contents of these inclusions melt. Similar studies on aqueous inclusions from U271 and U366 were generally unsuccessful since decrepitation invariably occurred during heating-runs. However, it was evident that the solids (apart from the magnetic, black speck) dissolved completely in the aqueous fluid. Consequently, whereas the multisolid carbonate rich inclusions were formed by the trapping of a carbonate-rich melt, the aqueous inclusions are considered to represent the trapped portion of a co-existing, aqueous, alkali-bearing, fluid phase.

The apatites from the Uyi iolite (Plate 1.18) which has been invaded by sanidine (U319), depart from the tendency for apatites from unaffected iolites to contain inclusions composed predominately of solid material. The inclusions present in this sample are almost exclusively aqueous saline types. These inclusions, which are primary, usually occur as tubular cavities within the apatites and can reach lengths of up to 100 \(\mu\). They are exceedingly abundant although their large numbers may prove somewhat of a handicap since many closely-spaced inclusions within a single crystal show definite signs of necking-down. Only isolated, tubular inclusions, which appeared not to have been subjected to necking-down, were selected for study. These unaffected inclusions consist of a vapour phase which contracts in volume when the inclusion is opened in oil, an aqueous phase, and usually 5 or 6 solid daughter phases which generally account for 10-20% of the volume of the inclusion, but never exceed 40%. (However, necked-down specimens may surpass this value.)

It is fortunate that the inclusions are often large and uniform
since the nature of the solid phases present can be studied in greater
detail. The daughter minerals consist of two isotropic cubes and two
highly birefringent, euhedral crystals. These birefringent solids possess
an index of refraction in one direction which matches that of the aqueous
fluid in which it occurs. All four phases are present in approximately
the same proportion (by volume). One or two black, opaque, non-magnetic,
specks also occur as daughter minerals.

Heating-stage studies reveal that all of the solid phases,
apart from the black specks, dissolved in the aqueous fluid as the
temperature was increased. The birefringent solids, which effervesced
rapidly in acidified glycerol and dissolved almost instantly in aqueous
glycerol, dissolved in the inclusion fluid at temperatures below 150°C
during heating-runs. In view of their solubility, effervescence with
acid and optical properties, these birefringent daughters have been
identified as alkali bicarbonates (see Chapter 2).

It has been possible to extract the cubic daughter phases,
by cracking open suitable inclusions in immersion oil, and to obtain
an estimate of their refractive indices. The values obtained for
these two solids were 1.485 ± 0.005 and 1.545 ± 0.005. These are in
excellent agreement with the indices for sylvite (KCl, n = 1.490) and
halite (NaCl, n = 1.544) respectively. The cubic phases showed a marked
difference in their solubility as the inclusions were heated on the
heating-stage. One of the cubes dissolved readily and uniformly in
the inclusion fluid (complete solution of this phase at temperatures
between 88-107°C) whilst the other was sluggish to dissolve (complete
solution at temperatures between 225 and 340°C). On the basis of their
refractive indices and solubility differences these two cubic phases have
been identified as halite and sylvite (Plate 1.10a, b, c).

The black, opaque specks, which are without any distinctive crystallographic form, do not show any movement when a hand magnet is placed in close proximity to the specimen. Even a tentative identification of these specks could not be made.

CO₂-liquid has been observed only twice, but in view of the general lack of expansion of the gas phase upon opening the inclusions in oil, the presence of large amounts of CO₂ is not characteristic of these cavities. The occurrence of CO₂-liquid on the two rare occasions is probably the result of trapping an immiscible globule of compressed CO₂ together with aqueous saline fluid during the growth of the apatite crystal.

There is a notable absence of multisolid carbonate-rich or silicate melt inclusions in these apatites. Anomalous inclusions, which on first sight appear to be filled with orange/brown glass, are, on closer inspection, the result of leakage of fluid out from an original aqueous inclusion followed by iron-staining from secondary sources. Small fractures in the apatite crystal, which traverse the inclusion, have similarly been filled with this orange/brown material (Plate 1.10e, f).

In view of the dominance of aqueous inclusions, and the lack of inclusions composed essentially of solid material, it must be concluded that the apatites have crystallised from a highly saline, aqueous fluid with little evidence for the former presence of a melt. The inclusions in the apatites from carbonatites consist almost entirely of aqueous types (section 1.6.2). The similarity in the nature of these inclusions and those in U849 might suggest that the apatites from this ijolite (U849) are not primary products of an ijolitic melt, but
rather the result of invading carbonatitic fluids.

1.7.6. Gaseous inclusions

In all of the ijolites studied, very dark, tubular, spheroidal or irregular cavities are present within the apatites. Crushing-stage studies in oil confirm that these inclusions are gaseous. In most instances contraction of the gas in the inclusion is observed, although it is not unusual to find those which do not show any apparent volume change upon crushing, which indicates that such inclusions are held at approximately atmospheric pressure. In U366 however, not only are gaseous inclusions which expand in volume quite noticeably upon crushing observed, (Plate 1.19d), but also inclusions composed entirely of CO₂-liquid together with a small CO₂-gas bubble in constant Brownian motion.

Gaseous inclusions are rare in U488, U1256 and U303, and those which have been studied are either located along healed fractures or associated with fine cracks. Such inclusions are therefore not primary. Similar 'secondary' gas-filled inclusions occur in the apatites from U349. In U366, gaseous inclusions are sometimes secondary features (Plate 1.19f), but the presence of CO₂-liquid and gaseous inclusions under pressure indicates that many are primary. Such inclusions represent the trapped portion of a CO₂-rich gas phase.

In U79, gaseous inclusions often reach sizes up to 70 μ (Plate 1.19e). Fine cracks are often associated with these cavities indicating that their original contents were lost either during sample preparation or, more likely, at some stage during the geological history of the apatites. Expansion of the gas has never been observed from these
inclusions during crushing studies, and a secondary origin can be assigned to all of them.

In sample U271, gaseous inclusions are widespread and hundreds of such cavities may be present in one single apatite crystal. Often small amounts of birefringent carbonate are present within these inclusions. Crushing-stage studies have revealed that most of these inclusions show a considerable volume expansion. In view of their widespread occurrence and the lack of any features suggestive of a secondary origin, these inclusions are regarded as primary and representative of a low-density vapour phase present at the time of crystallisation.

1.7.7. Inclusions of calcite

Inclusions composed entirely of a single crystal of calcite together with small amounts of fluid are only observed in a few instances in U79, U303, U271 but more commonly in U649 and U366 (Plates 1.19a, b, c). They have not been seen in U1256. These solid calcite inclusions are usually composed of one single irregular or rounded crystal and are similar to the calcite inclusions in carbonatite apatites (but not nearly so widespread). The calcite inclusions are large and enveloped completely by their apatite host. Secondary features, such as necking-down and fracturing, are not associated with these inclusions.

Such inclusions have evidently been formed by the trapping of a solid calcite crystal present at the time of crystallisation. They are not considered to be the result of crystallisation in situ within the inclusion of a calcitic melt, simply because of the exceedingly high
temperature (1340°C) at which pure calcium carbonate melts (Smyth and Adams, 1923).

1.8. **INCLUSIONS IN APATITES FROM OTHER ROCK-TYPES OF THE WASAKI AREA**

1.8.1. **The Usaki pyroxenite U1087**

Inclusions are scarce in apatites from this specimen and when they do occur they are extremely small, seldom exceeding 20 μ in size. Inclusions have been observed which consist of green, brown and colourless speckles of presumably silicate minerals in a glassy matrix. All these inclusions are associated with cracks (Plate 1.20d), and are not hermetically sealed within the apatite. A positive primary origin cannot be assigned to such inclusions, but their presence does indicate that a silicate melt was present at some time during the history of this rock.

Gaseous inclusions have been found which do not show a volume expansion after crushing. In all instances a secondary origin can be deduced for these inclusions from the numerous microfractures which criss-cross the apatites and traverse the inclusions (Plate 1.20a). A particularly interesting, although rare group of inclusions, essentially the same as those found in apatites from carbonatites, are aqueous CO₂-rich types. These are usually well-formed, tubular cavities which consist of one or two bicarbonate daughters, an aqueous saline phase, and CO₂-gas plus CO₂-liquid. The proportion of bicarbonates to CO₂-liquid to CO₂-gas to aqueous fluid is highly variable. A black, magnetic, opaque speck may also occur as a daughter phase. It is doubtful whether these inclusions are primary
since many lie in planes which seem to be the result of healed fractures (Plate 1.20b, c). Large, obviously primary inclusions are absent.

In summary, inclusions are sparse in this sample and when they do occur their primary nature is not convincing enough to consider them as samples of the environment in which the pyroxenite crystallised.

1.8.2. The fenites (U244, SK 10)

Two samples (U244 and SK 10) of apatite-bearing fenites are available for study; both from the fenites surrounding the Usaki ijolite intrusion. Inclusions are very abundant in both specimens and are almost entirely gaseous types (Plate 1.21). Their shape is most often spheroidal or tubular and their size may range up to approximately 75 μ.

There is little doubt that these inclusions are primary. Their very large numbers and lack of features which point to a secondary origin attest to this. Solid phases have not, in general, been recognised within the inclusions, although a small periphery of liquid, presumably aqueous fluid, is present on occasions. The behaviour of 52 inclusions has been studied on the crushing-stage. 47 showed mild contraction and 5 showed a very mild expansion. CO₂-liquid has never been observed, and it would appear that the inclusions result from the trapping of a low-pressure vapour phase.

Aqueous inclusions (containing at least 50% aqueous fluid) account for about one inclusion in every thousand. Unfortunately, their scarcity does not permit a detailed study of their nature, although their occurrence suggests that aqueous liquid was present together with
the low-pressure vapour phase at the time the apatites crystallised.

No other inclusion-types have been observed in these two samples.

1.8.3. The phonolites (UL220, UL223 and U256)

Inclusions are uncommon in apatites from the phonolite lavas (UL220, UL223) and only occur as minute (less than ~ 10 μm) cavities. The minute size of the inclusions restricts the amount of information obtainable from these cavities, but primary gaseous types, and clear isotropic glassy types containing an immobile vapour bubble, have been observed (Plate 1.20c and f).

Apatites occur in calcite-rich "amygdales" within the matrix of the Nyamaji phonolite (U256). In these apatites the inclusions are once again small and scarce. Gaseous and gas/liquid inclusions are present together with inclusions containing carbonate material composed principally of calcite (identified on the basis of very high order interference colours and the similarity of one of the refractive indices of the calcite to that of the host apatite). These inclusions (Plate 1.20f, g), which can actually be classed as multisolid inclusions, also contain a small, black, opaque mineral together with minor amounts of other, unidentified, carbonate phases. Vapour and liquid are occasionally present in small quantities within these inclusions. These calcite-rich inclusions may represent a portion of a carbonate-rich melt which existed together with an aqueous fluid and vapour phase in the phonolite magma. This supposition is highly speculative, but subsequent petrological studies on this sample may lend additional weight to this hypothesis.
1.9. SUMMARY AND CONCLUSIONS

1.9.1. Inclusions as samples of the crystallising medium

The preceding studies have revealed marked differences in inclusion-types present in the apatites from different rock-types of the Wasaki area. The inclusions are often complex and difficult to study because processes such as necking-down, leakage and secondary alteration have taken place to a large extent. In spite of this, it has been possible to assign a positive primary origin to many inclusions. These can be used to determine the nature of the fluids responsible for the deposition of these rocks.

In section 1.1.7, it was stated that, in general, primary inclusions represent only a portion of the crystallising medium and that this portion may not be representative of the entire environment of crystallisation. Apatites however, are particularly suitable for inclusion studies because of their pronounced tendency to trap large primary inclusions, and the experimental evidence which has shown that inclusions in apatites formed from synthetic melts are indeed representative portions of the crystallising medium (Wyllie et al., 1962).

It is possible to obtain a considerable amount of data from inclusion studies provided that the processes which form, and subsequently change inclusions, are understood. It must also be remembered that inclusions, although actual samples of the environment of crystallisation of minerals, may not reveal its exact nature, since phases which were present during crystallisation may not necessarily be preserved as inclusions. By studying literally thousands of these cavities in
apatites from the Wasaki area it is most likely that the phases present during crystallisation are represented by the inclusions.

1.9.2. Environment of crystallisation of the carbonatites

It is evident, from the overwhelming predominance of aqueous inclusions in apatites from carbonatites (U785, U876, U624, U693) and from their primary origin, that the medium from which the apatites have crystallised consisted of a highly fluid, essentially aqueous, medium. This fluid, which is in contrast to the usual concept of a classical molten magma, was composed of CO₂ and H₂O and was capable of transporting substantial quantities of solid material. Sodium and probably potassium, present in bicarbonate daughter minerals within the inclusions, were the principle cationic species present. Calcium must also have been present at some stage during the history of this fluid since solid calcite crystals are also preserved as inclusions. These evidently co-existed with the aqueous phase at the time the apatites crystallised. The ability of this fluid to transport appreciable amounts of ore metal is demonstrated by the common appearance of iron-bearing ore minerals within the inclusions as black, opaque, magnetic, daughter phases.

1.9.3. Environment of crystallisation of the iitolites

The inclusions within the apatites from most ijolitic rock-types are exceedingly complex. The dominant, inclusion-types present are melt inclusions (multisolid inclusions and silicate melt inclusions) which shows that the ijolite apatites have crystallised in the presence of a melt.
The exact nature of this melt is difficult to ascertain. In some cases silicate melt inclusions occur (U1256, U366), indicating that the medium from which the ijoites have crystallised was, in part, a silicate melt. Multisolid, carbonate-rich inclusions are, however, more widespread, which demonstrates that carbonate-rich melts also constitute part of the ijolitic fluid (U1256, U366, U400, U303). There is convincing evidence from the existence of co-genetic, multisolid carbonate-rich and silicate melt inclusions (U1256, U366), and complex silicate/carbonate inclusions (U1256), that co-existing carbonate-, and silicate-rich melts were present as immiscible fractions in the ijolitic fluid. Immiscibility between silicate and carbonate melts has been demonstrated experimentally by Koster van Groos and Wyllie (1963) and it would appear that such a relationship does indeed exist in natural ijolitic magmas. Some samples (U488, U303) have trapped carbonate-rich melts and show no evidence for the existence of silicate melt inclusions. This does not necessarily mean that such a melt was absent, but may mean either that the apatites preferentially trapped the carbonate-rich melt or that the silicate fraction had already crystallised before the apatites, the multisolid carbonate-rich inclusions merely representing the residual fraction.

The apatites from U271, and to a lesser extent from U79, also contain inclusions composed predominately of a mineral phase which has been tentatively identified as cancrinite. It has been beyond the scope of the present study to ascertain fully the nature and significance of this phase within the inclusions, although it is feasible that a positive identification may throw some light on the reasons for the mineralogical differences observed in different
ijolitic rock-types. It would therefore seem a worthwhile topic for future studies.

Aqueous inclusions are present in the apatites from all of the ijolite samples studied, but in most samples they are exceedingly rare. However, in U271 and U366 a large number of inclusions are aqueous types. The presence of these inclusions, which consist of a CO₂-rich, alkali-bearing aqueous fluid, show that an aqueous phase was also present in the ijolitic fluid at the time these apatites crystallised. Furthermore, gaseous CO₂-rich inclusions have been noted in U271 and U366. These inclusions represent a separate CO₂ vapour phase also present in the ijolitic fluid.

In conclusion, the ijolite apatites have crystallised from a silicate/carbonate-rich melt. The presence of an aqueous phase, preserved as nahcolite-bearing inclusions, and a CO₂-rich vapour phase, show that this melt was not 'dry'. The relationship between ijolites and carbonatites is well established, but whether ijolites are the precursors of carbonatites or vice versa has remained an issue under considerable dispute (Heinrich, 1966). The fact that carbonate-rich fluids (carbonate-rich melts and nahcolite-bearing aqueous fluids) exist in ijolitic magmas leaves little doubt of the possibility that carbonatitic fluids can be derived from these magmas.

1.9.4. Environment of crystallisation of the fenites

Inclusions in apatite from fenite consist almost exclusively of low-pressure gaseous-types. In view of the noticeable absence of other inclusion-types it must be concluded that the environment of crystallisation of the fenites involved a low-density gas phase as the
major constituent. Fenitisation occurs not only around carbonatites but also in association with ijolites (Heinrich, 1966). Consequently, fenitising solutions must be considered as being derived both from ijolitic and carbonatitic fluids. Aqueous, alkali-rich fluids, which are also capable of transporting iron (evident from the occurrence of minute specks of magnetic solids), are preserved as aqueous inclusions in apatites from carbonatites and could well give rise to the fenitisation process. Similarly, aqueous, alkali-rich fluids, which contain large amounts of alkalis, exist in ijolitic fluids. These fluids, which are preserved as nahcolite-bearing aqueous inclusions in U366 and U271, can also be considered as fenitising fluids.

1.9.5. Environment of crystallisation of phonolites

Inclusions in apatites from phonolite lavas (U1220, U1223) are scarce. However, the presence of glassy and gaseous inclusions indicate that these rocks have formed from a silicate melt co-existing with a low pressure gas phase. In U256 carbonate-rich (calcite) inclusions, showing a marked similarity to the multisolid carbonate-rich types from ijolite apatites, are present in apatites which occur in calcite-rich patches within the lava. In view of this similarity, and the evidence to suggest that immiscibility between carbonate and silicate melts can occur in ijolitic melts, it seems possible, that by analogy, these apatite/calcite patches may be the result of crystallisation from a separate carbonate-rich liquid present within the silicate lava.
1.9.6. **Environment of crystallisation of other rock-types**

Inclusions in apatites from the Usaki pyroxenite (U1037) are uncommon, but there is evidence in the form of glassy and aqueous inclusions that a silicate melt and associated carbonate-bearing, CO₂-rich, aqueous fluid were present at some stage during the history of the rock. The lack of suitable primary inclusions does not permit inferences to be drawn from these inclusions, which may be secondary, about the nature of the primary crystallising fluid.

The inclusions in apatite from the Uyi ijolite which has been invaded by sovite (U8149) are very similar to those observed in apatites from carbonatites, and it is inferred that the apatites may be products of the invading carbonatic fluid. The apatites from the Okuge carbonatite show features which suggest that they are not primary products of the medium responsible for crystallisation of the bulk of the carbonatite. The dissimilarity of inclusions present in the central core of the apatite crystals compared to those present in apatite from other carbonatites attest to this fact.
Plate 1.1  The morphology of aqueous inclusions

(a) Monophase aqueous inclusion in apatite (ap). The inclusion consists of an aqueous solution (aq) and a small, black, opaque, daughter (?) mineral on the right hand side of the cavity wall. Apatite from a specimen of ijolite (HC 424) from Homa mountain (Bar = 10 μ).

(b) Monophase aqueous inclusion (aq) in apatite (ap) from the same ijolite specimen (HC 424). The rectangular shape of the inclusion, whose longest sides are parallel to the c-axis of the apatite host, can be considered as a negative crystal shape (Bar = 10 μ).

(c) Numerous rectangular and cubic negative crystal shaped inclusions in a large crystal of sodium chloride grown in the laboratory from a saturated NaCl solution. Most of the inclusions contain only an aqueous solution, but the larger cavity also contains a small, spheroidal vapour bubble (arrowed) resulting from leakage of the aqueous fluid out from the inclusion (Bar = 100 μ).

(d) Elongate apatite crystal (ap) in immersion oil (n = 1.56) containing two tubular cavities which follow the c-axis of the apatite host. The larger inclusion can be seen to contain a vapour bubble (V) in an aqueous solution. To the left of this vapour bubble several daughter minerals, which have precipitated out from the inclusion fluid as it cooled, are discernible. The apatite is from a sample of ijolite (HC 576) from Homa mountain (Bar = 20 μ).

(e) A two-phase inclusion in apatite (ap) containing an aqueous solution (aq) and a small vapour bubble (V). The inclusion is viewed down the c-axis of the host apatite crystal and shows a hexagonal negative crystal morphology. A smaller inclusion (X), slightly out of focus and above the larger inclusion, also shows a hexagonal outline. The apatite is from a sample of ijolite (HC 596) from Homa mountain (Bar = 10 μ).

(f) A crystal of apatite (ap), in 1.56 immersion oil, containing a dark spheroidal cavity. A small crack (arrowed) traverses the inclusion. The original aqueous fluid contents of the cavity have leaked completely leaving the empty, apparently gas-filled, inclusion. Apatite from the Uyi sowe (U076) from the Wasaki complex (Bar = 100 μ).
Plate 1.2  Non-hermetic sealing of inclusions as shown by scanning electron microscopy

(a) Scanning electron photomicrograph of the fractured surface of an apatite (ap) crystal (0001). The basal fracture has traversed an inclusion and emptied its contents. All that remains of the cavity is the shallow depression on the (0001) cleavage face. A small tube (T) leading from the inclusion into the interior of the crystal can be seen which indicates that this inclusion has necked. Two further holes (×), leading from the inclusion to the hexagonal prism face (1010) of the host apatite crystal, are also apparent. These minute "tubes" show that the inclusion was not hermetically sealed within the crystal and had undoubtedly leaked during its history (Bar = 5 μ).

(b) Close-up of the inside wall of the cavity shown in (a), but viewed in a different orientation. The arrow indicates the tube which leads to the (1010) face (Bar = 2 μ).

(c) As (b) above but viewed in a slightly different orientation. Once again the darkened interior of the tube (arrowed) can be seen (Bar = 2 μ). The apatite is from a sample of ijolite (HC 476) from Homa mountain.
Plate 1.3  Apatite crystals extracted from rocks of the Wasaki complex

(a) Separated apatite grains from the Uyi carbonatite (U876) of the Wasaki complex, (Bar = 1mm). Oil immersion (n = 1.56).

(b) Single, rounded apatite crystal from the Uyi carbonatite (U876), (Bar = 100 μ ). Oil immersion (n = 1.56).

(c) Elongate apatite crystal extracted from the Usaki pegmatite ijolite (U366). Note the pyramidal terminations and lack of any central cavities, (Bar = 200 μ ). Oil immersion (n = 1.56).

(d) Elongate apatite crystal with pyramidal terminations and containing two, large, central, tubular cavities which are aligned parallel to the c-axis of the apatite crystal. The cavities contain solid material composed, in part, of isotropic silicate glass, (Bar = 150 μ ). Oil immersion (n = 1.60). Apatite from the Usaki ijolite pegmatite (U366).
Plate 1.4  Inclusions in calcite from carbonatite

Calcite containing numerous planes of minute, secondary, aqueous inclusions, one of which is shown by the arrow. Photomicrograph taken from a thin section of the Uyi sovite (U876) from the Wasaki complex, (Bar = 10 μ).
Primary aqueous inclusions in apatite from the Uyi carbonatite (U876)

(a) Numerous primary aqueous inclusions aligned parallel to the c-axis of the host apatite crystal (ap). Oil immersion ($n = 1.60$). Bar = 100 $\mu$m.

(b) Large, primary, three-phase, inclusion occupying the central portion of the host apatite crystal (ap). Oil immersion ($n = 1.56$). Bar = 50 $\mu$m.

(c) Three spheroidal inclusions in apatite. Oil immersion ($n = 1.56$). Bar = 50 $\mu$m.

(d) Numerous tubular inclusions aligned parallel to the c-axis of the apatite host. Bar = 20 $\mu$m.

(e) Flat, primary inclusion in apatite containing a vapour bubble (V), an aqueous solution (aq), nahcolite daughter (nh), and two small specks of other unidentified (carbonate?) solids. Bar = 20 $\mu$m.

(f) Flat, tubular inclusion containing large nahcolite daughter mineral (nh). Several other solid phases are also discernible to the right of the nahcolite daughter, and a small, black, opaque speck is shown by the arrow. Bar = 20 $\mu$m.
Plate 1.6. Primary aqueous inclusions in apatite from a carbonatite xenolith in Nyamaji phonolite (U693)

(a) Basal section of apatite crystal containing centrally-located aqueous inclusion. The inclusion has a distinct hexagonal outline and is a negative crystal shaped cavity. Oil immersion (n = 1.62). Bar = 100 μ.

(b) Two regular inclusions containing daughter phases (not readily apparent from these photomicrographs). The inclusions actually contain birefringent needles, bicarbonate daughter minerals and a small isotropic cube (halite). The difficulty of observing inclusions in this sample is due to the poor optical properties of the host apatite which are often corroded and usually extensively iron-stained. Bar = 20 μ.

(c) Tubular inclusion containing plate-like crystal of pyrrhotite (arrowed). Bar = 10 μ.

(d) As (c) above but after a hand magnet has been placed near to the specimen. The subsequent movement of the pyrrhotite (arrowed) is evident from the way in which this daughter has flipped over to expose its roughly hexagonal outline.
Plate 1.7 Primary aqueous inclusions in apatite from the Sokolo carbonatite (U785)

(a), (b) and (c) Large primary inclusions in apatite (ap) containing daughter minerals and a CO$_2$-rich bubble (arrowed). Note the typical irregular shape of the cavities. Oil immersion ($n = 1.56$). Bar = 50 $\mu$.

(d) Irregular, tubular inclusion aligned roughly parallel to the $c$-axis of the host apatite crystal. Bar = 50 $\mu$.

(e) Large, aqueous inclusion containing three, large, bicarbonate daughter minerals ($\times$), a CO$_2$-rich bubble (arrowed), and a small, black, highly magnetic daughter to the right of the bubble. Bar = 50 $\mu$.

(f) Spheroidal inclusion containing a CO$_2$-rich bubble which is actually composed of CO$_2$-gas (g) and an outer rim of CO$_2$-liquid ($L_2$). $L_{11}$ denotes the aqueous solution which occupies most of the volume of the cavity. The meniscus, which separates the CO$_2$-liquid from CO$_2$-gas, is rather blurred owing to the constant Brownian motion of the CO$_2$-gas bubble within the liquid ($L_2$). Bar = 10 $\mu$.

(g) Necking-down of inclusions. The smaller inclusion in the right hand corner of the photomicrograph still possesses a small tail (arrowed), and has evidently necked from the larger, elongate inclusion. Bar = 10 $\mu$.

(h) Inclusion produced by necking-down. Note the small tail (arrowed) which indicates that this process has taken place. Bicarbonate daughter minerals ($\times$) can also be seen in the inclusion. Bar = 10 $\mu$. 
Plate 1.8 The expansion of the vapour bubble in a primary aqueous inclusion in apatite from the Uyi carbonatite (U876) on crushing

(a) Apatite grain (ap), immersed in an inert hydrocarbon oil, showing a spheroidal inclusion before crushing.

(b) After opening the inclusion on the microscope crushing-stage. Note the large expansion of vapour bubble (V) indicating that the vapour phase within the inclusion is held under considerable pressure. Bar = 500 μ.
Plate 1.9  Inclusions in apatite from the Okuge carbonatite (U331)

(a) and (b) Zoned apatite crystals in immersion oil \((n = 1.58)\). A sharp optical discontinuity (denoted by \(x\)) is evident between the inner fluorapatite core and the outer carbonate-apatite zone. Small inclusions (arrowed) are located entirely in the inner zone of the crystal. \(\text{Bar} = 20 \mu \text{m}\).

(c) Large, central, primary inclusion in the inner fluorapatite part of the crystal. Oil immersion \((n = 1.58)\). \(\text{Bar} = 20 \mu \text{m}\).

(d) Close up of (c) showing inclusion packed with solid phases; about 50\% of the volume of the inclusion is occupied by an aqueous solution \((\text{aq})\). \(\text{Bar} = 20 \mu \text{m}\).
Plate 1.10  Solid calcite inclusions in apatite from carbonatites from the Wasaki area

(a) Apatite crystal (ap) containing two, rounded, solid calcite inclusions (calc) co-existing with two normal aqueous inclusions (inc). The calcite solid inclusions are aligned parallel to the c-axis of the apatite crystal. Apatite from UG76, oil immersion \((n = 1.60)\). Bar = 100 \(\mu\) m.

(b) Large, solid calcite inclusion (calc) in apatite from UG76. Oil immersion \((n = 1.56)\). Bar = 100 \(\mu\) m.

(c) Two, large, irregular, solid calcite inclusions in apatite (ap) from U785. A cogenetic aqueous inclusion is also present in the lower right hand portion of the apatite crystal. The small, black specks in the calcite crystals are minute (secondary?) inclusions. Hence we have inclusions in calcite which in turn are inclusions in apatite. Oil immersion \((n = 1.60)\). Bar = 100 \(\mu\) m.

(d) Hour-glass shaped solid calcite inclusion (arrowed) in apatite from UG76, viewed under crossed polars. Bar = 100 \(\mu\) m.

(e) Irregular solid calcite inclusion (calc) in apatite (ap) from U785, viewed under crossed polars. Bar = 100 \(\mu\) m.

(f) Complex inclusion consisting of an aqueous solution (aq), a vapour bubble \((V)\), and a large calcite crystal (calc). This inclusion was formed by the simultaneous entrapment of the calcite crystal together with a portion of aqueous fluid. Apatite from UG76. Bar = 50 \(\mu\) m.
Plate 1.11    Secondary inclusions and leakage of primary inclusions in apatites from carbonatites of the Wasaki complex.

(a) Apatite crystal (ap) traversed by a small plane of secondary inclusions (arrowed) which are located along the healed basal cleavage of the crystal. Apatite from U876. Oil immersion (n = 1.62). Bar = 100 µ. A large, primary aqueous inclusion is also visible.

(b) Apparent gaseous inclusion resulting from the leakage of an original aqueous inclusion in apatite from U876. A small crack (arrowed) is just discernible leading to the surface of the apatite crystal. Oil immersion (n = 1.56). Bar = 100 µ.

(c) Anomalous inclusion produced by the digestion of a non-hermetically sealed solid calcite inclusion during sample preparation. The inclusion is now partially filled by immersion oil (n = 1.56). Undigested calcite residue is also seen within the inclusion (x). Apatite from U876. Bar = 100 µ.

(d) Small plane of secondary inclusions (arrowed) in apatite from U785. Oil immersion (n = 1.56). Bar = 100 µ.

(e) Apparent gaseous inclusions in apatite from U785 resulting from leakage of original aqueous inclusions. No fractures are discernible but crushing-stage studies on this sample have shown that the 'gas' within the inclusions is held at approximately atmospheric pressure. Apatite from U785. Oil immersion (n = 1.56). Bar = 100 µ.

(f) Apatite crystal from U785 containing complex network of interconnected cavities (x). The inclusion contents have leaked via the small crack (arrowed) which traverses the apatite, and the cavities are now filled with immersion oil (n = 1.56). Bar = 100 µ.
Plate 1.12 Primary, multisolid inclusions in apatite from ijolites

(a) Numerous, multisolid, carbonate-rich inclusions in apatite (Ap) from U1256.

(b) Single, multisolid, carbonate-rich inclusion in apatite from U1256. The inclusion is aligned parallel to the c-axis of the apatite crystal.

(c) Primary, multisolid inclusions composed mainly of an unidentified, non-carbonate material (×) in apatite (Ap) from U79.

(d) Numerous, multisolid, tubular inclusions in apatite from U366. Note the large tubular cavity (arrowed) which extends along almost the whole length of the apatite crystal.

(e) Multisolid, carbonate-rich inclusion in apatite from U303 showing alignment with the c-axis of the apatite.

(f) Multisolid, carbonate-rich inclusion in apatite from U303. The inclusion is equant in shape and occupies a large portion of the apatite fragment.

Oil immersion:  

\[ n = 1.56 \]  (a, c, f)  

\[ n = 1.60 \]  (b, d, e)
Plate 1.12

a

Oil

b

c

Ap

BAR = 50 μ
Plate 1.13  Multisolid, carbonate-rich inclusions in apatite from ioclites

(a) Inclusion in apatite (ap) from U486. The inclusion contains colourless solid material (c), a small amount of vapour (v) and two, black, opaque specks of magnetite (X).

(b) Large, multisolid inclusion from U366. The bulk of the inclusion is composed of granular, microcrystalline, colourless carbonate-rich material. A black speck of magnetite (X) is also apparent.

(c) Typical multisolid, carbonate-rich inclusion from U303. A small amount of vapour (V) and a black speck of magnetite (X) are shown. A smaller inclusion is also evident above the larger one.

(d) Two small inclusions from U1256 showing fine-grained, carbonate-rich solid material and a small amount of vapour (V).

(e) Inclusion from U366 containing colourless carbonate-rich material (c), magnetite (x) and a small amount of vapour.

(f) Inclusion from U1256.

(g) Two multisolid carbonate-rich inclusions from U486 showing colourless solid material (c), a small amount of aqueous fluid (l) and vapour (V). The left hand portion of the inclusion is shown in greater detail in the photomicrograph below (h).

(h) Close-up of the left hand side of (g) above. Showing black, opaque magnetite (X) together with a small amount of vapour. A light brown hexagonal plate of mica (M) is also shown.
Solid silicate melt inclusions in apatite from ijolite pegmatite (U366 and U1256)

(a) Spheroidal silicate melt inclusion in apatite (Ap) from U1256. Bar = 20 μ.

(b) A fractured, spheroidal, silicate melt inclusion in apatite (Ap) showing part of the inclusion (arrowed) protruding into the immersion oil (n = 1.55). Bar = 20 μ.

(c) Elongate, tubular inclusion in apatite from U1256. The inclusion is a complex silicate/carbonate-rich inclusion composed of colourless carbonate-rich material (c) and a large patch of silicate minerals (s). Bar = 20 μ.

(d) Large, elongate, tubular silicate melt inclusion centrally located in apatite from U366. The left hand side of the inclusion protrudes into the immersion oil (n = 1.55). The large brown/black patch, common in all such inclusions, is identified tentatively as melanite and is shown by the arrow. The bulk of the inclusion is composed of a silicate glass (gl). Bar = 50 μ.

(e) Large silicate melt inclusion (gl) in apatite (Ap) from U366, non-hermetically sealed within the apatite. Oil immersion (n = 1.60). Bar = 50 μ.

(f) Hermetically sealed silicate melt inclusion (gl) showing speckled appearance and relatively large melanite crystal (arrowed). Bar = 20 μ.
Plate 1.15  Silicate melt inclusions in apatite from the ijolite pegmatite U366.

(a) Silicate melt inclusion (gl) in apatite (ap) protruding into immersion oil (n = 1.55). The near perfect match between the refractive indices of the oil and the silicate glass of the inclusion is evident. The speckled appearance of the inclusion is exemplified in this photomicrograph.

(b) As (a) above, but under crossed-polars, showing the isotropism of the bulk of the protruding part of the inclusion. Bar = 50 μ.

(c) Silicate melt inclusion (gl) in 1.56 immersion oil, extracted intact from a crushed apatite grain. Note the melanite crystal (black speck) within the inclusion.

(d) As (c) above, after fracturing the extracted inclusion contents on the microscope crushing-stage. The irregular fracture is shown on the right hand side of the inclusion. Bar = 50 μ.
Plate 1.16 Scanning electron photomicrographs of inclusion in apatite from ijolite pegmatite (U366)

(a) Apatite grain (ap) showing silicate melt inclusion (arrowed) protruding out of the fractured surface of the apatite crystal. Bar = 10 μ.

(b) Close-up of (a) above showing the smooth surface of the silicate melt inclusion. Bar = 2 μ.

(c) Close-up of (b) above showing the minute, irregular fractures on the surface of the inclusion. Bar = 0.1 μ.

(d) The fractured surface of an apatite crystal (ap). The indentations on this surface are minute, secondary inclusions which occur in an irregular plane over the whole of the fractured surface. Bar = 10 μ.

(e) Close up of (d) above, showing even smaller planes of inclusions on the fractured surface. Bar = 5 μ.

(f) Another view of (e) above, showing two secondary inclusions which have necked-down. The arrow shows the point at which the two inclusions were originally joined. Bar = 2 μ.
Plate 1.17  Inclusions in apatite from the Usaki ijolite (U271)

(a) Apatite crystal (Ap) in immersion oil \((n = 1.56)\) showing large numbers of small, primary inclusions. These consist of multisolid, carbonate-poor (see section 1.7.i) inclusions and aqueous inclusions. Necking-down has been extensive in this sample. Bar = 20 \(\mu m\).

(b) Close up of (a) above showing the irregularity and complexity of the inclusions. Bar = 10 \(\mu m\).

(c) Small, isolated, aqueous inclusion containing a vapour bubble (V) and an aqueous solution (aq). Several daughter minerals are present within the inclusion but are not readily distinguishable from this photomicrograph. Bar = 10 \(\mu m\).
Plate 1.18 Inclusions in apatite from ijolite invaded by s ovite
(U849)

(a) Large, spheroidal, aqueous inclusion containing a CO₂-poor
vapour bubble (v), aqueous solution (aq), cubes of halite
(h) and sylvite (s), and two bicarbonate daughter minerals
(c). Bar = 20 μ.

(b) Tubular aqueous inclusion containing phases described above.
Bar = 20 μ.

(c) Similar inclusion to (b) above. The daughter phases are,
from left to right: sylvite, bicarbonate (single crystal)
and halite. Bar = 10 μ.

(d) Aqueous inclusion containing several daughter phases including
a small, black, irregular solid (arrowed). Bar = 20 μ.

(e) Apatite crystal in oil, showing a large fracture. The fracture
has traversed an inclusion (f), and the cavity is filled with
secondary material. Oil immersion (n = 1.56). Bar = 50 μ.

(f) As (e) above, the fracture is shown by the arrow. The
inclusion (f) is coated with dark brown, iron-bearing material
of secondary origin. Bar = 50 μ.
Plate 1.19 Calcite inclusions and gaseous inclusions in apatite from ijolites

(a) Rounded calcite crystal (cal) associated with a small amount of vapour (v) in apatite from U849. Bar = 20 μ.

(b) Elongate inclusion in apatite (Ap) from U849, containing a large, irregular single crystal of calcite. Oil immersion (n = 1.60). Bar = 20 μ.

(c) Monocystalline inclusion of calcite (cal) in apatite from U366. A small amount of vapour (v) is also present. Bar = 20 μ.

(d) Numerous primary gaseous inclusions in apatite from U366. Bar = 50 μ.

(e) Large, irregularly-shaped, gas-filled inclusion (g) in apatite from U79. Crushing-stage studies on this inclusion have shown that the gas is held at less than atmospheric pressure. The inclusion is considered to be secondary in origin. Bar = 50 μ.

(f) Gaseous inclusion (g) in apatite from U366. Note the small "tail" (arrowed) connected to the inclusion, indicating that this inclusion has been produced by necking-down. Bar = 20 μ.
Plate 1.20  Inclusions in apatite from pyroxenite and phonolite.

(a) Apatite from pyroxenite (UL087) showing plane of secondary inclusions. Bar = 20 \( \mu \). Oil immersion \( n = 1.61 \).

(b) Plane of minute aqueous inclusions in apatite from pyroxenite. Necking-down has been extensive in these inclusions. The two inclusions shown by arrows contain nahcolite daughter minerals. Bar = 10 \( \mu \).

(c) Large aqueous inclusion in apatite (Ap) from pyroxenite (arrowed) showing association with numerous minute secondary inclusions. Oil immersion \( n = 1.63 \). Bar = 20 \( \mu \).

(d) Spheroidal silicate-rich inclusion (s) in apatite from pyroxenite. The cracks (arrowed) leading from the inclusion to the surface of the apatite crystal show that the inclusion is non-hermetically sealed. Bar = 20 \( \mu \).

(e) Gaseous inclusions in apatite from phonolite (UL220). Bar = 10 \( \mu \).

(f) Spheroidal inclusion in apatite (Ap) from phonolite (U256). The inclusion contains a large amount of calcite (cal) and a black opaque mineral (x). Bar = 10 \( \mu \).

(g) Co-genetic gaseous inclusion (g) and calcite-rich inclusion (arrowed) which contains a black opaque mineral. Apatite from U256. Bar = 10 \( \mu \).

(h) Inclusion in apatite from phonolite (UL223) consisting entirely of glass (gl) and a small immobile vapour bubble (v). Bar = 10 \( \mu \).
Plate 1.21  Gaseous inclusions in apatite from fenite (U244)

(a) and (b) Dark gas-filled inclusions (g) in apatite (Ap). Oil immersion (n = 1.56). Bar = 50 μ.

(c) Large gas-filled inclusion (g) in apatite (Ap). Oil immersion (n = 1.60). Bar = 50 μ.
The inclusion, trapped at temperature $T_1$, consists of a homogeneous fluid. The development of a vapour bubble and a small daughter mineral (stippled cube) takes place, over time, as the host crystal cools to $T_2$. At $T_3$ the inclusion starts to neck, and at $T_4$, the part of the inclusion containing the vapour bubble has necked completely. Further cooling causes another portion of the inclusion to neck and at room temperature $T_6$, three separate inclusions with widely varying phase ratios are produced.
FIGURE 1.1 THE NECKING-DOWN OF A FLUID INCLUSION.
CHAPTER 2

NAHCOLITE (NaHCO₃) IN INCLUSIONS IN APATITES FROM SOME

E. AFRICAN IJOLITES AND CARBONATITES

2.1 INTRODUCTION

Fluid inclusions in minerals can provide a unique opportunity of studying the physical and chemical nature of crystallising fluids. The presence of daughter minerals which have precipitated from the fluid inside the inclusion as it cooled, are particularly useful in determining the actual composition of this fluid, although the difficulties posed by their minute size and inaccessibility often precludes a definite identification of such phases (Roedder, 1972, p. 719). By a combination of optical, crystallographic, and chemical methods, it has been possible to show that nahcolite is present in inclusions in apatites from ijolites and carbonatites of the Wasaki, Ruri, Homa and Tororo complexes of East Africa, described by King, Le Bas and Sutherland (1972).

2.2 INVESTIGATION OF THE BICARBONATE DAUGHTER MINERALS WITHIN INCLUSIONS PRIOR TO EXTRACTION.

Primary aqueous inclusions containing precipitated daughter phases are present in the apatites from some East African carbonatites and ijolites (Le Bas, Mills, and Rankin, 1972; Rankin and Le Bas, 1973), and although the exact nature and composition of these inclusions varies from sample to sample, a characteristic feature of many of these fluid-filled cavities is the existence of highly birefringent, water-soluble, crystalline daughter phases such as are now reported as nahcolite (NaHCO₃).
These crystals are observed within the inclusions as minute (less than $10 \mu$), colourless, anisotropic solids exhibiting very high interference colours, usually third order (Plates 3.1 and 3.2). Crushing - stage studies (Roedder, 1970) in dilute acidified (HCl) glycerol show that these birefringent solids dissolve instantly with rapid effervescence and evolution of gas bubbles when the acid medium comes into contact with them, which coupled with the high birefringence, is indicative of a carbonate mineral. Similar studies showed that this carbonate phase dissolves instantly without any apparent reaction when the inclusion is opened in pure distilled water on the microscope crushing-stage. This marked solubility in an aqueous medium would further suggest that this phase is an alkali carbonate.

Flame emission micro-techniques have been used to study the alkalis present within the inclusions, and the results have demonstrated that sodium is present in substantial amounts within the aqueous fluids. Aqueous extracts leached from crushed apatite samples containing abundant inclusions have further shown, using an EEL flame photometer, that sodium is always in excess of potassium (Chapter 7). The sodium to potassium weight ratios (wt. Na$^+$: wt. K$^+$) range from 1.3:1 - 3.8:1 for the extracts from ijolite apatites and from 3.1:1 - 16.0:1 for those from carbonatite apatites.

Another most useful observation is the extreme difference in refractive indices of the alkali carbonate. In some orientations the index matches exactly that of the aqueous fluid within the inclusions, whilst in other orientations it exceeds that of the fluid, (Plate 2.1B and C). The refractive index for pure water
is 1.333 and seldom exceeds about 1.39 for saturated aqueous solutions of inorganic salts. Concentrated solutions of alkali carbonates are no exception, for example,

\[ n_D = 1.3409 \text{ for a } 6\% \text{ NaHCO}_3 \text{ solution and } n_D = 1.3652 \text{ for a } 15\% \text{ Na}_2\text{CO}_3.10\text{H}_2\text{O solution} \] (Weast, 1965, pp.D127-D165)

Water-soluble carbonates of sodium and potassium which possess an index of refraction less than 1.39 are restricted to nahcolite (NaHCO\(_3\), \(\alpha = 1.376\)) and kalicinite (KHCO\(_3\), \(\alpha = 1.380\)), (Winchell and Winchell, 1964, p.89). No other synthetic or naturally occurring water-soluble sodium or potassium carbonates having an index of refraction less than 1.405 are known to exist (Winchell and Winchell, 1964; Porter and Spiller, 1956). Nor do the properties correspond to those of natron and trona. These preliminary studies therefore indicated that alkali bicarbonates are present and, since soda is in excess of potash, suggested that nahcolite would be expected to be the dominant bicarbonate daughter phase within the inclusion. This is confirmed by the optical and crystallographic data given below.

2.3 EXTRACTION AND CRYSTALLOGRAPHIC MEASUREMENTS OF NAHCOLITE

In spite of the exceedingly small size of the nahcolite crystals which rarely exceed 10 \(\mu\), it has been possible to extract the solids from large (up to 150 \(\mu\)) well-formed inclusions present in the apatites from a few specimens, (U876, U366, U765) by gently opening the cavities in suitable oils (usually \(n = 1.56\)) on the microscope crushing-stége. In most cases, however, the crystal
either remains lodged within the inclusions or else it is crushed and scattered among the apatite debris as minute fragments.

The crystal morphology (Plate 2.3) at first suggested low symmetry orthorhombic but the subsequent discovery of twinned crystals (Plate 2.4A-D) indicated monoclinic symmetry. Due to the close coincidence of the $\alpha$ vibration direction and the pole to the (101) face which is prominent (fig. 2.1), the crystals give the appearance of having straight extinction apparently confirming the orthorhombic symmetry. The true monoclinic symmetry was determined by plotting stereographically all the morphological and optical data from twinned and untwinned crystals (fig. 2.2A) of nahcolite extracted from the inclusions. The difficulty of the identification largely arises from the fact that for nahcolite $\beta = 93^\circ 19'$ giving near orthorhombic symmetry in some orientations.

Refractive index measurements on the extracted specimens gave the following results:

$\alpha 1.378 \pm 0.003$, $\beta 1.502 \pm 0.005$, $\gamma 1.579 \pm 0.003$,

which compare favourably with those obtained by Fahey (1962) for nahcolite from the Green River Formation ($\alpha 1.375$, $\beta 1.593$, $\gamma 1.533$, all $\pm 0.002$). In shattered specimens the minute nahcolite fragments sometimes showed a marked conchoidal fracture but on other occasions good cleavages were visible though the directions could not be ascertained. Some of the crystals extracted could be rolled into various orientations directly under the microscope by gently stirring the immersion oil (R.I. = 1.54) with a fine-pointed steel probe. These crystals together with those in situ within the inclusions were photographed in various orientations at high power and the photomicro-
graphs enlarged (Plates 2.1 to 2.4). Interfacial angles and also angles to edges were measured from these photomicrographs and further measurements were made directly on the microscope-stage. The results of numerous measurements on five extracted crystals from U366 and U876 were used to determine the axial ratios. One of the extracted crystals showed perfect twinning (Plate 2.4A) which is a characteristic feature of synthetic nahcolite crystals (Winchell and Winchell, 1964, p.89), as shown in Plate 2.4E.

2.4 RESULTS OF CRYSTALLOGRAPHIC MEASUREMENTS

Some of the crystals of nahcolite measured are shown in Plates 2.3 and 2.4. The measurements, made with a simple goniometer were plotted on a stereographic projection and at first, when it was believed the mineral was orthorhombic, an apparent close fit of the axes and some prominent faces to those of pirssonite (\( \text{Na}_2\text{Ca(CO}_3\text{)}_2\cdot2\text{H}_2\text{O} \)) was obtained though the habit was unusual. Furthermore, since pirssonite is only partially soluble in water, this possibility had to be ruled out. When the twinned crystal was discovered and the monoclinic symmetry realised, the data were replotted (fig. 2.2A) and nahcolite recognised, and later confirmed by refractive index determinations.

Owing to the difficulty of measuring accurately the crystallographic angles of all the faces from the highly enlarged photographs, some use had to be made of the properties of zones of faces and the Law of Rational Indices to improve the measurements. Location of the optical vibration directions also assisted in the construction of the stereogram (fig. 2.2A). The axial constants obtained are
$a:b:c::0.755:1:0.355 (\pm 0.01), \beta = 93.5^\circ$ which compare favourably with the values quoted by Dana (Palache et al., 1951, p.134) of $0.7645:1:0.3582, \beta = 93^\circ 19'$.

The principal form developed is \{010\} and most crystals when extracted from the inclusions rest on this face (Plate 2.3A, F, G, H, J, K). In that orientation, the forms \{100\}, \{101\} and \{101\} are seen in profile with the angles between the poles being $62^\circ$, $50^\circ$ and $68^\circ$. These measurements (+ 1°) were repeated on innumerable different crystals from photomicrographs and directly under the microscope. The $\alpha$ vibration direction lies less than 1° away from the pole to (101) and towards the $z$ axis. Other forms present in all the crystals are \{110\}, \{111\} and \{111\}. The twinned crystal (fig. 2.2A) has its composition plane parallel to (101).

### 2.5 OTHER BICARBONATE DAUGHTER MINERALS

Even though nahcolite has been positively identified within the inclusions it became apparent during the course of these investigations, in view of the presence of potassium as well as sodium within the inclusions, that kalicinite ($\text{KHCO}_3$) might also be present, particularly in specimens which gave a low $\text{Na}^+:\text{K}^+$ weight ratio. When two or more seemingly identical bicarbonate phases are observed within the inclusions (Plate 2.2) it is feasible to suppose that one of them may be kalicinite (probably the smaller one), particularly since Roedder (1972, p.1129) cites evidence to suggest that, in general, only one single crystal of / precipitated daughter phase would be expected within a fluid-filled inclusion. Kalicinite has never been observed before in a rock, the only known previous occurrence was "found as a
result of recent decomposition under a dead tree at Chypis, Canton Wallis, Switzerland" (Palache et al., 1951, p.136). It is also said to occur with trone in Hungary (op.cit.).

The crystallographic distinction between naehcolite and kalicinite is not easy as they appear to have similar habits (Plate 2.4F, G, H, I). The principal forms of kalicinite are \( \{101\}, \{201\}, \{100\} \) and \( \{110\} \) according to Porter and Spiller (1956, M.387), giving the angles 74°, 52.5°, 53.5°, 74°, 52.5°, 53.5° in the \( [010] \) zone, with \( \alpha \) vibration only 7° from the (101) pole (Fig. 2.2B).

However, some synthetic crystals show the forms \( \{010\}, \{101\} \) and \( \{100\} \) with only minor development of \( \{110\} \) faces, such crystals usually rest on \( (010) \), being the larger face, and are elongated parallel to \( (101) \) face giving near-straight extinction optics. The \( \{001\} \) and \( \{210\} \) forms also seem to be likely faces. It has not been possible to positively identify crystals of either the Porter and Spiller habit or the "synthetic" habit, though several daughter minerals with crystallographic outlines approximating to one or other of these are suspected to be kalicinite (Plate 2.2A, B).

### 2.6 SUMMARY AND CONCLUSIONS

Nahcolite has been positively identified in aqueous inclusions in apatite from carbonatites and ijolites of the Wasaki complex. This is the first reported occurrence of this mineral in igneous rocks. It also occurs as a daughter mineral in aqueous inclusions in apatite from the Home, Tororo and N.Ruri rocks.

The nahcolite-bearing inclusions in the Usaki pegmatite
ijolite (U366) co-exist with melt inclusions. They represent trapped portions of an aqueous, saline, carbonate-bearing fluid phase present in the ijolitic melt at the time the apatites crystallised (section 1.9.3).

The aqueous inclusions in the carbonatite apatites (U876, U785) are the trapped portions of the fluid from which the apatites have crystallised (section 1.9.2). The presence of large amounts of naccolite within these inclusions shows that this fluid was rich in alkalis.
Plate 2.1 Nahcolite Crystals as Daughter Minerals in Aqueous inclusions in apatite from carbonatite

A. Three-phase inclusion in apatite (Ap) showing gas bubble (G), aqueous solution (L), nahcolite (Nh), ?kalicinite (Kh), and unidentified anisotropic solids (U).

B. As A, rolled through ~90°, showing normal habit of nahcolite, and 'disappearance' of the ?kalicinite crystal. If it is taken that the disappearance is due to viewing it with vibration in the plane of the photograph, then the crystal outlines observed in A may be correlated with the {210} and {100} forms in Fig. 6b.

C.D.E. Inclusion in apatite showing nahcolite crystals in several orientations.

F. Inclusion in apatite with nahcolite (Nh) and suspected kalicinite (Kh) showing normal habits.

G. Tubular inclusion in apatite, with great abundance of various carbonates, principally nahcolite.

The host rock in each case is Usaki ijolite pegmatite (U366)
Plate 2.1 Nahcolite crystals as daughter minerals in aqueous inclusions in apatite from carbonatite

A. Apatite crystal (Ap) containing large three-phase primary inclusion containing gas (G), liquid (L) and nahcolite daughter mineral (Nh).

B. Similar inclusion to A containing well-formed nahcolite crystal (Nh) with small amounts of other carbonate daughter minerals and an unidentified black opaque mineral alongside. Viewed in ppl with plane of polarisation \( \perp \) to length of inclusion.

C. Same inclusion as B viewed in ppl with plane of polarization parallel to length of inclusion. It shows the exact match of the refractive index of the liquid with the approximate vibration direction of the nahcolite.

D. Primary three-phase inclusion in apatite, similar to A.

E. Enlargement of inclusion in D, showing euhedral nahcolite (Nh).

F. As E, but rolled \( \sim 90^\circ \), showing different view of nahcolite crystal.

The host rock in each case in the Wasaki carbonatite (U876)
plate 2.1

A

B

C

D

E

F

Nh
L
G

Ap

Nh
L
G

Nh

Nh

Nh

50μ

10μ

10μ

50μ

10μ
Plate 2.3  Extracted Nahcolite Crystals

A. B. C  Three views of single nahcolite crystal extracted from inclusion in apatite from the Usaki ijolite pegmatite (U366). A is viewed down [010]-axis.

D. E. F. Another extracted nahcolite crystal from U366. F is viewed down [010]-axis. See also Fig. 5.

G. Another nahcolite crystal from U366, resting on side pinacoid.

H. Nahcolite crystal elongated along (101) extracted from a primary inclusion in apatite from the Sokolo carbonatite (U735). Viewed down [010]-axis.

I. As H, rolled about length of crystal.

J. K. L. Three views of rolled nahcolite crystal extracted from a primary inclusion in apatite from the Wasaki carbonatite (U376). K is viewed down [010]-axis.
Plate 2.4  Synthetic nahcolite and kalicinite crystals

A. B. C. D. Four views of twinned nahcolite crystal from Usaki ijolite pegmatite (U366).

E. Twinned crystal of synthetic nahcolite showing same habit as in A.

F. Normal habit of synthetic nahcolite, comparable with those in Plate 2.3.

G. Common habit of synthetic nahcolite, as in Plate 2.2B.

H. I. Normal habits of synthetic kalicinite. They are similar to F and G as discussed in text.
Fig. 2.1  The forms developed in nahcolite crystals extracted from inclusions

A. Nahcolite crystal showing the normally developed outline of faces and optical orientation. Drawn from Plate 2.3F.

B. Nahcolite crystal drawn from several photographs including Plate 2.3B and E. This is the normal habit. Letters correspond in Fig. 2.2A.

C. Twinned crystal of nahcolite as illustrated in Plate 2.4A, showing composition plane (dashed) and the $\alpha$ vibration direction which is common to both halves of the twin.

D. Kalicinite crystal, as in Plate 2.4H with faces indexed.

E. Kalicinite crystal, as in Plate 2.4I showing optical orientation of common habit with $\alpha \wedge (10\overline{1}) = 7^\circ$. 
Fig. 2.2 Stereograms of nahcolite and kalicinite crystals

A. Stereogram of nahcolite derived from angular measurements of natural crystals as shown in Figs. 3 and 4. Dots indicate faces identified, other faces also likely to be present are also plotted. X indicates vibration directions.

B. Stereogram of kalicinite constructed from data for synthetic crystals. Note the similarities of some of the zones and the optical orientation with those of nahcolite.
CHAPTER 3

A THERMOMETRIC STUDY OF AQUEOUS INCLUSIONS IN APATITES
FROM CARBONATITES OF THE WASAKI AREA OF E. AFRICA

3.1 INTRODUCTION

Apart from their usefulness as indicators of the chemical and physical nature of crystallising fluids, fluid inclusions have also been used extensively as reliable geothermometers in elucidating the formation temperatures of rocks and minerals (Roedder, 1972). The temperature at which a heterogeneous inclusion becomes homogeneous, the so-called homogenisation temperature ($T_h$), represents the minimum temperature of formation of the host material. Past (Smith, 1953) and present literature (Roedder, 1972) abound with results obtained from homogenisation temperature determinations, but in spite of innumerable references to fluid-filled cavities in minerals from carbonatites (Chapter 1, Table 1.1), American and European geologists have completely neglected their potential as geothermometers, although some results are scattered amongst the Russian literature (Panina and Kostyuk, 1971; Romanchev, 1972; Yevzikova and Moskalyuk, 1964; Kukharenko and Dontsova, 1964).

The apatites from the Sokolo carbonatite (U785), the Uyi sovite (U976) and the carbonatite xenolith in phonolite (U693) from the Wasaki complex of W.Kenya (King et al., 1972) contain numerous, well-formed, primary, aqueous inclusions suitable for a thermometric study using a microscope heating-stage. These aqueous inclusions, which have been described in detail in Chapter 1, usually consist of large
(up to 100μ) spheroidal, tubular or semi-regular cavities. The cavities contain an aqueous saline fluid, a CO₂-rich gas bubble (which in U785 may be composed entirely of CO₂-liquid) and substantial amounts of crystalline daughter phases. Naheeolite (Chapter 2) is the largest and most abundant daughter phase present in all samples and may occupy up to 25% of the total volume of the inclusion. Black opaque magnetic specks are observed in minor amounts in all specimens. In U693, additional cubes of halite and birefringent needles of an unidentified water-soluble carbonate phase are also present. Other daughter phases observed within the inclusions in apatite from U876, U785 and U693 consist of minute, highly birefringent, carbonate specks which, because of their miniscule size (never exceeding 0.1% of the total volume of the inclusion) may go unnoticed.

A specimen of ijolite invaded by sovite (U8149) has been included in this study owing to the large numbers of well-formed aqueous present in the apatites. These inclusions contain a low-pressure gas phase, an aqueous saline solution, and usually five daughter mineral phases which consist of halite, sylvite, and two bicarbonate phases (NaHCO₃ and possibly KHCO₃) together with a small, black opaque mineral whose exact nature could not be determined (section 1.7).

3.2 THE HEATING-STAGE

A commercially produced Leitz 1350 microscope heating-stage was used throughout this study. The specimen was placed in a small, water-cooled heating compartment. Heat was supplied to the sample by means of a minute resistance furnace, and temperature measured on a previously calibrated Pt/Rh-Pt thermocouple. Correction factors have
to be applied to the temperature recorded by the thermocouple at temperatures above 600°C (Appendix A). All temperatures reported in the text are believed to be accurate to ±2°C up to 400°C, ±4°C from 400-600°C and ±8°C for temperatures above 600°C.

3.3 SAMPLE PREPARATION AND SELECTED INCLUSIONS

The usual procedure in fluid inclusion homogenisation temperature determinations of using thin (1-2mm) polished plates (Harker, 1971) could not be adopted in this study because of the minute size of the apatite crystals (usually less than 0.5mm). It was decided that the only feasible way in which heating studies could be carried out on such small crystals was to use single separated apatite grains in the hope that their morphology and regularity would be sufficiently uniform to enable their inclusions to be optically resolvable. Whenever possible, single crystals containing only one large primary inclusion were selected in order to avoid the possibility of studying necked-down inclusions.

3.4 RESULTS OF HEATING-STAGE STUDIES

3.4.1. The Sokolo carbonatite U785

Despite innumerable attempts to homogenise the inclusions in this sample, the apatite crystals repeatedly decrpetitated before homogenisation could be achieved. Even when very slow heating-rates were used (less than 1°C/mm) the specimen exploded, often violently, at some elevated temperature, and it was only possible to obtain two single homogenisation temperatures at 338°C and 260°C from the forty specimens studied.
The temperature at which the inclusions decrepitated ranged from 88°C - 367°C, and although Fig. 3.1 shows a maximum frequency of decrepitation at between 150 and 200°C these results cannot be directly related to the actual formation temperature of the host mineral. The fact that virtually every sample studied decrepitated before homogenisation, indicates that the inclusion contents exert a substantial pressure, undoubtedly due, in this instance, to the presence of large amounts of highly compressed CO₂-liquid and -gas. The reasons why inclusions should decrepitate at a certain temperature are complex. The important variables which influence this temperature would appear to be the size, shape, internal pressure within the inclusion, its distance from the surface of the crystal and the resistance of the host material to fractures and cleavages in different directions.

Inclusions which did not decrepitate until reasonably high temperatures showed distinct changes in their contents as the temperature was increased. The birefringent bicarbonate daughter phases (NaHcolite) dissolved completely at temperatures between 122 and 175°C, and the CO₂-rich bubble contracted uniformly in volume with increasing temperature.

3.4.2. The carbonatite xenolith in phonolite (U693)

Homogenisation temperatures were recorded for 36 primary aqueous inclusions from a total of 30 individual apatite crystals selected from the thousands studied. The progress of homogenisation was the same in every instance; starting with solution of bicarbonate daughter minerals at temperatures between 103 and 125°C, and followed by
solution of halite crystals at temperatures up to about 200°C. The black, hexagonal, magnetic platelet, previously identified as pyrrhotite, did not dissolve completely even after prolonged heating at temperatures between about 150 and 200°C for periods of up to 12 hours. This phenomenon is not unknown in fluid inclusion studies and several reports exist in the literature where opaque mineral phases fail to dissolve completely at elevated temperatures, even though they are true daughter minerals derived from the inclusion fluid (Bazarova, 1965; Kelly and Turneaure, 1970, p.663). All inclusions studied finally homogenised to the liquid phase (i.e. the vapour bubble contracted uniformly in volume so that, at the moment of homogenisation, the bubble had disappeared completely and the cavity was filled entirely by the liquid aqueous solution) at temperatures between 204 and 207°C. The majority of the inclusions homogenised at temperatures between 260 and 280°C (fig. 3.2).

Although precautions were taken to minimise the possibility of studying necked-down inclusions, three homogenisation temperatures at 125°C, 166°C and 173°C were suspect, and since such low temperatures are usually indicative of necking-down (Sawkins, 1966), these results were not considered further.

Decrepitation occurred on only one occasion before complete homogenisation of the gas and liquid phases took place. In several instances however, the course of homogenisation could no longer be observed since the vapour bubble moved to a darkened part of the inclusion and remained obscured from further observation.
3.4.3. The Uyi ijolite invaded by sovite (U842)

A total of 60 apatite crystals were selected from this sample, and although 41 homogenisation temperatures were obtained, decrepitation took place before homogenisation could be attained in 25 of these apatite crystals. During the initial part of this study relatively fast heating-rates were used (up to 20°C/min), but when slower heating-rates were employed (usually 5°C/min) the number of specimens which decrepitated was reduced.

In all inclusions studied, homogenisation occurred to the liquid phase. Sylvite (KCl) dissolved rapidly at temperatures between 88 and 107°C. The bicarbonate daughters also dissolved rapidly, with complete solution taking place at temperatures between 115 and 157°C. Halite (NaCl) was typically rather reluctant to dissolve and only did so at substantially higher temperatures (225 - 340°C). The black, opaque speck, observed on several occasions, did not dissolve completely even when the inclusions were kept at elevated (300 - 600°C) temperatures for several hours.

The homogenisation temperatures obtained (fig. 3.3b) give an extremely wide spread of values ranging from 248 to 892°C. This large temperature range may be due, in part, to necking-down processes which have affected many of these inclusions. But since precautions were taken to avoid the likelihood of studying necked inclusions, this spread is considered to be real and probably reflects the variable conditions prevailing at the time the apatites crystallised.

Decrepitation temperatures, for inclusions which exploded before homogenisation, could be achieved, ranged from 330 to 790°C. The majority of the inclusions decrepitated at temperatures between 400
and 600°C (fig. 3.3a). Once again these decrepitation temperatures are of little significance but they do show that, since most inclusions decrepitated at temperatures above about 400°C, homogenisation temperatures above this value would have been achieved if these inclusions had not exploded.

3.4.4. The Uyil carbonatite (U876)

66 homogenisation temperatures have been recorded from single apatite crystals containing one, solitary, primary aqueous inclusion. A further 32 temperatures have also been obtained from apatite crystals containing two or more primary inclusions. Strict precautions were taken against the possibility of studying necked-down inclusions in specimens which contained more than one inclusion, and only those samples whose inclusions gave consistently uniform homogenisation temperatures were used (Fig. 3.4). Samples whose inclusions gave widely varying or very low temperatures were rejected (about 5% of the total number studied).

Solution of the nahcolite daughter minerals proceeded uniformly in all inclusions as the temperature was increased (Fig. 3.5), and complete solution of these solid bicarbonates occurred at temperatures between 99 and 183°C. Minute specks of other carbonate phases, although difficult to observe, usually dissolved at temperatures between 220 and 380°C. Complete solution of the black, opaque speck, occasionally present in the inclusions, did not take place even at temperatures well above the actual homogenisation temperatures. After the initial solution of these daughter phases, final homogenisation of the gas and liquid within the inclusions occurred in one of three distinct ways.
(a) **Homogenisation to the liquid phase (30 inclusions)**

This type of homogenisation took place by the gradual expansion of the liquid phase so that, at the moment of homogenisation, the cavity was completely filled by liquid (Plate 3.1) in exactly the same manner as previous samples (U693, U349, U735).

(b) **Homogenisation to the gas phase (65 inclusions)**

Inclusions which homogenised to the gas phase always showed a characteristic 'inversion' at some temperature during the course of their homogenisation. Initially, the vapour phase contracted uniformly in volume until a certain temperature (the inversion temperature), but then began to expand rapidly until, at the moment of homogenisation, the cavity was completely filled by gas. The behaviour of a typical fluid inclusion showing this type of homogenisation, with an inversion point at about 380°C, is depicted graphically in Fig. 3.6. In general, the inversion temperature ranged from about 360°C to 430°C depending upon the final homogenisation temperature. Yermakov (1965, Chapter 7) has also observed homogenisation of aqueous inclusions in quartz, topaz and beryl from Volynia (U.S.S.R.) which homogenised to the gas phase and showed similar inversion points at elevated temperatures.

(c) **Homogenisation by fading of meniscus (3 inclusions)**

This type of homogenisation, which can be considered as intermediate between the two types previously described, takes place by the gradual and progressive fading of the meniscus which separates the liquid from the vapour phase within the inclusion, until, at the moment of homogenisation, the meniscus has disappeared completely (see Appendix B and especially Plate B.1).
Inclusions showing this type of homogenisation have evidently been trapped at the critical density (see Appendix B) and the temperature at which homogenisation occurs is the critical temperature for the fluid in question. It is not uncommon to find inclusions which exhibit this type of behaviour up to a few degrees before the actual homogenisation temperature, but then, in these last few degrees, proceed as usual to homogenise either to the gas or liquid phase. Roedder (1972, p.JJ17) gives an explanation for this phenomenon by stating that although there is only one single critical point for any given fluid system, a consequence of the pronounced flattened top of the P.V.T. curve separating the two phase region from the single phase region, for most fluid systems, is that inclusions whose density is close to critical will appear to go through a critical point if relatively fast heating-rates are used. Several inclusions in this study which showed homogenisation with critical phenomenon (fading of meniscus) when fast heating-rates were used, subsequently showed a distinct but rapid homogenisation to gas or liquid over the last few degrees when substantially slower heating-rates were used. However, three homogenisation temperatures of 63°C, 62°C and 59°C were recorded for inclusions which homogenised at the critical point despite the use of laboriously slow heating-rates of less than 1°C/min.

The temperatures for 65 inclusions which homogenised to the gas phase and 30 inclusions which homogenised to the liquid phase are presented in Fig. 3.7a and Fig. 3.7b respectively. Fig. 3.7c depicts the combined data from both types of homogenisation together with the three values obtained for homogenisation with fading of the meniscus. It can be seen that the two sets of data in Fig. 3.7a and Fig.3.7b are
closely comparable. The temperature range was 383-418°C for inclusions homogenising to the gas phase and 484-371°C for inclusions homogenising to the liquid phase.

3.4.5. The nature and significance of the transient phase precipitated at high temperatures in aqueous inclusions from U876

When aqueous inclusions in samples U849 and U693 were heated up to 100°C beyond their homogenisation temperature, decrepitation or leakage occurred and no phase changes could be seen within the inclusions. However, when heating-stage studies on inclusions from U876 were continued past their homogenisation temperatures, a further phase precipitated from the aqueous fluid in some of these inclusions at, or very close to, their homogenisation temperatures. Continued heating caused this phase to enlarge until it occupied up to 5% of the total volume of the cavity. When these inclusions were heated still further, this phase subsequently "redissolved" in the fluid at some elevated temperature well above the original homogenisation temperature. The growth and subsequent "dissolution" of this transient phase was difficult to observe because of its small size and tendency to cling to the sides of the inclusion, and only 14 reliable "solution" temperatures (Ts\textsuperscript{1}) could be obtained (Table 3.1).

When the inclusions were allowed to cool from the "solution" temperature (Ts\textsuperscript{1}), this precipitated phase reappeared almost immediately, very often as several dispersed specks which continued to grow in size and on three occasions coalesced to form a single, large globule. Further cooling caused this phase to disappear completely at a temperature very close to the original homogenisation
Table 3.1  SOLUTION TEMPERATURES ($T_{s}^{-1}$) FOR THE PHASE PRECIPITATED FROM THE INCLUSiON FLUID AT HIGH TEMPERATURES (U376)

<table>
<thead>
<tr>
<th>Homogenisation Temperature in °C</th>
<th>Mode of Homogenisation</th>
<th>Solution Temperature ($T_{s}^{-1}$) in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>447</td>
<td>To gas</td>
<td>563</td>
</tr>
<tr>
<td>447</td>
<td>To gas</td>
<td>544</td>
</tr>
<tr>
<td>432</td>
<td>To gas</td>
<td>563</td>
</tr>
<tr>
<td>432</td>
<td>To gas</td>
<td>500</td>
</tr>
<tr>
<td>438</td>
<td>To gas</td>
<td>590</td>
</tr>
<tr>
<td>432</td>
<td>To gas</td>
<td>536</td>
</tr>
<tr>
<td>425</td>
<td>To gas</td>
<td>553</td>
</tr>
<tr>
<td>456</td>
<td>To gas</td>
<td>533</td>
</tr>
<tr>
<td>441</td>
<td>To gas</td>
<td>595</td>
</tr>
<tr>
<td>452</td>
<td>To liquid</td>
<td>523</td>
</tr>
<tr>
<td>438</td>
<td>To liquid</td>
<td>523</td>
</tr>
<tr>
<td>426</td>
<td>To liquid</td>
<td>538</td>
</tr>
<tr>
<td>428</td>
<td>To liquid</td>
<td>524</td>
</tr>
<tr>
<td>374</td>
<td>To liquid</td>
<td>570</td>
</tr>
</tbody>
</table>
temperature (Fig. 3.8).

Previous accounts (LeBas et al., 1972; Rankin and LeBas, 1973) have indicated that this phase is solid. However, its liquid nature is now evident from its tendency to form globules on cooling which may subsequently coalesce into larger globules, and its ability to "wet" the inclusion walls. A most likely explanation for the nature and occurrence of this phase, based upon the knowledge that the inclusions are composed predominately of NaHCO$_3$ (nahcolite), CO$_2$ and H$_2$O, is that sodium carbonate (Na$_2$CO$_3$) is produced by the gradual decomposition of the sodium bicarbonate solution with increasing temperature (Equation 1).

$$2\text{NaHCO}_3(\text{aq.}) \rightleftharpoons \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad (1)$$

Sodium carbonate exhibits retrograde solubility in aqueous solutions (i.e. it becomes increasingly insoluble as temperature is increased) and is almost totally insoluble at 348°C (Waldeck et al., 1932). Therefore when reaction (1) occurs within the inclusions, the sodium carbonate so produced precipitates continuously as the equilibrium shifts further to the right with increasing temperature. Koster van Groos and Wyllie (1968) have deduced that the "solubility" of sodium carbonate in aqueous fluid or vapour increases with increasing temperature above the interval of retrograde solubility. This indicates that sodium carbonate would be expected to "redissolve" in the inclusion fluid at high (> 348°C) temperatures. The liquid nature of the precipitated sodium carbonate phase, present in inclusions at temperatures above the homogenisation temperature, is undoubtedly the result of lowering of the liquidus temperature (872°C at one kilobar pressure) of pure Na$_2$CO$_3$ (Koster van Groos and [Additional text here...])
Wyllie, 1966) by additional components such as CO₂ and H₂O. For example, Koster van Groos and Wyllie (1968) have shown that Na₂CO₃ reacts with excess water at about 750°C to form a liquid containing approximately 20% water at one kilobar pressure. Attempts by these same authors to study the melting relationships in the system Na₂CO₃ - H₂O - CO₂, using standard methods, were unsuccessful because no criteria could be found to distinguish between solid Na₂CO₃ and quench products formed from Na₂CO₃ melts. However, it seems feasible that a melt (Na₂CO₃-rich liquid) may exist at substantially lower temperatures (down to about 450°C) in this system, particularly since it has been established that liquidus temperatures for CaCO₃ melts in the analogous CaCO₃ - H₂O - CO₂ system are very low indeed (Wyllie and Tuttle, 1960).

3.4.6. Summary of homogenisation temperature data

The results of homogenisation temperature determinations for primary aqueous inclusions in apatites together with the values derived for the standard deviation and confidence limits at the 95% level are shown in Table 3.2.

The range of temperatures obtained for each sample reflect the varying conditions which prevailed during crystallisation. In U649 this variation is large (S.D. = 145.1) but in U693 and U376 it is relatively small (S.D. = 20.8 and 21.6 respectively). It must be remembered that homogenisation temperatures represent the minimum temperature of formation of the host crystal. Unless the fluid was boiling at the time of entrapment, a positive temperature correction must be added to take into account the effect of external pressure.
### Table 3.2
**SUMMARY OF HOMOGENISATION TEMPERATURE DATA FROM FLUID INCLUSIONS IN APATITES FROM CARBONATITES OF THE WASAKI AREA**

<table>
<thead>
<tr>
<th>Source Material</th>
<th>Locality Number</th>
<th>Mode of Homogenisation</th>
<th>$T_h$ Min.</th>
<th>$T_h$ Max.</th>
<th>$T_h$ Mean</th>
<th>$n$</th>
<th>Standard Deviation</th>
<th>Confidence Limits at 95% level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sekelo Carbonatite</td>
<td>U735</td>
<td>To Liquid</td>
<td>260</td>
<td>338</td>
<td>299</td>
<td>2</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Carbonatite Xenolith</td>
<td>U693</td>
<td>To Liquid</td>
<td>203</td>
<td>284</td>
<td>263</td>
<td>36</td>
<td>20.8</td>
<td>7.0</td>
</tr>
<tr>
<td>Ijelite Invaded by Sovite</td>
<td>U349</td>
<td>To Liquid</td>
<td>253</td>
<td>880</td>
<td>493</td>
<td>1</td>
<td>145.1</td>
<td>45.8</td>
</tr>
<tr>
<td>Uyi Carbonatite</td>
<td>U376</td>
<td>To Liquid</td>
<td>374</td>
<td>484</td>
<td>430</td>
<td>30</td>
<td>28.6</td>
<td>10.6</td>
</tr>
<tr>
<td>Uyi Carbonatite</td>
<td>U376</td>
<td>To Gas</td>
<td>418</td>
<td>483</td>
<td>446</td>
<td>65</td>
<td>14.2</td>
<td>3.5</td>
</tr>
<tr>
<td>Uyi Carbonatite</td>
<td>U376</td>
<td>All Types</td>
<td>374*</td>
<td>484*</td>
<td>441</td>
<td>93</td>
<td>21.6</td>
<td>4.2</td>
</tr>
</tbody>
</table>

All Temperatures are given in °C

* Homogenisation to Liquid Phase

n.d. Insufficient Data to Analyse

$T_h$ = Homogenisation Temperature
on the fluid in order to obtain the true temperature of formation (Roedder, 1962, 1967a).

3.5 REPRODUCIBILITY OF RESULTS

3.5.1. Duplicate runs

Whenever possible, homogenisation temperatures obtained were checked by duplicate runs on the same inclusion. Obviously checks on decrepitation temperatures could not be made and errors in this temperature measurement may be as high as ±10°C. It is advisable to obtain at least two determinations of the homogenisation temperature for every inclusion, not only as a check but also to ascertain whether leakage has taken place during the course of homogenisation runs. If leakage has occurred, the second homogenisation temperature will be higher than the first by a value in excess of the experimental error (section 3.2) for inclusions which show homogenisation to the liquid phase. However, in U876, leakage of inclusions which homogenise to the gas phase will be evident if the second homogenisation temperature is lower than the first. Fortunately, leakage does not appear to be a problem in these samples and has only been evident on 6 separate occasions (once in U876, twice in U693 and three times in U649).

Even repeated homogenisation of selected inclusions still gave results which were well within the acceptable experimental error.

3.5.2. Effect of heating-rate on the homogenisation temperature

It is well-known that the homogenisation temperature of a fluid inclusion depends, in part, on the heating-rate used.
Exceptionally fast heating-rates of more than $40^\circ\mathrm{C}/\mathrm{min}$ usually give anomalously high homogenisation temperatures simply because insufficient time is allowed for thermal equilibrium between the heating-stage and specimen to be attained. Harker (1971) was able to show that the homogenisation temperatures for aqueous inclusions in fluorite depend upon the thickness of the mineral slice containing the inclusions. The homogenisation temperature recorded for such inclusions in thick sections ($\sim 2\,\mathrm{mm}$) was found to be much lower when the thickness of the slice was decreased.

In this present study, since minute apatite crystals less than $0.5\,\mathrm{mm}$ were used, the effect of thickness upon the homogenisation temperature is negligible, but in order to ascertain whether variations in heating-rates affected the homogenisation temperatures obtained, several inclusions were repeatedly homogenised using different heating-rates. It was found that even relatively fast heating-rates of $10-20^\circ\mathrm{C}/\mathrm{min}.$ gave results which were comparable, within the experimental error, to those obtained when slower heating-rates of between 2 and $10^\circ\mathrm{C}/\mathrm{min}.$ were used.

Although it is evident that the heating-rate is not critical, provided that it is kept below about $15^\circ\mathrm{C}/\mathrm{min}.$, it is imperative to use a very slow heating-rate of about $2-5^\circ\mathrm{C}/\mathrm{min}.$ when an inclusion is about to homogenise. This is because the time-lapse between observing the moment of homogenisation and reading the temperature on the potentiometer may be large and give erroneously high readings.
3.6 THE TRAPPING OF SUPERCRITICAL FLUIDS IN INCLUSIONS

3.6.1. Evidence to suggest that inclusions in U876 are trapped portions of a supercritical fluid

The manner in which homogenisation occurs in inclusions in apatites from U876 indicates that the contents of those cavities have been trapped either as homogeneous supercritical fluids or as heterogeneous boiling liquids. In their study of Bolivian tin deposits Kelly and Turneaure (1970) found inclusions which homogenised to the liquid phase co-existing with inclusions which homogenised, over the same temperature range, to the gas phase. These authors concluded that these inclusions represent the trapped vapour and liquid portions of a boiling fluid. Other authors (Roedder, 1973; Roedder and Coombs, 1967) have also found evidence, in the form of co-existing low density and high density inclusions in minerals, that boiling conditions have prevailed during crystallisation. These authors were able to show that the trapped portions of the vapour phase were considerably different in density and composition to the trapped portions of the liquid phase. Such a sharp distinction cannot be made between those inclusions which homogenise to the gas and those which homogenise to the liquid phase in apatites from U876. It is therefore inferred that these inclusions are the result of trapping of a supercritical fluid rather than a subcritical heterogeneous boiling liquid. Evidence to substantiate this view is as follows:

(1) The percentage of the total volume of the inclusion occupied by the gas phase (a measure of the density of the inclusion) varies from about 65% to 25%, with the majority containing between about 55 and 30% gas. If trapping of a boiling liquid had occurred, then two distinct
inclusion-types would be expected: a low density (large percentage gas) type and a high density (small percentage gas) type. A very small number of intermediate types might also occur as a consequence of the fortuitous, simultaneous trapping of portions of gas and liquid within the same inclusion.

(2) The composition of the inclusions is virtually identical irrespective of whether they homogenise to gas or liquid. This is evident from the similar quantities of nahcolite present within the inclusions (up to 20% by volume) and the fact that the volume expansion of the gas phase, upon opening the inclusions on the crushing-stage (an indication of the amount of CO\textsubscript{2} present) is the same order of magnitude for inclusions which homogenised to the gas phase and those which homogenised to the liquid phase. A boiling fluid would be expected to give rise to a CO\textsubscript{2}-rich gas phase, and a CO\textsubscript{2}-poor aqueous solution containing substantially larger quantities of dissolved salts.

(3) The solution temperature of nahcolite (Ts) and the 'solution' temperature of the sodium carbonate phase (Ts\textsuperscript{1}) precipitated at high temperatures, occur in the same temperature ranges and are independent of the mode of homogenisation (Tables 3.1 and 3.3). This also shows the similarity in composition of the inclusions studied.

(4) Homogenisation with critical phenomenon has been observed within some of the inclusions indicating that they have been trapped at critical density. Most other inclusions which homogenise to gas or liquid show a distinct fading of the meniscus as they approach their homogenisation temperature indicating that these inclusions have been trapped close to the critical density of the fluid.
Table 3.3  SOLUTION TEMPERATURES ($T_g$) FOR NAHCOLITE DAUGHTER MINERALS IN THE AQUEOUS FLUIDS IN INCLUSIONS (U976)

<table>
<thead>
<tr>
<th>Homogenisation Temperature in °C</th>
<th>Mode of Homogenisation</th>
<th>Solution Temperature ($T_g$) in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>147</td>
<td>To gas</td>
<td>118</td>
</tr>
<tr>
<td>147</td>
<td>To gas</td>
<td>124</td>
</tr>
<tr>
<td>151</td>
<td>To gas</td>
<td>173</td>
</tr>
<tr>
<td>132</td>
<td>To gas</td>
<td>145</td>
</tr>
<tr>
<td>153</td>
<td>To gas</td>
<td>115</td>
</tr>
<tr>
<td>125</td>
<td>To gas</td>
<td>103</td>
</tr>
<tr>
<td>156</td>
<td>To gas</td>
<td>115</td>
</tr>
<tr>
<td>141</td>
<td>To gas</td>
<td>142</td>
</tr>
<tr>
<td>140</td>
<td>To gas</td>
<td>79</td>
</tr>
<tr>
<td>424</td>
<td>To liquid</td>
<td>144</td>
</tr>
<tr>
<td>438</td>
<td>To liquid</td>
<td>104</td>
</tr>
<tr>
<td>422</td>
<td>To liquid</td>
<td>99</td>
</tr>
<tr>
<td>404</td>
<td>To liquid</td>
<td>123</td>
</tr>
<tr>
<td>412</td>
<td>To liquid</td>
<td>109</td>
</tr>
<tr>
<td>395</td>
<td>To liquid</td>
<td>137</td>
</tr>
<tr>
<td>420</td>
<td>To liquid</td>
<td>120</td>
</tr>
<tr>
<td>374</td>
<td>To liquid</td>
<td>145</td>
</tr>
</tbody>
</table>
3.6.2. The critical temperatures of fluids trapped in inclusions in apatites from the Uyi carbonatite (U376)

The temperature at which inclusions homogenise after the gradual and progressive fading of the meniscus is an approximate value for the critical temperature for the inclusion fluid. The three values obtained (section 3.6.1.c) indicate that this temperature is between 459 and 462°C. However, the critical temperature for any static, compositionally uniform fluid system is a value which can be altered even if only small compositional changes occur within the fluid. Sourirajan and Kennedy (1962) have shown, in their study of the system NaCl - H₂O at elevated temperatures and pressures, that the critical point for pure water at 374°C is increased to 425°C when 5 weight per cent sodium chloride is added. The critical temperature is increased still further when the amount of sodium chloride in solution is increased, and a 25 wt.% NaCl solution would have a critical temperature at about 650°C (op.cit.). If volatile components such as CO₂ are added to an aqueous fluid system, the critical temperature is lowered. Takenouchi and Kennedy (1964) have shown that the critical temperature for pure water is reduced from 374°C to 350°C by the addition of about 22 wt.% CO₂. In cases where both volatile (e.g. CO₂) and non-volatile components (e.g. NaCl or NaHCO₃) are present in an aqueous fluid, a balancing out of the effects of these two types of components on the critical temperature for pure water takes place, and depending upon the component which exhibits the greatest influence, the critical temperature may be increased or decreased.

The fluids present in inclusions in apatites from U376 do
exhibit minor variations in their composition as shown by the variable amounts of nahcolite daughters present in the inclusions (Chapter I, Table 1.7). Therefore a range of critical temperatures would be expected for these fluids.

In order to obtain an approximate range for the critical temperature and critical degree of filling (relative proportion of gas to liquid at 23°C), several well-defined, tubular cavities, whose percentage by volume of the gas phase could be measured accurately within a micrometer eyepiece, were homogenised on the heating-stage. A plot of the percentage of the total volume of the inclusion occupied by the gas phase was made against the homogenisation temperature (Fig. 3.10). These results show that those inclusions which homogenise to the gas phase contain at least 49% gas and that those homogenising to the liquid contain less than 50% gas. The curve (Fig. 3.10) represents the approximate division between the single phase region and the two phase (liquid and gas) region, and the maximum point on this curve is the critical temperature. It can be seen that many of the points do not lie on this curve which is a result of the slightly varying composition of the fluids. However, a realistic estimate for the critical temperature range (Tc) would be 460 - 490°C and between 47.5 and 52.5% for the critical degree of filling (Fc) of the inclusion by the gas phase (Fig. 3.10).

3.6.3. Critical phenomena and supercritical fluids in inclusions in apatite from samples U785, U693 and U689

The inclusions from all three samples, in every instance, showed homogenisation to the liquid phase. Critical phenomenon has never been
observed in any inclusion and there is no evidence to suggest that the inclusions are the result of trapping of a supercritical fluid.

3.7 DISCUSSION OF RESULTS

3.7.1. Homogenisation temperatures as indicators of the formation temperature of the apatites

The homogenisation temperature of a fluid inclusion merely represents the minimum temperature of formation of the host mineral and unless the fluid was boiling at the time of entrapment, a positive temperature correction needs to be added to the trapping temperature to take into account the effect of pressure on the fluid during crystallisation (Roedder, 1962; 1967a).

Data on the compressibility of saline fluids are needed for estimates of this temperature correction for pressure, but although P.V.T. relationships are well documented for aqueous NaCl solutions (Klevtsov and Lemmlein, 1960), data on other systems are not yet available. Homogenisation temperatures are quoted by most authors as being "uncorrected for pressure", this is not only due to the lack of compressibility data for fluid systems, but also primarily because the pressure at the time of entrapment is generally unknown (For example see Roedder and Coombs (1967)). Similarly, in view of the absence of compressibility data on the H$_2$O - CO$_2$ - NaHCO$_3$ - NaCl system and the unknown pressure at the time of entrapment, estimates of temperature corrections for pressure cannot be made for homogenisation temperatures obtained in this study.

In the case of inclusions in U876, which precipitate sodium carbonate at temperatures close to the gas-liquid homogenisation temperature, the "solution temperature" of this phase is the actual
temperature at which true homogenisation takes place and thus allows a higher estimate of the formation temperature to be obtained. Reliable temperatures, accurate to ±10°C, were recorded for 14 specimens (Table 3.1) and ranged from 500 to 595°C (mean = 547°C).

This higher estimate of the formation temperature, which is far above the estimated critical temperature range for the inclusion fluids, confirms that these fluids were supercritical at the time of entrapment.

3.7.2. The importance of supercritical fluids in the formation of carbonatites

The role of supercritical fluids in the formation of carbonatites has been discussed previously by several authors. Bailey (1960), in his study of a pyroclastic carbonatite from the Rufunsa valley of N.Rhodesia (Zambia), suggests that the carbonate material originated as a hot, dense, supercritical fluid composed predominately of CO₂ together with lesser amounts of other volatiles such as H₂O, Cl and F, but carrying high concentrations of Ca, Na, K and other metallic ions. Similarly, Balashov and Pozharitskaya (1968) consider that the early carbonatites of the West Siberian Massif were produced by supercritical CO₂ - H₂O solutions. Recent isotope studies (Pineau and Allegre, 1972) also indicate that a hot, CO₂ - H₂O fluid played an important role in the formation of carbonatites.

Heating-studies of inclusions from U876 indeed suggest that supercritical fluids rich in CO₂ and H₂O may play a dominant role in carbonatite formation. The ability of this fluid to transport considerable amounts of carbonate material and lesser amounts of ore
metals is indicated by the presence of significant amounts of nahcolite and black, opaque daughter minerals in the fluids.

3.7.3. The significance of homogenisation temperatures of inclusions in apatite from the sample of ijolite invaded by sovite (U849)

In a previous chapter (Chapter I, section 1.7.5) the broad similarity between the inclusions in apatites from carbonatites (U876, U693, U705, U624) and those in apatites from the specimen of ijolite invaded by sovite (U849) was shown. It was further suggested that since the inclusions in U849 differ considerably from those in apatites from other ijolites (section 1.7), it might be supposed that the apatites from U849 are the result of the invading carbonatitic fluid rather than primary products of the ijolitic melt. However, the high homogenisation temperatures observed for some inclusions (up to 880°C) are well within the range of magmatic temperatures for silicate melts, whilst others are compatible with temperatures obtained for carbonatite apatites (down to 253°C), and evidence to support or negate this supposition cannot be cited on homogenisation temperature data alone.

3.3 SUMMARY AND CONCLUSIONS

Homogenisation temperature data have been obtained from primary aqueous inclusions in apatites from carbonatitic rocks of the Wasaki area of W.Kenya. These temperatures, which may be subject to a significant positive temperature correction for pressure, give an estimate of the minimum temperature of formation for apatites in the carbonatites. The values obtained range from 284 - 208°C for
the carbonatite xenolith in phonolite (U693), 338 - 260°C for the Sokoło carbonatite and 464 - 374°C for the Uyi carbonatite, and are well in agreement with temperatures derived by other methods for the formation temperature of other carbonatites (Heinrich, 1966, p.281).

In inclusions in apatites from the Uyi carbonatite (U876), a precipitated phase exists at temperatures above the gas/liquid homogenisation temperature. The "solution" temperature of this phase, most probably a sodium carbonate melt, allows a higher estimate of the formation temperature of apatites in U876 to be obtained (595 - 500°C).

The mode of homogenisation of inclusions in U876 indicates that the inclusions were trapped as supercritical fluids. An approximate critical temperature range has been obtained for these fluids (480 - 460°C) and it has been shown that the critical degree of filling (percentage gas) is within the range 17.5 - 52.5 per cent. No evidence exists to suppose that the inclusions in other specimens (U735, U693, U849) were trapped as supercritical fluids, and in these cases it is probable that they represent portions of a subcritical aqueous solution.

The sample of ijolite invaded by sovite (U849) gives an extremely wide range of homogenisation temperatures (253 - 330°C). The apatites within this sample have been derived either from the primary ijolitic melt or from the invading sovitic fluid, but it has not been possible to deduce the most likely origin for these apatites on the basis of homogenisation temperature data alone.

Decrepitation of inclusions before homogenisation could be
attained, occurred extensively in U785, and to a lesser extent in U049. The temperature at which decrепitation takes place does not bear a direct relationship to the formation temperature of the host mineral and cannot be used with any accuracy to determine crystallisation temperatures.
Plate 3.1 The homogenisation to the liquid phase of a primary aqueous inclusion in apatite from the Uyi carbonatite (U076)

The inclusion at room temperature (A) contains a vapour bubble (V), an aqueous solution (L) and a nahcolite daughter mineral (Nh). Slight heating of the inclusion causes the vapour bubble to shift to the left hand side of the inclusion (B). As temperature is increased the nahcolite daughter mineral dissolves rapidly until at 137°C (F) complete solution takes place. Little change in the volume occupied by the vapour phase is noticed until temperatures of 375°C (H) are attained. The bubble then gradually diminishes in size (that is, the liquid expands) with a noticeable fading of the boundary which separates the liquid from vapour (I, J). Complete homogenisation occurred at 396°C.
FIG 3.1 DECREPITATION TEMPERATURES FOR INCLUSIONS IN APATITE FROM THE SOKOLO CARBONATITE (U785).
FIGURE 3.2 HOMOGENISATION TEMPERATURES OBTAINED FOR 36 AQUEOUS INCLUSIONS IN APATITE FROM THE CARBONATITE XENOLITH (U693).
FIG. 3.3  DECREPITATION AND HOMOGENISATION TEMPERATURES OBTAINED FOR 66 AQUEOUS INCLUSIONS IN APATITES FROM THE UYI IJOLITE INVADED BY SOVITE (U849).
FIG. 3.4  THE CONSISTENCY OF HOMOGENISATION TEMPERATURES FROM CRYSTALS CONTAINING SEVERAL INCLUSIONS.
(APATITE FROM THE UYI CARBONATITE, U876.)

ALL TEMPERATURES GIVEN IN °C.
G DENOTES HOMOGENISATION TO GAS PHASE.
L DENOTES HOMOGENISATION TO LIQUID PHASE.
n.d. TEMPERATURE NOT RECORDED.
Fig. 3.5

The amount of nahcolite dissolved was determined from photomicrographs of the inclusion taken at various temperatures during an homogenisation run. X denotes the unknown weight of nahcolite in solution at 24°C. The amount of undissolved nahcolite at room temperature (23°C) was determined from plasticine models made of the inclusion, and was found to be L weight units. Thus L + X weight units of nahcolite would be in solution at the solution temperature (T_s). The amount of dissolved nahcolite at any given temperature was obtained by determining the amount of nahcolite left undissolved (in arbitrary weight units) from plasticine models of photomicrographs and subtracting this value from L + X.
FIG 3.5 THE SOLUBILITY OF NAHCOLITE IN AN AQUEOUS INCLUSION IN APATITE FROM U876.

![Graph showing the solubility of nahcolite with temperature and amount of nahcolite dissolved.](image-url)
Fig. 3.6

Fig. 3.6 shows a plot of temperature versus the areal length ($X$) of the vapour phase determined at each temperature, with a micrometer eyepiece, for a large, flat, tubular inclusion in apatite from U876. Heating the inclusion from 23°C to 380°C (the inversion temperature, $T_1$) causes the vapour bubble to contract uniformly in volume. After the inversion temperature, the vapour phase expanded in volume very rapidly until, at the moment of homogenisation, ($T_h = 451°C$) the cavity was completely filled by gas.
FIG 3.6 THE THERMAL BEHAVIOUR OF A TUBULAR AQUEOUS INCLUSION IN APATITE FROM U876 WHICH HOMOGENISED TO THE GAS PHASE AND SHOWED INVERSION DURING THE COURSE OF HOMOGENISATION.
FIG 3.7 HOMOGENISATION TEMPERATURES FOR 98 AQUEOUS INCLUSIONS IN APATITE FROM THE WASAKI CARBONATITE (U876).

□ = HOMOGENISATION TO GAS PHASE.

= HOMOGENISATION TO LIQUID PHASE.

= HOMOGENISATION BY FADING OF MENISCUS.

HOMOGENISATION TEMPERATURE (°C)
Fig. 3.8

Fig. 3.8 shows diagrammatically the behaviour of a typical fluid inclusion in sample U876 as it is heated up to, and beyond its homogenisation temperature (in this case homogenisation is to the gas phase). Initial heating from (a) to (c) causes the nahcolite daughter mineral to dissolve until complete solution of this phase occurs at (d), the solution temperature ($T_s$). Homogenisation to the gas phase occurs at (f) and a second phase precipitates as a minute speck which continues to grow in size from (f) to (i) but subsequently "redissolves" at some elevated temperature ($T_{s1}$) above the original homogenisation temperature. On cooling the inclusion, this second phase reappears almost immediately, usually as several individual blebs. Continued cooling (k) to (l) causes this phase to grow in size but it then diminishes in size until it completely disappears just below the homogenisation temperature at (c). Nahcolite precipitates as a daughter mineral as the inclusion is cooled still further, and finally at room temperature (t) the inclusion returns to its original constitution.
Fig. 3.8 A diagrammatic representation of the behaviour of a typical fluid inclusion U876 as it is heated up to and beyond its homogenisation temperature showing the precipitation of sodium carbonate at elevated temperatures.

$T_s^1$

COOLING

j

i

h

g

f

e

Ts

d

c

HEATING

b

a

$T_s$ Nahcolite at(d)

$T_h$ To gas phase at(f)
FIG 3.9 PLOT OF SOLUTION TEMPERATURES OF NAHCOLITE DAUGHTERS ($T_S$) AND OF THE SODIUM CARBONATE PHASE ($T_{S'}$), WHICH PRECIPITATED OUT FROM THE INCLUSION FLUID AT ELEVATED TEMPERATURES, VERSUS HOMOGENISATION TEMPERATURE. APATITE FROM THE WASAKI CARBONATITE (U876).

- Single phase region

- Two phase region

- Homogenisation to gas

- Homogenisation to liquid
CHAPTER 11

HEATING STUDIES ON MELT INCLUSIONS IN APATITES FROM
IJOLITES OF THE WASAKI AREA: EVIDENCE FOR LIQUID
IMMISCIBILITY IN IJOLITIC MELTS

4.1 INTRODUCTION

Trapped portions of a melt, which have subsequently crystallised
to form multicroystalline inclusions, composed essentially of solid
material, are present in apatites from ijolites of the Wasaki area
of W. Kenya (Chapter 1). When such inclusions are studied on the
microscope heating-stage, changes occur within the inclusions as
temperature is increased until, at some elevated temperature, the
contents of the cavity are completely molten.

With the development of suitable high-temperature microscope
heating-stages (Kalyuzhnyi, 1960; Dolgov and Bazarova, 1965), several
authors have attempted to use crystallised melt inclusions in minerals
from alkaline igneous rocks as geothermometers (Valyashko and Kogarko,
1966; Naumov et al., 1972; Romanchev, 1972; Sobolev et al., 1972).
However, these studies have been subject to serious limitations such
as the small number of inclusions studied and the constant problem of
leakage and decrepitation during heating-runs.

This present study is concerned mainly with the observation and
interpretation of the phase changes which occur within the inclusions
during heating-runs. The multisolid inclusions in apatite from the
Usaki ijolite pegmatite (UL256) have proved particularly informative.
Positive evidence, which shows that liquid immiscibility exists
between carbonate-rich melts and silicate melts in ijolitic fluids,
has been gained from their study at high temperatures.

Although the multisolid inclusions in the ijolite apatites could not be used as reliable geothermometers, some indication of the temperature of formation of the host apatites has been determined from the melting temperatures of the inclusion contents.

4.2 THE MICROSCOPE HEATING-STAGE

Heating-studies were conducted on the Leitz 1350 microscope heating-stage which had been previously calibrated up to 1100°C using "specpure" inorganic substances with known melting points (Appendix A). Correction factors had to be added to all temperatures recorded above 600°C (Appendix A) since large, static, thermal gradients were found to exist within the heating-chamber above this temperature. These correction factors have been applied to all temperatures reported in the text.

In order to maintain thermal equilibrium between the sample (apatite crystal containing the inclusion) and heating-chamber, slow heating-rates of between 5 and 10°C/min. have been used throughout this study.

Observation of the contents of the inclusions become progressively more difficult as the temperature was increased above 800°C, because of the incandescent glow from the heating-chamber and sample. Heating-studies could not be performed beyond about 1100°C since above this temperature the glow had become so intense that the outline of the inclusion and its contents had become too diffuse for further observation.
4.3 SAMPLE SELECTION AND PREPARATION

Sample preparation for heating-stage studies of melt inclusions in apatites from ijolitic rock-types was the same as the method previously described for thermometric studies of aqueous inclusions in apatites from carbonatites (Chapter 3). Individual apatite grains used for heating-stage studies at high temperatures must be chosen with care.

It is necessary to select apatite crystals whose inclusions are large enough and sufficiently uniform to enable their contents to be seen clearly. It is also imperative that the selected grain rests on a smooth, flat, crystal face to ensure that the best possible thermal contact is made between the sample and the heating-stage object carrier. If irregular grains are used, this thermal contact may be poor and will result in large errors in temperature determinations during heating-runs. Unfortunately, because of these stringent requirements very few inclusions were suitable for study.

Heating-studies were carried out on multisolid, carbonate-rich inclusions in apatites from the following ijolitic rocks of the Wasaki area of W. Kenya:

- Ijolite xenolith in Nyamaji phonolite (U688)
- Usaki wollastonite-melanite ijolite (U303)
- Usaki pegmatite ijolite (U366), (U1256)

Similar studies were also conducted on multisolid, carbonate-poor inclusions in apatite from the Usaki wollastonite-urtite (U79) and on silicate melt inclusions in U366 and U1256. All attempts to homogenise aqueous-rich, nahcolite-bearing inclusions (section 1.7.5) in U366 were unsuccessful. Decrepitation or leakage occurred in every instance.
before the contents of the inclusion had homogenised.

4.4 THE RESULTS OF THE HEATING-STAGE STUDIES

4.4.1 The multisolid carbonate-rich inclusions in U488, U303 and U366

Changes in the contents of the inclusions were not apparent until temperatures in excess of 500°C were attained. Above this temperature the colourless, crystalline solids, which occupied between 75% and 95% of the total volume of the inclusion, began to melt. The melting occurred abruptly and most (about 90%) of these solids had melted over a very small temperature range (Table 4.1). In inclusions from U488 and U303, all of these colourless crystalline solids were completely molten by 675°C and 690°C respectively, but in U366 a very small amount of colourless crystalline material persisted up to temperatures between 690°C and 860°C (6 specimens) until it too melted. These results are summarised in Table 4.1 below.

<table>
<thead>
<tr>
<th>Table 4.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample reference number</td>
</tr>
<tr>
<td>Number of inclusions studied</td>
</tr>
<tr>
<td>Temperature range over which the bulk of the colourless solids melted (°C)</td>
</tr>
<tr>
<td>Maximum temperature at which all of the colourless solids had melted (°C)</td>
</tr>
</tbody>
</table>

A small, light-brown, pleochroic mineral, previously identified as mica (section 1.7), is present in some of the inclusions. It is
particularly common in inclusions from U188 but only occasionally apparent in those from U366 and U303. The behaviour of the mica, was only observed on three occasions (all from U188). In these three instances it remained unaffected until the bulk of the colourless crystalline solids within the inclusions had melted (between about 550°C and 650°C). It then began to dissolve very rapidly in the resulting melt, and had completely dissolved at temperatures of 700°C, 735°C and 820°C.

Small, black, magnetic specks, identified as magnetite (section 1.7), are also seen in the inclusions from all three samples studied. These specks dissolved in the molten contents of the inclusion over the following temperature range:

- U188: 780 - 950°C (8 specimens)
- U303: 680 - 820°C (5 specimens)
- U366: 685 - 790°C (7 specimens)

Magnetite was the last solid phase to dissolve in the melt (except in eight inclusions in U366 where a small amount of colourless, solid material dissolved at temperatures higher than this). In U188, when the mica and magnetite were both present in the same inclusion (3 specimens), the mica dissolved independently, always at temperatures lower than the solution temperature of the magnetite.

Over half of all inclusions studied, visibly leaked during heating-runs. The results from such inclusions therefore had to be discarded. When leakage occurred at temperatures above about 650°C, the molten contents of the inclusion were rapidly extruded onto the surface of the apatite crystal where they immediately recrystallised to a very fine-grained aggregate. This immediate
solidification is presumably because the melt loses its volatile components as it breaks out from the inclusion. The rate at which the fluid was extruded, even at these relatively low temperatures (∼650°C), shows that these melts are exceedingly mobile.

When the inclusions were cooled from temperatures approximately 50°C above the final solution temperature of the magnetite, all of the solid phases, originally present within the inclusion, recrystallised. Magnetite crystallised out first as a small, euhedral, monocrystalline speck at temperatures 20–40°C below its original solution temperature. Similarly, the mica in U88 crystallised immediately after the magnetite at temperatures approximately 40°C lower than its original solution temperature. Continued cooling down to temperatures between 650°C and 500°C resulted in the immediate crystallisation of the colourless solids from the melt. No molten material was observed in any instance below 490°C. Cooling-rates were generally between 10 and 20°C/mm. On no occasion did any of the molten contents of the inclusion quench to a glass, even when the fastest cooling-rates possible (approx. 200°C/mm) were used.

So far, only the behaviour of solid phases on heating has been described. However, most of the multisolid inclusions also contain a small amount of vapour (section 1.7). After the bulk of the colourless crystalline solids within the inclusions have melted, the vapour phase takes the form of a single bubble which moves with relative ease within the molten contents of the inclusion (which once again shows the marked fluidity of this melt).

As the temperature was increased the vapour bubble gradually diminished in size and reciprocally the melt expanded. Complete
'solution' of this vapour bubble within the melt below 1100°C was achieved in less than half of all inclusions studied (heating-studies had to be terminated at about 1100°C). Only two inclusions, both in U438, were devoid of a vapour bubble at all stages during heating-runs. When inclusions which contained this vapour bubble had become completely homogeneous, the bubble was always the last phase to homogenise in U303 and U366. This was generally the case in U438, but three inclusions did not conform. In these three instances, although a vapour bubble was present within the melt it dissolved before the solution of magnetite, also present in the inclusions, had taken place. Complete homogenisation for these three samples occurred at the solution temperature of the magnetite (950, 855, 830°C).

Table 4.2 summarises the results obtained for the temperature of solution of the gas bubble for all samples studied.

Duplicate heating-runs were performed whenever possible. In most inclusions, the melting temperature range of the colourless, crystalline solids, the solution temperatures of the mica (when present) and magnetite, and the solution temperature of the vapour bubble (when it occurred) were reproducible to within ±20°C. A few inclusions (about 10% of the number studied), when heated for a second time, showed visible signs of leakage (that is, a significant portion of the molten contents of the inclusion had been extruded, and a larger vapour bubble than was originally present was observed).

Inclusions in which the vapour bubble failed to dissolve in the molten contents of the inclusion below 1100°C, still showed this same behaviour even after replicate runs. Three of these inclusions (all from U366) were held at temperatures between 900 and 950°C for
twelve hours in the hope that such an extended period of heating might bring about the complete solution of the vapour bubble. However, even after heating for this length of time, the vapour bubble still failed to dissolve, instead the bubble increased in size (presumably because of leakage).

Table 4.2 Summary of the behaviour of the vapour phase, in multisolid inclusions in apatite from Wessakijolites, on heating

<table>
<thead>
<tr>
<th>Sample ref. number</th>
<th>U488</th>
<th>U303</th>
<th>U366</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total number of inclusions studied</td>
<td>19</td>
<td>13</td>
<td>39</td>
</tr>
<tr>
<td>Number of inclusions which did not contain a vapour bubble</td>
<td>2</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>Number of inclusions in which the bubble failed to dissolve in the molten contents of the inclusion below 1100°C</td>
<td>10</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Number of inclusions in which complete solution of the vapour bubble occurred</td>
<td>7</td>
<td>3</td>
<td>17</td>
</tr>
<tr>
<td>Temperature range obtained for the solution of this vapour bubble below 1100°C (in °C). (i.e. the temperature at which these inclusions become completely homogeneous)</td>
<td>850-1050 820-930 750-1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Complete range of homogenisation temperatures for all inclusions studied (in °C)</td>
<td>850-1100 820-1100 750-1100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.4.2 Inclusions composed predominately of a non-carbonate solid phase (U79)

Multisolid, carbonate-rich inclusions are not characteristically present in the apatites from the Wessakijolite-urtite (U79), and those which have been observed are unsuitable for detailed heating studies. The dominant inclusion-type present in those apatites (U79) (possibly cancrinite), usually consist of a single crystal of an unidentified/non-carbonate
solid (section 1.7.1) together with a small amount of vapour. Heating-studies have been possible on eight of these non-carbonate, crystallised melt inclusions.

No visible change occurred in the contents of the inclusions on heating from 23°C to about 600°C, although one of the inclusions decrepitated at 263°C. The unidentified mineral phase, which was the only solid present in these inclusions, began to melt slowly at about 600°C. By 650°C, approximately one fifth of this mineral had melted and the vapour phase present in all of these inclusions formed a large, rounded bubble within the melt. Further heating caused decrepitation in two of these inclusions (at 705 and 690°C), but in the other five, melting of the remainder of the crystalline solid occurred abruptly at temperatures between 730 and 810°C. At these temperatures the inclusion contents were completely molten, although the vapour bubble still remained undissolved. On cooling, the unidentified mineral phase crystallised from the melt at temperatures between 715 and 685°C and continued to grow down to temperatures of about 580°C. Below this temperature all of the melt had crystallised. Rapid cooling failed to produce a glass.

The vapour bubble, present in all of the inclusions studied and occupying between one tenth and one quarter of the total volume of the inclusion at about 350°C, failed to dissolve in the melt. Continued heating up to temperatures of 950°C simply caused all inclusions to decrepitate or leak.

4.4.3. Multisolid inclusions in U1256

Multisolid inclusions, which contain large amounts of colourless,
crystalline material, are present in the apatites from U1256. Crushing-stage studies in acidified glycerol have shown that these colourless solids react instantly with the acid medium; this reaction being accompanied by rapid effervescence (section 1.7). These inclusions are therefore similar to the carbonate-rich, multisolid inclusions in apatites from other ijolite samples (U488, U303, U366). However, in contrast to the multisolid inclusions in apatites from these ijolites, those from U1256 may also contain substantial and variable amounts of small green, brown and black mineral phases (mainly silicates but probably magnetite as well). For the sake of convenience, when discussing their behaviour on heating, the multisolid inclusions from U1256 have been subdivided as follows:

1. Type A inclusions which contain only a few minute, crystalline specks of coloured and black mineral phases.

2. Type B inclusions which contain significant amounts of these green, brown and black crystalline solids and which occupy between 10 and 25% of the volume of the inclusion.

3. Type C inclusions in which the volume of the inclusion occupied by these small, coloured and opaque crystals ranges from about 25% to 50%.

Preliminary studies on the inclusions were unsuccessful, and although the contents were seen to melt at high temperatures, the small size of the inclusions studied did not permit a reliable estimate of the temperature of melting of the solid phases. Moreover, phase changes were exceedingly difficult to observe although some of the inclusions were seen to contain two separate fluid phases (melts) above 900°C. To assess the nature of these fluid phases, an
intensive search was made for inclusions suitable for heating studies. Eight such inclusions were found: two type A, four type B and two type C.

When these eight inclusions were heated, the colourless solids began to melt above about 500°C. At temperatures between 575 and 640°C, approximately two thirds of these colourless solids had melted. By 710°C they were completely molten. The small green, brown and black crystals, apparent in type A inclusions, dissolved in the melt at temperatures between 790 and 870°C. Above 870°C, all of the solids within these inclusions had melted or dissolved. In type B inclusions, many of the green, brown and black crystalline solids dissolved in the melt between 610 and 870°C, but the remainder did not. Instead they melted independently to form pale green globules of immiscible liquid. These globules formed at temperatures between 820 and 900°C. Continued heating caused the globules to gradually "dissolve" in the colourless carbonate-rich melt. Complete "solution" of the globules occurred at temperatures of 950, 970, 930 and 1030°C. The phase changes which occur on heating one of these inclusions are shown in Plate 4.1.

The behaviour of the coloured and black, opaque, crystalline solids in type C inclusions was similar, with the formation of pale green globules at about 850°C. However, instead of dissolving completely in the carbonate melt, these globules coalesced into a single large globule and remained immiscible at temperatures above 1100°C. In both inclusions the globules still occupied a large proportion of the cavity volume (approx. 20%) at this temperature.

A vapour bubble was present in six of the inclusions studied.
It failed to dissolve in the melt on five occasions and was still apparent at 1100°C. However, in one of the type A inclusions it dissolved completely at 950°C. At this temperature the inclusion contents had completely homogenised. Complete homogenisation was attained only on one other occasion. In this instance a type B inclusion, which did not contain a vapour bubble, homogenised at 980°C; the temperature at which the pale green globules dissolved.

When type A inclusions were cooled from about 1000°C, the contents of the inclusions crystallised completely. The small, coloured and black crystals reappeared at temperatures between 855°C and 780°C, and the colourless solids crystallised at temperatures between 590 and 505°C.

The behaviour of type B inclusions on cooling is shown in plates 4.2 and 4.3. When these inclusions were cooled slowly, (using cooling rates of between 10 and 20°C/mm.), the molten contents of the inclusion separated to form two distinct immiscible liquid phases; the green globules and the colourless melt. Continued cooling caused precipitation of a few small, brown and black crystalline phases from these globules, notably brown/black, euhedral, isotropic solids (Plate 4.4b). However, most of the globules quenched to form a pale-green, isotropic glass (Plate 4.4a, b, c). The colourless carbonate-rich melt crystallised at temperatures between 575°C and 500°C.

The behaviour of type C inclusions on cooling was similar. Most of the green coloured globules quenched to form a glass (Plate 4.4d) but the colourless melt sample recrystallised at temperatures between 560 and 490°C.
4.4.4. Silicate melt inclusions

Silicate melt inclusions are also present in the apatites from U1256 and U366 (section 1.7.3). In U366, most of the inclusions are visibly non-hermetically sealed within the apatites (see Plate 1.14d, e). However, some of the smaller inclusions, which appear completely sealed within the apatite crystal, were studied on the microscope heating-stage. On heating, the contents of the inclusion progressively darkened until, at about 700°C, the darkening had become so acute that observation was no longer possible. Further heating to 950°C did not cause any noticeable change within the inclusion. This darkness was still apparent after the inclusions had been cooled to room temperature.

Heating studies on silicate melt inclusions in apatite from U1256 resulted in a similar progressive darkening of the contents of the inclusions. Small cracks leading from the inclusion into the apatite crystal, not observed before heating-runs, became readily apparent during heating-runs. This shows that such inclusions did not remain hermetically sealed during the course of heating studies. However, two very small (≈ 10 μm) inclusions did not show this characteristic darkening. These inclusions were far too small for detailed observations during heating-runs, but after heating to 950°C, the specimen was cooled (cooling rate of between 20 and 30°C/mm.), removed from the heating-stage and the inclusions studied at very high magnification (x 1200) using oil immersion. The contents of the inclusion were seen to consist of a pale green, isotropic glass which contained a small vapour bubble (Plate 4.4e, f). This glass was the same pale green colour, and possessed the same approximate refractive
index (as indicated by its relief relative to the apatite crystal in contact with it) as the partly crystallised glassy globules observed in type B and type C multisolid inclusions (Plate 4.4). It is therefore concluded that these two glasses are essentially the same.

4.5 DISCUSSION OF RESULTS

4.5.1. Multisolid melt inclusions as indicators of the temperature of formation of the apatites

Sobolev et al. (1972) have recently presented experimental evidence to show that melt inclusions can be used, in exactly the same way as aqueous inclusions, to determine the formation temperature of minerals. The temperature at which a crystallised melt (multisolid) inclusion becomes homogeneous represents the temperature at which the host mineral has crystallised. However, this is only true if the inclusion was originally trapped as an homogeneous melt. If the inclusion represents an heterogeneous (for example, gas plus melt or two immiscible melts) portion to the magma, the homogenisation temperature does not give any indication of the formation temperature. Furthermore, if leakage occurs during homogenisation runs, the final homogenisation temperature obtained (if any) will be an over estimate of the formation temperature.

The multisolid inclusions studied here often contain a very large vapour bubble which still occupies a large percentage of the total volume of the cavity, even at about 1100°C. Leakage has been particularly noticeable on many occasions and although inclusions which had obviously leaked (that is, when the molten contents were seen to spill out onto the surface of the apatite crystal) were disregarded, it may be exceedingly difficult to spot partial leakage during heating-
runs. If leakage is slow and continues gradually over a wide temperature range it may go unnoticed, and the final homogenisation temperature obtained will be considerably higher than the formation temperature. Other workers have been hampered by this constant problem of leakage of melt inclusions at high temperatures. Valyashko and Kogarko (1966), in particular, suspect that the homogenisation temperatures which they obtained may be erroneously high due to partial leakage. Because leakage has been so widespread in the inclusions studied here it is similarly concluded that their homogenisation temperatures (especially those greater than 1100°C) do not give a reliable indication of the formation temperature of the host apatite. Furthermore, the multisolid type B and type C inclusions in apatite from U1256 result from the trapping of a heterogeneous portion of the environment of crystallisation. Consequently the homogenisation temperature for these inclusions will be an overestimate of the formation temperature.

Since the homogenisation temperature for most inclusions cannot be used to obtain an estimate of the crystallisation temperature of the apatites with any degree of certainty, it would appear that these multisolid inclusions cannot be used as geothermometers. However, a minimum temperature of formation can be deduced from the temperature at which the crystalline contents of the inclusion had completely melted or dissolved. This temperature may be as much as 300°C lower than the actual formation temperature, but it certainly is more reliable than the temperature of complete homogenisation (i.e. solution of the vapour bubble in the melt) for these inclusions. The results are summarised in Table 4.3.
Table 4.3  Summary of the temperature at which the crystalline contents of multisolid inclusions have completely melted or dissolved

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Number of results obtained</th>
<th>Temperature range* over which last solid phase dissolved or melted</th>
<th>Nature of the last solid phase to melt or dissolve</th>
</tr>
</thead>
<tbody>
<tr>
<td>U138</td>
<td>3</td>
<td>780-950°C</td>
<td>Black spock (magnetite)</td>
</tr>
<tr>
<td>U303</td>
<td>5</td>
<td>630-820°C</td>
<td>Black spock (magnetite)</td>
</tr>
<tr>
<td>U366</td>
<td>7</td>
<td>635-790°C</td>
<td>Black spock (magnetite)</td>
</tr>
<tr>
<td>U366</td>
<td>4</td>
<td>690-860°C</td>
<td>Colourless solid</td>
</tr>
<tr>
<td>U79</td>
<td>5</td>
<td>730-810°C</td>
<td>Colourless solid</td>
</tr>
<tr>
<td>U1256 (Type a)</td>
<td>2</td>
<td>790-870°C</td>
<td>Various coloured specks</td>
</tr>
<tr>
<td>U1256 (Type b)</td>
<td>4</td>
<td>810-870°C</td>
<td>(Melting of various coloured phases to form immiscible green coloured globules)</td>
</tr>
<tr>
<td>U1256 (Type c)</td>
<td>1</td>
<td>350</td>
<td></td>
</tr>
</tbody>
</table>

* The Temperature at which the last solid phase dissolved represents the minimum formation temperature of the apatite.

4.5.2. Immiscibility in ijolite melts as indicated by the study of melt inclusions in apatite from U1256

Two distinct types of melt inclusion are present in the apatites from U1256 and U366. They consist of silicate melt inclusions and carbonate-rich multisolid inclusions. Since these two inclusion-types are co-genetic in the same apatite crystal it has been suggested (Chapter 1, section 1.9.3.) that they represent the trapped portions of immiscible carbonate-rich and silicate melts which co-existed in the ijolite magma. The results obtained from heating studies of melt inclusions in apatites from U1256 confirm that these two melts do
indeed show an immiscibility relationship as summarised below.

Type A multisolled inclusions and the silicate melt inclusions represent separate portions of two co-existing melts. When portions of these two melts (carbonate-rich and silicate melts) are trapped contemporaneously within the same inclusion, type B and type C inclusions are formed. Heating studies on these two inclusion types have shown that two coexisting liquid phases are present within the inclusions at high temperatures ($> 810^\circ$C). These liquids consist of a silicate melt (green globules) and a carbonate-rich melt (colourless liquid). This immiscibility is particularly noticeable during cooling of the inclusions from elevated temperatures (Plate 4.2 and 4.3). At high temperatures the two melts are partly miscible as shown by the solubility of the globules in the carbonate-rich melt at temperatures between 950 and 1030$^\circ$C in type B inclusions. However, complete miscibility does not occur at these temperatures since type C inclusions, which contain a larger portion of silicate melt, still showed immiscibility above about 1100$^\circ$C. Unfortunately, it has not been possible to determine the temperature at which these two liquids become totally miscible.

The idea that immiscibility between carbonate and silicate melts could play an important role in the derivation of carbonatite magmas from a parent carbonated silicate melt is not new (von Eckermann, 1967). From their study of calcite phenocrysts from ijolite porphyry, Zhabin and Samsonova (1968) have also suggested that primary carbonate melts may occur in ijolitic magmas. Recently, Koster van Groos and Wyllie (1968), who studied the join NaAlSi$_3$O$_8$ - Na$_2$CO$_3$ - H$_2$O, have demonstrated that immiscibility between carbonate and silicate melts
can indeed occur. These authors considered that carbonatite magmas could be derived from a carbonated silicate magma by a process of liquid immiscibility.

Immiscibility between carbonate-rich and silicate melts has actually been observed in inclusions in apatites from U1256. Therefore, since these inclusions are primary and represent the trapped portions of the environment of the ijolites, these observations show that immiscibility does exist, at least in this instance, in naturally occurring ijolitic magmas. Romanchev (1972) has also observed immiscibility between carbonate and silicate melts in inclusions in nepheline and pyroxene from the Kiwaraha nephelinites of Tanzania. It is therefore apparent that this present observation of liquid immiscibility is not unique to the sample studied here (U1256).

Carbonate material is present in the multisolid inclusions in apatites from the Usaki ijolites. The possibility that carbonatitic fluids could originate from ijolite magmas has been outlined in a previous chapter (Chapter 1, and section 1.9.3.). That such fluids can be derived by a process of liquid immiscibility is now evident from this present study.

4.6 SUMMARY AND CONCLUSIONS

Serious problems of leakage and decrepitation have often been encountered during these preliminary heating studies of melt inclusions in apatites from the Usaki area. The complete homogenisation temperatures for most inclusions are considered to be erroneously high mainly due to partial leakage of the inclusion contents at high temperatures during heating-runs. Consequently, these temperatures
cannot be used as reliable indicators of the formation temperatures of the apatites.

The temperature at which the contents of the multisolid carbonate-rich inclusions \((U_{1256}, U_{303}, U_{366})\), the multisolid carbonate-rich/silicate inclusions \((U_{1256})\), and the melt inclusions composed essentially of a non-carbonate crystalline solid become completely molten does give a value for the minimum formation temperature of the apatites. The temperature range obtained (Table 4.3) shows that the ijolite apatites have crystallised at temperatures substantially higher than carbonatite apatites from the same complex (chapter 3).

Heating studies of inclusions in apatite from \(U_{1256}\) have shown that an immiscibility relationship exists between carbonate-rich melts and silicate melts in natural ijolite melts. That carbonatite magmas (carbonate-rich fluids) can be derived from ijolitic melts by a process of liquid immiscibility is now evident from this present study.

The precise nature of this carbonate-rich fluid (preserved as multisolid, carbonate-rich inclusions) is not yet fully understood. However, heating studies on these inclusions \((U_{1256}, U_{303}, U_{366}, U_{1256})\) have shown that the carbonate-rich melts are highly mobile, volatile-rich and can maintain their fluidity down to relatively low temperatures (approximately 500-600°C). It is also particularly interesting to note the sequence of crystallisation of the contents of the carbonate-rich, multisolid inclusions as they are cooled from high temperatures produced during heating-runs. Magnetite is almost always the first mineral to crystallise; followed by the mica, when present, and
finally the bulk of the colourless, carbonate-bearing minerals. This sequence of crystallisation is well in agreement with the general crystallisation sequence of minerals in most carbonatites, where magnetite and mica are usually early mineral phases (Heinrich, 1966, pp. 212-213).

Detailed studies on the homogenisation of melt inclusions together with an appraisal of the possible sources of error (e.g. leakage) are needed before they can be used as accurate indicators of the formation temperature of minerals. In particular, the absence of a vapour bubble in some multisolid inclusions (2 from Ul68 and 2 from Ul256) needs to be explained. It is beyond the scope of this present work, which is only intended as a preliminary study, to give an adequate answer to all the questions which arise from this study.
The behaviour of the contents of a complex multisolid carbonate-rich/silicate melt inclusion from U1256 on heating

The inclusion (type B) at room temperature (23°C) consists of a vapour bubble (v), colourless carbonate-rich solids (c), and numerous, small, crystalline specks of green, brown and black mineral phases, seen as black and dark grey patches in A. Heating to 422°C causes very little change, but at 620°C the colourless carbonate-rich material has melted. Progressive heating to 850°C causes only slight solution of the remaining mineral phases (black, brown and green specks). Above 850°C these specks dissolve noticeably. However, at 890°C pale green coloured globules have formed (some of which are arrowed). Continued heating causes these globules to dissolve in the carbonate melt. Complete solution has taken place at 960°C at which temperature only one single homogenous melt exists together with the vapour bubble (v) which failed to dissolve even at 1100°C.

The behaviour of this same inclusion on cooling is shown in Plate 4.2
The behaviour of the molten contents of a complex multisolid carbonate-rich/silicate melt inclusion from U1256, as it is cooled from elevated temperatures.

The behaviour of this inclusion on heating was shown in Plate 4.2. As the inclusion is cooled from 960 to 940°C the green coloured globules (some of which are arrowed) separate from the melt. At 900°C two separate co-existing melts are seen: the green globules (gg) and the colourless carbonate rich melt (cm). Note also the vapour bubble (v). At 805°C no phase changes have occurred except that some of the globules have coalesced to form larger ones. At 670°C some of the globules have crystallised, but others simply quench to a glass. At 553°C the colourless carbonate-rich melt crystallises and a colourless solid (c) appears. Further cooling results in complete crystallisation of this melt. At 451°C the left hand side of the inclusion has darkened (indicating that further crystallisation has occurred, but it has not been possible to observe the exact nature of this change). The inclusion at 23°C, was then removed from the heating chamber and viewed under high magnification using oil immersion (see Plate 4.4a).
Plate 4.3 Liquid immiscibility in a complex multisolid carbonate-rich/silicate inclusion from U1256

The inclusion shown in Plates 4.1 and 4.2 was reheated up to 970°C and cooled. At 960°C a few globules are apparent, but at 950°C numerous, pale green coloured globules appear spontaneously. These immiscible globules continue to grow in size down to 885°C. At 705°C small, black, crystalline solids are discernible within some of these globules. Note also that many of the globules apparent in E have coalesced to form larger globules as shown in F.
Plate h.4

(a) The inclusion shown in Plate h.28. Note the vapour bubble (v), colourless solids (c), and the dark patch (arrowed) which consists of brown and black isotropic solids. Three of the green coloured globules (gg) have quenched to a glass. Bar = 20 μ. 

(b) The two immiscible liquids (colourless melt and green globules) which appeared in this inclusion during heating-runs became completely miscible at 900°C. On cooling, the melt unmixed again. A black solid (arrowed) formed from one of these globules, but most quenched to form a green coloured glass. The colourless melt crystallised completely as colourless solids. The vapour bubble (v) occupies a large percentage of the inclusions volume, leakage during heating runs has undoubtedly occurred. Bar = 20 μ. 

(c) A close-up of (b) above showing numerous glass globules (arrowed) colourless solids (c) and the unidentified black mineral phase which had crystallised from one of the globules. Bar = 10 μ. 

(d) A type C inclusion showing glass globules (some arrowed), formed on cooling. A vapour bubble (v) is also seen. The remainder of the volume of the inclusion is composed of colourless solids (c) which crystallised from the colourless melt. Bar = 20 μ. 

(e) and (f) Silicate melt inclusions after heating to 950°C, quenched to a pale green isotropic glass (GG) identical to the glassy globules observed in type (c) and type (b) multisolid inclusions. A vapour bubble is observed in both inclusions. Bar = 10 μ.
CHAPTER 5

A THERMOMETRIC STUDY OF AQUEOUS INCLUSIONS IN APATITE
FROM CARBONATITES OF THE TORORO COMPLEX OF E.UGANDA

5.1. INTRODUCTION

The Tororo complex of south-east Uganda consists of two separate masses of carbonatite; Tororo Rock, and to the south Limekiln Hill (King and Sutherland, 1966, p.80). Magnetite, aegirine and apatite are common accessory minerals in the carbonatites. The apatites contain inclusions similar to those previously described in apatites from carbonatites of the Wasaki area (section 1.6). A detailed study of these inclusions has been made and their nature and origin discussed. Homogenisation temperatures were recorded for 200 aqueous inclusions. The results give an indication of the temperatures prevailing during the crystallisation of the carbonatites. Thin sections from a total of 18 separate apatite-rich carbonatite samples, at present housed in the Geology Department, Leicester University, were studied. However, only 6 of these samples (Table 5.1) contained sufficient numbers of inclusions for further studies.

5.2. THE AQUEOUS INCLUSIONS

5.2.1. Size, shape and abundance

The inclusions within the apatites from the selected carbonatites consist almost exclusively of aqueous saline types (Plate 5.1) similar to those described previously in apatites from carbonatites of the Wasaki area of W.Kenya (section 1.6.2). The
Table 5.1  CARBONATITE SAMPLES FROM THE TORORO COMPLEX
SELECTED FOR FLUID INCLUSION STUDIES

<table>
<thead>
<tr>
<th>Locality</th>
<th>Sample Number</th>
<th>Rock-Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limekiln Hill</td>
<td>SUTO 20</td>
<td>Apatite-Sovite</td>
</tr>
<tr>
<td>Limekiln Hill</td>
<td>SUTO 22</td>
<td>Aegirine-Apatite-Sovite</td>
</tr>
<tr>
<td>Limekiln Hill</td>
<td>SUTO 26</td>
<td>Aegirine-Apatite-Sovite</td>
</tr>
<tr>
<td>Limekiln Hill</td>
<td>SUTO 607</td>
<td>Apatite-Carbonatite</td>
</tr>
</tbody>
</table>
| Tororo Rock   | SUTO 103      | Apatite-Magnetite-
Carbonatite              |
| Tororo Rock   | SUTO 112      | Apatite-Magnetite-
Carbonatite              |
abundance of the inclusions within the apatites from the Tororo carbonatites varies from sample to sample and from apatite to apatite crystal in the same sample as shown in Table 5.2. The size of the inclusions rarely exceeds about 50 $\mu$, most being smaller than 20 $\mu$ (Table 5.3). Their shape is usually spheroidal (SUTO 20, SUTO 22, SUTO 103, SUTO 111) although a large number of irregular inclusions predominate in other samples (SUTO 26, SUTO 607). Tubular, negative crystal-shaped cavities are not particularly common in any of the apatites studied and are only observed in significant numbers (10-20% of all inclusions observed) in SUTO 103 and SUTO 20.

The primary nature of these inclusions is readily apparent from their large size relative to the host apatite (Plate 5.1b), and also from the occurrence of enlongate or tubular cavities running the length of the apatite crystal (Plate 5.1a). Necking-down of inclusions has been operative to a large extent in all samples. Small tails on some inclusions (Plate 5.2f) are positive evidence that such inclusions have necked, and many instances have been recorded where inclusions are seen in various stages of necking-down (Plate 5.2d, e). In SUTO 607 so many inclusions appear to have necked that it proved exceedingly difficult to find isolated inclusions unaffected by necking-down processes, consequently this sample proved unsuitable for further studies.

5.2.2. Phases present

The inclusions consist of an aqueous solution containing a mobile gas bubble and often one or more crystalline daughter phases. In all samples studied, the gas bubble showed a distinct but small
Table 5.2

ESTIMATES OF THE ABUNDANCE OF AQUEOUS INCLUSIONS IN APATITES FROM CARBONATITES OF THE TORORO COMPLEX

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Number of inclusions in apatites (as a percentage of the total number studied)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>None</td>
</tr>
<tr>
<td>SUTO 20</td>
<td>12</td>
</tr>
<tr>
<td>SUTO 22</td>
<td>17</td>
</tr>
<tr>
<td>SUTO 26</td>
<td>34</td>
</tr>
<tr>
<td>SUTO 607</td>
<td>2</td>
</tr>
<tr>
<td>SUTO 100</td>
<td>33</td>
</tr>
<tr>
<td>SUTO 112</td>
<td>63</td>
</tr>
</tbody>
</table>

These percentages were determined by counting the number of inclusions in 200 apatite crystals selected at random from each sample.

Inclusions less than \( \sim 1 \mu \) in size were not considered
Table 5.3  
THE SIZE RANGE OF 200 PRIMARY AQUEOUS INCLUSIONS IN APATITE SELECTED AT RANDOM FROM EACH SAMPLE, GIVEN AS PERCENTAGES OF THE TOTAL NUMBER STUDIED

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Percentage of inclusions within each size range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1-10μ</td>
</tr>
<tr>
<td>SUTO 20</td>
<td>51</td>
</tr>
<tr>
<td>SUTO 22</td>
<td>54.5</td>
</tr>
<tr>
<td>SUTO 26</td>
<td>71.5</td>
</tr>
<tr>
<td>SUTO 607</td>
<td>33</td>
</tr>
<tr>
<td>SUTO 108</td>
<td>66</td>
</tr>
<tr>
<td>SUTO 112</td>
<td>81</td>
</tr>
</tbody>
</table>

Only inclusions greater than 1μ were considered.

tr. = Very occasional occurrence of inclusions in the size range specified (less than 0.5% of the total number of inclusions studied)

n.o. = Inclusions within this size range never observed
volume expansion (calculated to be up to about 27x volume expansion) when the inclusions were opened in an inert hydrocarbon oil (for example, liquid paraffin) on the microscope crushing-stage (Roedder, 1970). This indicates that the gas bubble is held under a significant positive pressure. No liquified CO₂ has been observed at room temperature in any of the inclusions from the Tororo apatites, but when cooling-studies were conducted down to about 0°C, a small rim of CO₂-liquid was evident in some inclusions (particularly SUTO 108 and SUTO 20). This confirms that the gas bubble is composed essentially of low-density carbon dioxide. The percentage of the total volume of the inclusion occupied by the gas phase varies greatly. This is a consequence of the extensive necking-down processes which have been operative in all specimens studied. Estimates of the volume occupied by the gas phase have been obtained from several, large, isolated inclusions which do not appear to have necked-down. The gas bubble present in these inclusions fills, on average, between about one fifth to one quarter of the volume of the cavity (Table 5.4).

The inclusions in apatite from SUTO 20, SUTO 22 and SUTO 26 usually contain a single, large, highly birefringent, water-soluble, alkali bicarbonate daughter mineral (Plate 5.1f) positively identified as nahcolite (see Chapter 2). The percentage of the total volume of the inclusion occupied by this phase usually ranges from 10-20%, although inclusions containing up to 30% by volume of this same phase are not unusual. A minute, black, anhedral, non-magnetic speck is observed in some inclusions from all three of these samples (SUTO 20, 22 and 26), but its exact nature could not be ascertained. Other daughter phases are notably absent. Minute amounts (less than 1% of
Table 5.4  THE PERCENTAGE OF THE TOTAL VOLUME OF THE INCLUSION
OCCUPIED BY THE GAS PHASE IN SELECTED PRIMARY
AQUEOUS INCLUSIONS UNAFFECTED BY NECKING-DOWN
PROCESSES

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Percentage of the Total Volume of Inclusion filled by Gas</th>
<th>Number of Determinations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range</td>
<td>Mean</td>
</tr>
<tr>
<td>SUTO 20</td>
<td>16-23</td>
<td>21.5</td>
</tr>
<tr>
<td>SUTO 22</td>
<td>20-25</td>
<td>21.5</td>
</tr>
<tr>
<td>SUTO 26</td>
<td>20-30</td>
<td>24.5</td>
</tr>
<tr>
<td>SUTO 108</td>
<td>21-27</td>
<td>25.5</td>
</tr>
<tr>
<td>SUTO 112</td>
<td>19-28</td>
<td>23.5</td>
</tr>
</tbody>
</table>

The volume per cent. (+ 1%) of the gas phase was obtained from plasticine models of the inclusions fashioned from photomicrographs of the cavities taken in various orientations.
the total volume of the inclusion) of other unidentified specks of birefringent daughter minerals are only observed in a few inclusions.

In SUTO 112 the aqueous inclusions are often simple two-phase, gas/liquid types (Table 5.5). However, nahcolite has been identified as a precipitated daughter phase in many inclusions (Plate 5.1e) and once again is the predominant daughter phase present. The only other commonly occurring daughter mineral is a small, black, opaque, hexagonal platelet which displays marked magnetic properties when a hand magnet is placed in close proximity to the inclusions. On the basis of the pronounced magnetism and the common occurrence of this phase as regular hexagonal platelets (Plate 5.1c, d), it has been identified as pyrrhotite. Similar daughter minerals, also identified as pyrrhotite, have been described previously in inclusions in apatite from a sample of carbonatite (U693) from the Wasaki area of W.Kenya (section 1.6.3.). Small specks of other anisotropic, unidentified daughter phases are only occasionally observed in some inclusions from SUTO 112.

Daughter phases are present in a little over half of the total number of inclusions studied in SUTO 108. Nahcolite daughters have been observed but only on rare occasions (Plate 5.1b), being noticeably absent in most of the inclusions and no longer occurring as the dominant daughter phase. Small, black, magnetic, hexagonal platelets identical to those described above (SUTO 112) and similarly identified as pyrrhotite are occasional daughter minerals. However, another solid phase, present in amounts which never exceed 5% of the total volume of the inclusion, is the most commonly encountered daughter mineral in the aqueous inclusions in apatites from this sample (SUTO 108) (Plate 5.1g, h). This phase is usually present as one or more moderately
birefringent (1st order colours), pale yellow to colourless solids whose crystallographic form could not be ascertained with any degree of certainty, although a crystal possessing a rectangular outline was observed in one instance. This crystal was length fast and showed straight extinction. The relief of these unidentified daughter phases relative to the aqueous fluid is high, and they dissolve readily in this fluid when heating-studies are conducted on those inclusions containing this phase. Attempts to extract this solid for optical and chemical tests were unsuccessful, and although a positive identification could not be made, its non-carbonate nature is evident from its low order interference colours.

A further unidentified daughter phase is occasionally seen as very small slender needles (Plate 5.1g). However, since the width of these needles never exceeds a fraction of a micron, even simple optical tests could not be made. These needles readily dissolved in the inclusion fluid during heating studies.

Table 5.5 summarises the daughter phases present within the inclusions together with the percentage of the volume of the inclusions occupied by each phase. It also shows the percentage of the total number of primary inclusions which do not contain precipitated daughter phases.

5.2.3. Alteration of the inclusions by secondary processes

Apart from the extensive necking-down of inclusions which has taken place in all samples studied (particularly SUTO 108 and SUTO 112), other secondary processes, which have brought about considerable changes in the original contents of the aqueous inclusions, are exceptionally
Table 5.5  FREQUENCY OF OCCURRENCE OF DAUGHTER MINERALS IN PRIMARY AQUEOUS INCLUSIONS FROM THE TORORO CARBONATITES

<table>
<thead>
<tr>
<th>Daughter Mineral</th>
<th>Percentage of inclusions containing indicated daughter mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SUTO</td>
</tr>
<tr>
<td>Nahcolite (Nh)</td>
<td>42</td>
</tr>
<tr>
<td>Non-magnetic black opaques</td>
<td>11</td>
</tr>
<tr>
<td>Pyrrhotite platelets</td>
<td>0</td>
</tr>
<tr>
<td>Acicular needles</td>
<td>0</td>
</tr>
<tr>
<td>Yellow-coloured anisotropic solids (Y)</td>
<td>0</td>
</tr>
<tr>
<td>Small specks of other birefringent solids</td>
<td>12</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Percentage of inclusions which do not contain any daughter minerals</th>
<th>SUTO</th>
<th>SUTO</th>
<th>SUTO</th>
<th>SUTO</th>
<th>SUTO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>31</td>
<td>30</td>
<td>36</td>
<td>48</td>
<td>52</td>
</tr>
</tbody>
</table>
common in apatite from the carbonatites of Tororo rock (SUTO 20, SUTO 22, SUTO 26). Numerous small planes of minute (less than 1 μ) secondary inclusions criss-cross these apatites at random, indicating several phases of fracturing and subsequent re healing (Plate 5.2a). When a fracture has traversed a primary aqueous inclusion but has not completely healed, the inclusion contents are emptied and anomalous 'gas-filled' inclusions produced (Plate 5.2c). More often, infilling of emptied inclusions is observed and two further types of anomalous inclusions are produced. The first of these two types results from infilling of the inclusion, and the fracture which has traversed it, with calcite. Similar inclusions have been observed in apatites from SUTO 112.

The second type are produced as a result of the invasion of the rock by late-stage ferruginous veinlets which traverse the inclusions in the apatites and fill them with brownish-red, granular solid material (Plate 5.2b). Sutherland (1966) has previously noted the existence of "numerous rod-like inclusions of a brownish material" in the apatites from these samples and it is evident now, from this study, that such inclusions are of secondary origin.

5.3. OTHER PRIMARY INCLUSIONS PRESENT IN THE APATITES

Single crystals of calcite occur as solid inclusions in apatite from all samples studied. These inclusions are usually hermetically sealed within the apatite and are not the same as similar inclusions which result from infilling of an original aqueous inclusion with secondary calcitic material as described above (section 5.2.3). These
primary calcite inclusions are observed as spheroidal, rounded, or even tubular, monocristalline solids. They are co-genetic with primary aqueous inclusions (Plate 5.3a, b) and were presumably present as already precipitated solids in equilibrium with the aqueous fluid during the growth of the apatite crystals. Occasionally, a small portion of aqueous fluid may be trapped together with these single calcite crystals, and complex gas/liquid/captured calcite inclusions are produced (Plate 5.3c). These complex inclusions show, once again, that the calcite solids and aqueous fluids co-existed in the original crystallising fluid.

A further inclusion-type has been recognised in apatites from SUTO 103 and SUTO 112. These inclusions consist of either one monocristalline solid (Plate 5.3d) or else as several closely-packed crystals of this same solid phase often together with a small amount of liquid (Plate 5.3e, f).

The solids (denoted by U in plate 5.3) are sometimes observed as elongate rectangular prisms with interference colours ranging from 1st order yellows to 2nd order blues. Measurements of the thickness of some of these crystals has enabled a birefringence of between 0.020 to 0.030 to be calculated. The refractive indices of the solid are considerably lower than the host apatite. Elongate crystals are length slow and exhibit straight extinction. Further studies on the nature of this solid phase were not made owing to its minute size and rare occurrence as uniform crystals. However, the similarity in optical properties and crystallographic habit between these solids and those observed in some inclusions in apatite from two samples of iolite (U79, U271) from the Wasaki area (section 1.7.4.) should be noted. In
view of this similarity it is quite possible that the unidentified solid phase here studied (U) is the same mineral as that observed in apatites from the Wasaki ijolites (U79, U271).

The presence of these crystalline solids as inclusions in apatites from SUTO 103 and SUTO 112 can be explained by one of two processes. They could merely represent a trapped solid phase similar to the calcite inclusions described above or else they could conceivably result from the trapping of a melt which subsequently crystallised in situ, within the apatite. The former explanation is favoured since instances have been recorded where normal aqueous inclusions appear to have captured a large crystal of this mineral phase (Plate 5.3e, f).

5.4. HEATING-STAGE STUDIES

5.4.1. The heating-stage and sample selection

A previously calibrated (Appendix A) Leitz 1350 microscope heating-stage was used throughout this study. All temperatures recorded in the text are believed to be accurate to within ±2°C. Whenever possible, the homogenisation temperature recorded was checked by duplicate runs on the same inclusion.

Extreme care had to be exercised in the selection of material suitable for heating studies. Inclusions which had obviously necked or leaked were discarded, and although it was often very difficult to find relatively large (> 20 μm) primary inclusions which had not been affected by these processes, a total of 200 reliable homogenisation temperatures were recorded (Fig. 5.1). A further 32 homogenisation runs had to be terminated either because leakage was seen to occur or
else the course of homogenisation could no longer be observed.

5.4.2. The course of homogenisation

195 of the 200 homogenisation temperatures recorded showed homogenisation to the liquid phase, and one inclusion from each of the five samples studied showed homogenisation to the gas phase.

In general, the daughter phases in all inclusions dissolved below the temperature of homogenisation of the gas and liquid phases. However, the black hexagonal platelets of pyrrhotite (SUTO 100, SUTO 112) proved very reluctant to dissolve, and although a distinct corrosion of the platelets was apparent after the inclusions had been held at elevated temperatures for up to 12 hours, complete solution of these daughter minerals was not achieved. Kelly and Turnearue (1970, p.663) and Bazarova (1965) have also noted the reluctance of similar opaque daughter minerals to dissolve in inclusion fluids even after long periods of heating. A possible explanation for this phenomenon is that equilibrium was not attained between this daughter mineral and the aqueous fluid during the short time (35-60mins) taken for most heating-runs.

Two inclusions, which contained a large, single, captive calcite crystal and a small amount of gas and liquid, were studied on the heating-stage. Homogenisation of the gas and liquid phase within these inclusions took place at 356°C and 395°C, but no noticeable solution of the calcite was observed. When these inclusions were heated past their gas/liquid homogenisation temperature a slight "solution" of the calcite was evident, but continued heating caused the inclusions to explode. Similar studies were also conducted on five aqueous
inclusions containing the captive mineral phase (U) described in the previous section (Plate 5.3e, f). Once again the gas and liquid part of the inclusion homogenised at temperatures between 335°C and 365°C with no noticeable solution of the captive mineral, but decrepitation occurred at temperatures a little above this homogenisation temperature.

Several normal aqueous inclusions were also heated past their homogenisation temperature in order to ascertain whether any phase changes similar to those described previously in inclusions in apatite from the Uyi sovite (U876), (section 3.4.3) could be observed. Decrepitation occurred at temperatures a little above the homogenisation temperature in all instances, with the exception of one inclusion (SU70 20) which did not decrepitate until 540°C, but no obvious phase changes could be seen.

5.5. DISCUSSION OF RESULTS

The results of 200 homogenisation determinations previously shown as histograms in Fig. 5.1 are presented in Table 5.6. The temperature range obtained for all samples studied is relatively large. Roedder (1967, p.558) believes that necking-down of inclusions accounts for a good part of the scatter so apparent in practically all careful thermometric studies. Although precautions were taken in this study to avoid the likelihood of studying necked inclusions it is conceivable, particularly in view of the extensive necking-down processes which have affected many inclusions, that the homogenisation temperatures for several necked inclusions may have also been inadvertently recorded.
Table 5.6  SUMMARY OF HOMOGENISATION TEMPERATURES RECORDED FOR AQUEOUS INCLUSIONS IN APATITES FROM THE TORORO CARBONATITES

<table>
<thead>
<tr>
<th>Sample Ref. Number</th>
<th>SUTO 20</th>
<th>SUTO 22</th>
<th>SUTO 26</th>
<th>SUTO 103</th>
<th>SUTO 112</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of determinations</td>
<td>47</td>
<td>36</td>
<td>34</td>
<td>46</td>
<td>37</td>
</tr>
<tr>
<td>Maximum Temperature (°C)</td>
<td>408*</td>
<td>466*</td>
<td>432*</td>
<td>436*</td>
<td>427*</td>
</tr>
<tr>
<td>Minimum Temperature (°C)</td>
<td>230</td>
<td>246</td>
<td>241</td>
<td>266</td>
<td>200</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>41.9</td>
<td>44.8</td>
<td>43.9</td>
<td>32.3</td>
<td>39.7</td>
</tr>
<tr>
<td>Mean Temperature (°C)</td>
<td>323</td>
<td>321</td>
<td>359</td>
<td>353</td>
<td>365</td>
</tr>
<tr>
<td>± Confidence limits of mean (at 95% level)</td>
<td>12.3</td>
<td>15.2</td>
<td>15.3</td>
<td>9.6</td>
<td>13.2</td>
</tr>
</tbody>
</table>

* Homogenisation was to gas phase in these five instances.
One single inclusion from each sample homogenised to the gas phase. This type of homogenisation, which is characteristic of many inclusions in apatite from the Uyi sovite (U876) previously studied (section 3.4.4.), cannot be considered typical for the inclusions studied here. It is thus concluded that such inclusions have necked, particularly since the homogenisation temperatures were, in all samples, the highest temperatures recorded.

Sawkins (1966) allows for the possibility of having determined the homogenisation temperature of necked-down inclusions by ignoring the top and bottom values of the homogenisation temperatures he recorded. Similarly, since necking-down has occurred in all samples studied here, a comparable 'polishing-up' of the data could be made. However, this procedure is inadvisable since the total number of necked inclusions studied (if any) is unknown and a great deal of subjectivity would be introduced if an arbitrary number of high and low values were discarded. The only recorded homogenisation temperatures considered with any degree of certainty to be due to necked inclusions are the five inclusions which homogenised to the gas phase.

The five samples studied can be divided into two groups; those from Limekiln Hill (SUTO 20, 22, 26) and those from Tororo Rock (SUTO 103, 112). In order to determine whether a significant difference exists between the homogenisation temperatures for samples within each of these two groups, student's t tests were applied to the data. The values obtained for t for the differences between the homogenisation temperature means of each sample from the two separate carbonatite masses (Limekiln Hill and Tororo Rock) are shown in Table 5.7. These results show that although there is no
<table>
<thead>
<tr>
<th>Locality</th>
<th>Number of Degrees of Freedom (N)</th>
<th>Value of t at 0.05 level for N degrees of Freedom</th>
<th>Whether a Significant Difference Exists</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tororo Rock</td>
<td>30</td>
<td>2.00</td>
<td>No</td>
</tr>
<tr>
<td>Suto 108 &amp; 102</td>
<td>91</td>
<td>2.00</td>
<td>No</td>
</tr>
<tr>
<td>Suto 20 &amp; 22</td>
<td>70</td>
<td>2.00</td>
<td>Yes</td>
</tr>
<tr>
<td>Suto 20 &amp; 26</td>
<td>63</td>
<td>2.00</td>
<td>Yes</td>
</tr>
<tr>
<td>Suto 22 &amp; 26</td>
<td>63</td>
<td>2.00</td>
<td>Yes</td>
</tr>
<tr>
<td>Limekiln Hill</td>
<td>30</td>
<td>2.00</td>
<td>Yes</td>
</tr>
</tbody>
</table>
significant difference between the two samples from Torero Rock, one sample from Limekiln Hill (SU TO 26) is significantly different, at the 0.05 level, from the other two (SU TO 20, SU TO 22). This shows that it is possible for small temperature differences to exist between samples from a single carbonatite mass. Unfortunately, it has not been possible to assess the extent to which these differences can occur since only five samples were available for study. To determine whether a significant difference exists between the homogenisation temperatures obtained for Limekiln Hill samples and Torero Rock samples, student's t test was again applied. However, it is necessary to weight each sample equally rather than each individual inclusion in the separate samples. Thus, the mean temperatures for each sample from the two carbonatite masses were used to determine the overall mean for these two separate masses of carbonatite, as shown in the table below.

<table>
<thead>
<tr>
<th>Carbonatite Mass</th>
<th>Number of Samples</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limekiln Hill</td>
<td>3 (328, 321, 359°C)</td>
<td>336°C ((\bar{X}_L))</td>
</tr>
<tr>
<td>Torero Rock</td>
<td>2 (353, 365°C)</td>
<td>359°C ((\bar{X}_T))</td>
</tr>
</tbody>
</table>

The value of t was found to be 1.46 and since \(t = 3.10\) for 3 degrees of freedom at the 0.05 level, there is no significant difference between the homogenisation temperatures obtained for Limekiln Hill apatites and Torero Rock apatites. However, since only five samples were available for study it is not really surprising that the difference (\(\bar{X}_L - \bar{X}_T\)) of 23°C is not significant.

These recorded homogenisation temperatures only allow a minimum
temperature of formation for the host apatites to be obtained. Significant temperature corrections need to be added to the homogenisation temperature in order to take into account the effect of external pressure upon the fluid during the crystallisation of the apatites. P.V.T. data on the compressibility of CO₂-rich, carbonate-bearing aqueous fluids are needed, together with an estimate of the pressure during crystallisation of the apatites, in order to calculate this temperature correction. Unfortunately, the pressure is unknown, and P.V.T. data on such fluids has not been determined. Nevertheless the "uncorrected" homogenisation temperatures still place some useful limits on the temperature at which carbonatitic minerals were formed.

5.6. SUMMARY AND CONCLUSIONS

The marked similarity of the primary aqueous inclusions studied here to those in apatites from the Wasaki carbonatites (section 1.6.2.) has been noted. The inclusions in apatite from the Tororo carbonatites, which consist of aqueous, CO₂-rich, carbonate-bearing (predominately nahcolite) solutions, represent trapped portions of the medium responsible for the deposition of the carbonatite apatites. Sutherland (1966) had previously recognised hydration as an important process associated with the emplacement of the Tororo carbonatites. The existence of aqueous fluid-filled cavities, within the apatites, leaves little doubt that such fluids have played an important part in the formation of these carbonatites.

Primary, rounded, monocryalline calcite inclusions are also common in apatite from all samples studied. Since they are co-genetic
with aqueous inclusions in many apatite crystals, calcite must have been present in the aqueous fluid at the time the apatites crystallised.

Despite the great extent to which most inclusions have been subjected to necking-down processes and to subsequent infilling by late-stage, calcite and ferruginous material, homogenisation temperature determinations on numerous, seemingly unaffected primary aqueous inclusions, selected from the thousands studied, have been made. Five of these inclusions showed homogenisation to the gas phase, but in view of the rare occurrence of this type of homogenisation and the anomalously high temperature at which it occurs, such inclusions are believed to have necked, and no convincing evidence exists to suppose that those inclusions were trapped as supercritical fluids (section 3.6.1.) or that boiling conditions (Roedder, 1973) had prevailed during crystallisation.

The homogenisation temperature range obtained for inclusions in apatite from Limekiln Hill samples (SUTO 20, 22, and 26) was 230-466°C and the range for the Tororo Rock samples (SUTO 108 and 112) was 200-436°C. These temperatures represent the minimum temperature of formation of the apatites. Student's t tests on the five separate sample means (Table 5.7) have shown that there is no significant difference between homogenisation temperatures recorded for inclusions from Tororo Rock apatites and those from Limekiln Hill. However, small differences may exist between different samples from the same carbonatite mass, as shown by student's t tests on SUTO 26 and SUTO 20 and 22.

The aqueous inclusions in apatite from Tororo Rock (SUTO 112,
SUTO 103) contained additional daughter minerals (pyrrhotite, acicular needles and an anisotropic, water-soluble, yellow to colourless solid) not observed in those from Limekiln Hill (SUTO 20, SUTO 22, SUTO 26). A further group of inclusions, which are considered to be the result of trapping of solid crystalline material, have also been recognised in apatites from Tororo Rock (SUTO 112, SUTO 108). These slight differences between the inclusions seem to indicate that, although the temperature conditions of formation of the two separate masses were similar, the composition of the fluid responsible for the formation of carbonatites from Tororo Rock differed slightly from that which formed the carbonatites at Limekiln Hill.

Further work on the nature of the daughter phases present would seem desirable in the hope that their identification may prove fruitful in elucidating the reasons for the mineralogical differences (Sutherland, 1966) which exist between the carbonatites of Limekiln Hill and those of Tororo Rock.
Plate 5.1  Aqueous inclusions in apatites from Tororo carbonatites.

(a) Elongate apatite crystal (ap) containing large, centrally located, tubular inclusion. Partial necking-down of this inclusion has taken place. Oil immersion (n = 1.56). Bar = 50 µ.

(b) Large, spheroidal inclusion containing a nahcolite daughter mineral (Nh). Note the absence of any other inclusion. Solitary inclusions such as these are particularly useful for thermometric studies since necking-down processes could not possibly have taken place. Oil immersion (n = 1.64). Bar = 50 µ.

(c) Rounded, aqueous inclusion containing a large vapour bubble. The photomicrograph is focused on the bottom of the inclusion. The top is out of focus. Bar = 20 µ.

(d) As (c) above but focused on the top of the inclusion. An hexagonal platelet of pyrrhotite (arrowed) is seen inside the inclusion attached to its sides. Bar = 20 µ.

(e) Tubular inclusion aligned parallel to the c-axis of the apatite host. A small nahcolite daughter mineral (arrowed) is visible within the inclusion. Bar = 20 µ.

(f) Inclusion containing an aqueous solution (aq), a vapour bubble (v) and a nahcolite daughter mineral (Nh). Bar = 20 µ.

(g) Inclusion containing an anisotropic pale yellow daughter mineral (y) and several anisotropic acicular daughters (d) (arrowed) showing curved habit. Bar = 20 µ.

(h) Regular-shaped inclusion containing a pale yellow daughter mineral (y). Nahcolite is also present within the inclusion (arrowed) but because it is viewed in its approximate α - vibration direction it is almost invisible. Bar = 20 µ.

(a), (b), (g), (h) are from SUTO 108
(c), (d), (e) are from SUTO 112
(f) is from SUTO 20
Plate 5.2
Leakage and necking-down of aqueous inclusions in apatite from the Tororo carbonatites

(a) Apatite crystal in immersion oil (n = 1.63) showing innumerable fractures and planes of secondary inclusion which are roughly parallel to the basal cleavage of the apatite. Bar = 50 μ.

(b) Thin section of the bulk rock sample (SUTO 20) showing apatite (ap) in calcite (calc). A small ferruginous veinlet (fer) traverses the calcite and the apatite crystals. The ferruginous material also coats the surface of the apatite crystal. A small inclusion (arrowed) has been infilled by this material. Bar = 100 μ.

(c) Apatite crystal (Ap) in immersion oil (n = 1.60). The apparent gas-filled inclusion has resulted from leakage of the original aqueous inclusion via the fracture (arrowed) which leads to the surface of the crystal. Bar = 20 μ.

(d) and (e) Necking-down of primary aqueous inclusions. Bar = 20 μ.

(f) Rounded, aqueous inclusion showing small tail protruding from the inclusion. Such tails are indicative of inclusions which have necked. Bar = 20 μ.

(a) is from SUTO 26
(b), (c), (e), (f) are from SUTO 20
(d) is from SUTO 22
Plate 5.3 Other primary inclusions in apatites from the Tororo carbonatites

(a) and (b) Co-genetic aqueous inclusion (aq) and spheroidal, monocrystalline inclusion of calcite (calc). Bar = 20 μm.

(c) Elongate inclusion of calcite (calc) in apatite (Ap). The dark patches in the inclusion probably result from partial digestion of the calcite by acetic acid during sample preparation. Bar = 50 μm.

(d) Monocrystalline inclusion of an unidentified solid (U), as discussed in section 5.3. Bar = 20 μm.

(e) and (f) Complex inclusion containing crystals of the unidentified solid (U). These inclusions result from the simultaneous entrapment of an aqueous fluid together with the crystalline solid. Bar = 20 μm.

(a), (b), (c), (d), (f) are from SUTO 108
(e) is from SUTO 112
CHAPTER 6

A THERMOMETRIC STUDY OF AQUEOUS INCLUSIONS IN APATITE
FROM CARBONATITE AND IJOLITE OF HOMA MOUNTAIN, W. KENYA

6.1 INTRODUCTION

The Homa peninsula of western Kenya is dominated by Homa mountain which marked the site of an active volcano during Tertiary and Pleistocene times. Subsequent erosion has exposed a multi-centered complex of nepheline syenite, carbonatites, ijolites and related rocks, (Heinrich, 1966, p.484). Saggerson (1952) has described the area and gives an account of the sequence of events which have taken place during the history of this complex (see also Heinrich, 1966, p.485), while the geology and petrology of the southern (Clarke, 1968) and the northern parts (Flegg, 1969) have recently been studied in more detail.

Apatite is present as an accessory mineral in both the carbonatitic and ijolitic rocks from this area, and occasional fluid-filled cavities have been observed in some of these apatites. Heating studies on these aqueous inclusions together with studies on the composition of the fluids (as determined from daughter phases present) have been made and the origin and environment of crystallisation of the apatites discussed.

The heating studies were performed on primary aqueous inclusions within single apatite grains extracted from the bulk rock sample by magnetic and heavy liquid separation. All temperatures reported in the text were recorded on a previously calibrated Leitz 1350 microscope heating-stage (Appendix A) using heating-rates of between 5 and 10°C/min.
6.2 INCLUSIONS IN Apatite FROM CARBONATITE

The apatites in the carbonatites from Homa mountain are noticeably devoid of inclusions, and suitable material available for study is limited to a sample of apatite-sovite (HC249) collected by M.C.G. Clarke in 1964. The cavities are universally small and rarely exceed 50 μ in size. Their shape is generally irregular, sometimes spheroidal and only very rarely tubular negative crystal shaped. The inclusions are so abundant that literally hundreds of small cavities, less than 10 μ in size, occur within a single apatite crystal (Plate 6.1a). It has been calculated that up to 10% of the volume of the apatite crystal may be occupied by these cavities.

In spite of this great abundance of inclusions, necking-down processes (see section 1.1.4.) have been operative to such a large extent that it has proved virtually impossible to locate large, isolated, unaffected primary inclusions. As a result of this extensive necking-down, the following inclusion-types, containing widely varying amounts of gas, liquid and precipitated daughter minerals, have been produced (Plate 6.1b, c):

(1) Simple gas/liquid inclusions in which the ratio of gas to liquid is highly variable and ranges from 0:1 to 1:0.

(2) Aqueous inclusions containing variable amounts of precipitated daughter minerals but devoid of a gas bubble.

(3) Inclusions containing gas, liquid and daughter minerals in which the amount of each phase present is highly variable.

The following phases have been recognised in these necked-down inclusions:
(a) **Nahcolite**

This is by far the most commonly encountered daughter phase. It has been identified on the basis of its high order interference colours and its very low $\alpha$ refractive index, so that when the crystal is viewed in its approximate $\alpha$ - vibration direction, a perfect match in refractive index between the daughter phase and the aqueous fluid within the inclusion is obtained. On one occasion a twinned crystal of this same daughter phase was observed in which both halves of the twin went into extinction simultaneously. This type of twinning is typical of both synthetic and naturally occurring crystals of nahcolite (Chapter 2).

(b) **Halite**

Small, isotropic, colourless cubes are sometimes present in the inclusions. The relief of these cubic daughter minerals relative to the inclusion fluid is high, and heating studies have shown that this phase is rather sluggish to dissolve in the inclusion fluid at high temperatures. Halite is a widely reported daughter mineral in aqueous inclusions in minerals from a wide variety of geological environments. Its high relief and reluctance to dissolve in the inclusion fluid are often reported as criteria upon which the identification of this daughter is based (Sillitoe and Sawkins, 1971; Kelly and Turneaure, 1970), and it is similarly concluded that the isotropic cube recorded in this study is halite, although confirmatory tests (e.g. refractive index measurements) have not been possible.

(c) **Small magnetic opaque speck**

Small (never exceeding 1-2 $\mu$ in size), black, opaque specks,
which exhibit marked magnetic properties are discernible in many of
the necked inclusions. Hexagonal platelets, so typical of other
magnetic, opaque, daughter minerals in apatite from carbonatites of
other East African complexes and previously identified as pyrrhotite
(see sections 1.6.3 and 5.2.2.) have not been observed. Instead,
the specks are ill-defined, and without any crystallographic form, and
although pyrrhotite cannot be ruled out as a possibility, it is
inferred that this phase is magnetite.

(d) **Liquified carbon dioxide**

A careful study at very high magnification, (x 1000) using
intense illumination and infra-red heat filters, of the 'gas' bubble
in many inclusions often reveals that the bubble is composed of liquid
plus gas, so that such inclusions actually contain three fluid phases
(Plate 6.1d). Mild heating studies reveal that this second liquid
phase and its associated gas bubble homogenise rapidly to a single
fluid phase always below about 31°C. Crushing-stage studies
(Roedder, 1970) have further shown that a large expansion of the
gas bubble is observed when such inclusions are opened in oil.
On the basis of these two observations this second liquid phase has
been positively identified as highly-compressed, liquified CO₂
(Plate 6.1d).

(e) **Other phases observed**

Significant amounts of other precipitated daughter phases are
absent in nearly all inclusions studied, but traces of small, highly
birefringent solids (carbonatos?) may occur in some of the larger
inclusions.
It is noteworthy that many of the larger inclusions contain all of the phases described above, and since it is probable that such large inclusions approximate more closely to the composition of the original "un-necked" inclusion than the smaller ones, it is concluded that the fluid was originally trapped as a CO$_2^-$, H$_2$O-rich fluid containing large amounts of dissolved sodium bicarbonate (nahcolite) and sodium chloride (halite), together with minor amounts of ore metals.

Apart from the extensive necking down processes which have occurred, a large number of microfractures are seen within the apatites, and numerous inclusions now composed of a low pressure (as determined from crushing-stage studies) gas are located along these cracks. These gas-filled inclusions undoubtedly represent original aqueous inclusions whose contents have leaked.

Inclusion-types other than those which can be ascribed to necking-down or leakage of aqueous inclusions are notably absent. Solid rounded calcite inclusions, commonly observed in apatites from the carbonatites of other complexes (see sections 1.6.6. and 5.3), have not been observed in the apatites from the sovite studied here.

### 6.3. INCLUSIONS IN APATITE FROM IJOLITES

#### 6.3.1. General remarks

Apatite containing abundant inclusions has been noted in two separate ijolite samples (HC176, HC934) collected by M.C.G. Clarke during visits to the Homa complex during the period 1961-1967.

Primary aqueous inclusions account for over 90% of all inclusion-types present in these apatites. They occur either as
elongate, tubular cavities, which are aligned parallel to the c-axis of the apatite crystal, or as equant, regular cavities whose shape approximates to a negative crystal (Plates 6.2 and 6.3). Spheroidal and irregular inclusions are rarely observed.

Equant cavities seldom exceed about 75 µ in size, but the tubular cavities may extend up to 150 µ in length, although their breadth never exceeds about 20 µ. The length to breadth ratio of these tubular cavities may be as high as 50:1, particularly in apatites from HG176, but such inclusions are usually too thin for any useful observations. Smaller inclusions less than 5 µ in size are uncommon.

Occasionally, a single apatite crystal may contain only one, large, central tubular cavity (Plate 6.3a, c). Such inclusions are obviously primary and have proved particularly useful for study since, in these instances, necking-down could not possibly have taken place. However, there is ample evidence, as shown by the widely varying phase ratios (ratio of liquid to gas to daughter minerals) observed in closely-spaced groups of inclusions in the same crystal, and by the presence of small tails attached to some inclusions (Plate 6.4a), that necking-down processes have taken place to some extent. Nevertheless, it is always possible to find large, isolated inclusions that have remained unaffected by these processes, and only these inclusions have been studied in detail.

Leakage from the aqueous inclusions has sometimes taken place, but when it has occurred it is not difficult to recognise. Inclusions whose contents have leaked completely may be mistaken for primary gas-filled inclusions, but crushing-stage studies have shown that the
contents are held at approximately atmospheric pressure which is indicative of leaked inclusions whose contents have been replaced by air (Roedder, 1970). Furthermore, many of those apparent gaseous inclusions are associated with microfractures along which the original aqueous fluid has evidently leaked.

The primary aqueous inclusions contain a vapour bubble which occupies between 10 and 20% of the total volume of the inclusions from HC476, and between 10 and 15% in those from HC934. Crushing-stage studies have shown that this vapour bubble contracts markedly in volume when the inclusions are opened in oil, indicating that the 'gas' bubbles are actually partial vacuums held at pressures substantially lower than atmospheric pressure. Only one inclusion in apatite from HC476 showed a small rim of condensed CO₂-liquid around the vapour phase. However, despite an extensive search to find similar inclusions, and innumerable crushing-stage studies on scores of inclusions, no evidence has been found to suggest that CO₂ is present in significant amounts within the inclusions. It is thus concluded that this unique, atypical, CO₂-liquid-bearing inclusion resulted from the fortuitous trapping of aqueous fluid together with a small immiscible globule of compressed CO₂. Similar inclusions formed in this manner have been reported by Kelly and Turneaure (1970) in minerals associated with Bolivian tin deposits.

An aqueous solution occupies most of the volume of the cavities, and several daughter minerals are usually present within this fluid. In large, tubular inclusions (Plates 6.2 and 6.3) many of the daughter minerals are sufficiently large in size to enable some positive identifications to be made.
6.3.2. Daughter phases present in inclusions in apatite from HC934

The inclusions in apatite from HC934 usually contain a large, isotropic, cubic daughter mineral (Plate 6.2a, b, c, d) which dissolves rapidly in the inclusion fluid when heating-stage studies are conducted on the inclusions. Normally, when attempts are made to extract daughter minerals from inclusions for optical and chemical tests, the host apatite crystals are crushed too violently and the daughter minerals are lost in the crushed debris (Chapter 2). However, on one occasion a large, tubular cavity in apatite from HC934 was gently opened and the cubic daughter mineral remained attached to the wall of the inclusion, but protruding slightly into the immersion oil. Since the crushing was performed in an oil with a refractive index of 1.540, and that of the cube was substantially lower than the oil, this phase could not possibly be halite (n = 1.544). When the apatite grain and its opened inclusion containing the cubic daughter were transferred to an oil of refractive index 1.490, a near perfect match between the refractive indices of the oil and the cube was obtained (the cube showed an exceedingly weak Becke line which was split into its component colours). Consequently this phase has been identified as sylvite (KCl, n = 1.490).

A second smaller, isotropic cube, showing a much higher relief relative to the inclusion fluid than sylvite, and which dissolves sluggishly in this fluid during heating-runs, is sometimes present. This smaller cube is, in all probability, halite (NaCl).

Many inclusions may also contain a further daughter phase which exhibits properties identical to those of nahcolite (Chapter 2);
that is, extremely high order interference colours, rapid solution response to heating, and a perfect match in refractive index between the inclusion fluid and the crystal in its approximate $\alpha$ vibration direction (Plate 6.2c and d). Well-formed crystals of this phase have not been observed and although its properties are characteristic of nahcolite (NaHCO$_3$), it is quite feasible to suppose that it is kalicinite (KHO$_3$), particularly in view of the substantial amounts of potassium, as indicated by the large sylvite daughters present, within the inclusion. However, the distinction between nahcolite and kalicinite is extremely difficult (Chapter 2) unless the crystallography can be determined with reasonable accuracy.

A black, opaque, non-magnetic speck is also present in many inclusions, and is sometimes associated with another non-magnetic, black, opaque phase which displays a hairlike habit (Plate 6.2b, c). A positive identification of these two daughters, which may actually be different habits of one and the same phase, could not be made.

Minor amounts of several other anisotropic and isotropic daughter minerals may occur within the inclusions from this sample (HC934) but their minuteness precludes even the simplest of optical tests.

6.3.3. Daughter phases present in inclusions in apatite from HC476

Many of the daughter minerals in inclusions in apatites from HC476 (Plate 6.3b, d) display properties similar to those described above (HC934). A large, isotropic cube, which dissolves rapidly in the inclusion fluid at high temperatures and which shows a low
positive relief relative to this fluid, is present in 74% of all inclusions studied. A smaller, isotropic cube possessing a higher relief and showing a greater reluctance to dissolve in the inclusion fluid at elevated temperatures than the larger cube is sometimes present. These two phases have been identified as sylvite and halite respectively. A bicarbonate phase (nahcolite or kalicinite) and an unidentifiable black, non-magnetic, anhedral speck are also common within the inclusions.

A further daughter phase, in many inclusions from this sample (HCl76), but never observed in inclusions from HC934, has been recognised. It usually consists of a rounded, anisotropic solid exhibiting moderate relief. In some of the larger inclusions it possesses a prismatic habit (Plate 6.3b, d). These somewhat elongate prisms are length fast, have a moderate birefringence (1st order colours) and show a large extinction angle of 32°. During heating-runs these daughters dissolved with such rapidity in the inclusion fluid that complete solution took place often only 30°C above room temperature (R.T. = 23°C). A positive identification could not be made, although a tentative proposition that this phase is a complex alkali chloro-carbonate would seem likely in view of the chemistry of these fluids.

Minor amounts of other daughter phases can be seen in many of the inclusions; some show very high order interference colours suggestive of carbonates. All of the daughter phases, which have been observed in apatite from this sample of ijolite (HCl76), are extremely well represented in the tubular inclusions shown in Plate 6.3b and d.
The frequency of occurrence of the phases described above and in section 6.3.3. for both ijolite samples (HC476, HG934) are shown in Table 6.1. The abbreviations used in this table (e.g. Sy, h, B) refer to the abbreviations used in Plates 6.2 and 6.3.

6.3.4. Other inclusion-types present in the apatites from HC476 and HG934

Very occasionally a normal aqueous inclusion may be seen attached to a large crystal of a foreign mineral. This type of inclusion results from the simultaneous trapping of aqueous fluid together with crystalline solid (Roedder, 1967, p.520). Sometimes the foreign mineral is calcite (Plate 6.4b), but more often it consists of one or more crystals of another unidentified mineral phase (Plate 6.4c and d). Elongate crystals of this mineral are often observed; these are length fast and have straight extinction. Birefringence estimates give a value of 0.030 ± 0.005, but attempts to extract this phase for more detailed study were unsuccessful. It is interesting to note the marked similarity between this solid (UK in Plate 6.4c, d) and those (U in Plate 5.3d, e, f) observed attached to aqueous inclusions from apatites of the Tororo carbonatites (section 5.3), and it is quite possible that they are one and the same phase.

Solid inclusions of this unidentified mineral and of calcite have been seen very occasionally in the apatites from HC476. In these instances no associated aqueous phase is present and such inclusions simply represent trapped solid crystalline material.

Inclusions other than those which result from necking-down or leakage of original, primary, aqueous inclusions are notably absent, and the overwhelming predominance of aqueous saline types in apatites from
### Table 6.1
**Daughter Minerals Present in the Aqueous Inclusions in Apatite from Two Separate Ijolites (HC 476, HC 934) from Homa Mountain**

<table>
<thead>
<tr>
<th>Daughter Mineral</th>
<th>Percentage of Inclusions Containing Daughter Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HC 934</td>
</tr>
<tr>
<td>(1) Isotropic, colourless cube, low relief, rapidly dissolves in the inclusion fluid at high temperatures (Sylvite, Sy).</td>
<td>90</td>
</tr>
<tr>
<td>(2) Isotropic, colourless cube, high relief, sluggish to dissolve in inclusion fluid at high temperatures (Halite, h).</td>
<td>15</td>
</tr>
<tr>
<td>(3) Highly birefringent, water-soluble solids (Alkali Bicarbonates, B).</td>
<td>11</td>
</tr>
<tr>
<td>(4) Small, black, non-magnetic, opaque mineral without any distinct crystallographic form (Not Identified, O).</td>
<td>60</td>
</tr>
<tr>
<td>(5) Black, opaque, non-magnetic mineral showing hairlike habit (Not Identified).</td>
<td>27</td>
</tr>
<tr>
<td>(6) Rounded, moderately birefringent, water-soluble mineral. Sometimes seen as elongate prisms, extinction angle of 32°, length fast (Alkali-Chloro-Carbonate?, X)</td>
<td>0</td>
</tr>
<tr>
<td>(7) Other specks of isotropic and anisotropic solids (Not Identified, Z)</td>
<td>48</td>
</tr>
</tbody>
</table>

Percentage of inclusions without any daughter minerals

<table>
<thead>
<tr>
<th>Percentage of inclusions without any daughter minerals</th>
<th>HC 934</th>
<th>HC 476</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
<td>8</td>
</tr>
</tbody>
</table>
the ijolites here studied is in marked contrast to the large number of multisolids melt inclusions present in the apatites from the Wasaki ijolites (see section 1.7).

6.4. **HEATING-STAGE STUDIES ON THE AQUEOUS INCLUSIONS**

6.4.1. **The apatite-sclvite (HC249)**

As a result of extensive necking-down processes, the inclusions from this sample (HC249) are generally unsuitable for detailed heating-stage studies. Preliminary studies on small (<20 μ) inclusions, which showed evidence of having necked-down their history, usually resulted in leakage or decrepitation before homogenisation could be obtained. Further studies were conducted on larger inclusions since it is probable that such inclusions have not undergone necking-down to the same extent as the smaller ones. If this assumption is correct, and if a sufficient number of these larger inclusions are studied, the mean temperature obtained would be a fair approximation of the minimum formation temperature of the host apatite, even though the actual temperature range obtained would be unrealistic. Unfortunately only 16 homogenisation temperatures could be recorded (Table 6.2). Homogenisation occurred to the liquid phase on every occasion. Solution of nahcolite and halite occurred at temperatures below the homogenisation temperature, although the black, opaque, magnetic (?) speck failed to dissolve completely even after prolonged heating.

6.4.2. **The ijolites (HC476, HC934)**

The inclusions in apatite from these two samples of ijolite were particularly suitable for heating-stage studies. Large,
Table 6.2 THE HOMOGENISATION TEMPERATURES RECORDED FOR 16 LARGE AQUEOUS INCLUSIONS IN APATITE FROM A SAMPLE OF APATITE SOVITE (HC 249)

<table>
<thead>
<tr>
<th>Homogenisation Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
</tr>
<tr>
<td>362</td>
</tr>
<tr>
<td>349</td>
</tr>
<tr>
<td>346</td>
</tr>
<tr>
<td>334</td>
</tr>
<tr>
<td>332</td>
</tr>
<tr>
<td>325</td>
</tr>
<tr>
<td>295</td>
</tr>
<tr>
<td>287</td>
</tr>
<tr>
<td>273</td>
</tr>
<tr>
<td>263</td>
</tr>
<tr>
<td>260</td>
</tr>
<tr>
<td>255</td>
</tr>
<tr>
<td>254</td>
</tr>
<tr>
<td>189</td>
</tr>
</tbody>
</table>

Mean = 299°C
Standard deviation = 49.7°C
Confidence limits at 95% level = 26.4°C
tubular inclusions, centrally located in the core of the apatite crystal, are undoubtedly primary in origin (Plate 6.3a, c). Necking-down could easily be recognised in these two samples, and only those inclusions which had obviously remained unaffected by the necking-down processes were selected for study.

Duplicate homogenisation temperature determinations were performed whenever possible. Some inclusions obviously leaked during the course of their homogenisation, and the results obtained from these leaked specimens were discarded. Decrepitation seldom occurred during homogenisation runs unless the inclusions were heated past their homogenisation temperature ($T_h$) in which case violent decrepitation took place at temperatures above $T_h$.

Homogenisation, in all instances occurred to the liquid phase. All daughter minerals, except the black, opaque specks, dissolved completely at temperatures well below the final homogenisation temperature ($T_h$). When some of the inclusions were held at high temperatures (between about 200 and 300°C) for periods up to 12 hours, the black, opaque mineral showing the hairlike habit dissolved, but the black speck failed to do so.

It is interesting to note that during homogenisation runs, when the vapour bubble moves freely within the inclusion fluid, the black speck may attach itself to the vapour bubble. When this happened the bubble and its attendant black speck spun around rapidly within aqueous fluid because of the small convection currents which are set up in the inclusion fluid during heating-runs. Rogers (1973, person. comm.) has also noted this behaviour in gas/liquid inclusions containing a small black ore mineral, in hydrothermal fluorite
deposits from the North Pennine orefield, but similar accounts of this phenomenon are absent in the literature.

A total of 79 homogenisation temperature determinations for inclusions in 48 different apatite crystals were recorded. Histograms of these results are shown in Fig. 6.1. and a statistical treatment of the data is presented in Table 6.3.

6.5. DISCUSSION OF RESULTS

6.5.1. Environment of crystallisation of the carbonatite apatites

Extensive necking-down processes have, unfortunately, masked much of the information discernible from the abundant primary inclusions present in the apatites. A study of numerous necked inclusions reveals that the environment of crystallisation of the apatites consisted of a CO₂-rich, aqueous fluid containing dissolved alkali bicarbonates (nahcolite) and halides (halite), together with small amounts of iron-bearing ore minerals (magnetite?). Whether this fluid was trapped as a single homogeneous fluid or as a heterogeneous fluid consisting of a CO₂-rich gas phase in equilibrium with an aqueous saline solution as envisaged for apatites from the Amba Dongar carbonatite (Roedder, 1973), could not be ascertained.

Since heating studies were performed on inclusions which had quite probably necked, only the mean temperature of 299°C (+ 26.4°C at the 95% confidence level) is considered to be a fair estimate of the minimum temperature of formation of the apatites.
### Table 6.3
SUMMARY OF HOMOGENISATION TEMPERATURE DATA
OBTAINED FROM PRIMARY AQUEOUS INCLUSIONS IN
APATITE FROM TWO IJOLITES (HC 476, HC 934)
FROM HOMA MOUNTAIN

<table>
<thead>
<tr>
<th>Sample Ref. Number</th>
<th>HC 476</th>
<th>HC 934</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Temperatures Obtained</td>
<td>49</td>
<td>30</td>
</tr>
<tr>
<td>Maximum Temperature (°C)</td>
<td>458</td>
<td>352</td>
</tr>
<tr>
<td>Minimum Temperature (°C)</td>
<td>232</td>
<td>250</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>53.9</td>
<td>27.6</td>
</tr>
<tr>
<td>Mean Temperature (°C)</td>
<td>357</td>
<td>321</td>
</tr>
<tr>
<td>Confidence Limits of Mean at 95% Interval</td>
<td>15.4</td>
<td>10.2</td>
</tr>
</tbody>
</table>
6.5.2. Environment of crystallisation of the ijolite apatites

The fact that the primary inclusions in all ijolite apatite crystals studied here consist exclusively of aqueous saline types must mean that the environment of crystallisation of these apatites consisted, in the main, of an aqueous saline solution. However, it might be argued that these inclusions simply result from the trapping of globules of aqueous fluid, present in a melt, which preferentially adhered to the growing surface of the apatite crystals (Roedder, 1967, p.521; Roedder and Coombs, 1967). Such a mechanism is unrealistic for the inclusions studied here since the presence of large, tubular cavities, which reduce the apatite host to a mere shell surrounding the captured liquid, could only be formed if the apatite actually grew from the aqueous fluid. If the apatites had formed from a melt then the central, tubular cavities present in many of the apatites would be filled by quench melt material, as shown by Wyllie, Cox and Biggar (1962) from their study of the habit of synthetic and naturally occurring apatites. Such inclusions, although common in the Wasaki ijolite apatites (Chapter 1), have not been observed in the Homa ijolite apatites.

On the basis of field, petrographic and chemical data, Clarke (1968) concludes that the Homa ijolites were intruded as a magma accompanied and followed by a very powerful volatile/metamorphic event which caused replacements to occur in the later minal phases of the ijolite. Clarke (1968) further believes that the apatite in these ijolites are mainly due to this late-stage, volatile-rich fraction.

The study of inclusions within the apatites confirms that they were indeed formed from a volatile-rich aqueous medium. The
presence of large amounts of alkali halides (halite and sylvite) and alkali bicarbonates (nahcolite and kalicinite) as daughter minerals within the inclusions, reveals that this medium consisted of a highly concentrated saline fluid. Other material (represented by the unidentified daughter minerals also present within the inclusions as depicted in Table 6.1) could also be carried in this fluid. CO$_2$, which has only been observed in one instance within an inclusion, was presumably present in this fluid as an immiscible fraction at the time the apatites crystallised. However, the general lack of significant amounts of CO$_2$ within most of the aqueous inclusions indicates that the crystallising fluid was CO$_2$-poor.

The homogenisation temperature data recorded for the primary aqueous inclusions (Table 6.3) are uncorrected for the effects of pressure (see Chapter 3, section 3.7.1.), and only allow a minimum temperature of formation to be deduced for the apatites. The mean homogenisation temperature obtained for the two separate ijolite samples show a difference of 36°C (HC476, mean = 357°C; HC934, mean = 321°C). In order to ascertain whether this difference is significant, student's t test was applied to the data. T was found to be 3.4, and since the value for t for 77 degrees of freedom at the 0.05 level is 2.00, a significant difference does exist between these two means. In fact this difference is highly significant, even at the 0.01 level, and the likelihood of it occurring by chance is less than one in one hundred.

The temperature range recorded (Fig. 6.1) cannot be attributed to necked-down inclusions, and it must, therefore, reflect the varying temperature of formation of the host apatites.
Even though necking-down processes have taken place to a very large extent, the study of inclusions in apatite from the apatite-sovite (HC249) has shown that the apatites have crystallised from a CO₂-rich aqueous solution which carried large amounts of alkalis and ore metals. An estimate of the mean minimum temperature of formation (299°C) of the apatites has been obtained.

The apatites from the Homa ijolites, which contain numerous aqueous inclusions (HC476 and HC934), have crystallised from a highly saline, CO₂-poor aqueous solution. This is in contrast to the apatites from the Wasaki ijolites which have crystallised from a silico-carbonate rich melt (Chapter 1). The presence of large amounts of sylvite (KCl) and smaller amounts of halite (NaCl) as daughter minerals in the aqueous inclusions from HC476 and HC934, indicates that this fluid was rich in potassium and relatively poor in sodium. The actual Na⁺:K⁺ weight ratio within the inclusions in apatite from HC476 has been determined by a flame photometric method (Chapter 7), and a value of 1.3:1 (Na⁺:K⁺) obtained for these aqueous fluids.

Although the inclusions are poor in free CO₂, they do contain substantial amounts of bicarbonate daughter minerals, which shows that these aqueous fluids are capable of transporting carbonate material. Furthermore, the existence of co-genetic aqueous inclusions and solid calcite inclusions within the apatites indicates that calcite has also crystallised in the presence of this aqueous saline fluid.

Homogenisation temperature determinations on these aqueous inclusions give a value for the minimum formation temperature of the
apartites. The range of temperatures obtained are as follows:

\[\text{H0476: } 232 - 458^\circ C\]
\[\text{H0934: } 250 - 352^\circ C\]

A significant difference was found to exist between these two sets of data.

To summarise, it is concluded that the apatites (and probably the calcite) within the ijolites have crystallised from an aqueous saline fluid at moderately high temperatures. These conclusions are in full agreement with Clarke's suggestion (Clarke, 1963) that the apatites may have crystallised from a late-stage aqueous fluid.
Plate 6.1 Inclusions in apatite from carbonatite (HC2h9), Hema mountain.

(a) Apatite crystal (Ap) containing numerous, irregular, primary inclusions. Oil immersion (n = 1.63). Bar = 20 μ.

(b) Three inclusions resulting from the necking-down of an originally larger inclusion. Inclusion 1 contains only gas plus liquid, inclusion 2 contains liquid plus daughter minerals, inclusion 3 contains only gas. Bar = 10 μ.

(c) Regular inclusion (arrowed) containing liquid, vapour, and daughter minerals. Bar = 10 μ.

(d) Three-phase inclusion in apatite (Ap) containing CO₂-vapour (V), CO₂-liquid (L) and an aqueous solution (Aq). Bar = 20 μ.
Plate 6.2 Primary aqueous inclusions in apatite from ijolite (HC 934) from Homa mountain.

(a) Regular inclusion containing vapour (V), aqueous solution (Aq), sylvite (SY) and an alkali bicarbonate phase (B). The bicarbonate daughter shows a near-perfect match in refractive index with the aqueous fluid. Bar = 20 μm.

(b) Two negative crystal shaped inclusions containing a large rectangular-shaped sylvite daughter mineral (SY). A black sword-shaped daughter phase is discernible in the more equant inclusion. Bar = 20 μm.

(c) Tubular inclusion aligned parallel to the c-axis of the apatite host crystal. Sylvite (SY) and an alkali bicarbonate daughter mineral (B) are present in the inclusion. A larger inclusion (out of focus) can be seen in the top left hand corner of the photomicrograph. Bar = 20 μm.

(d) As (c) above but with polariser rotated through 90°. The 'disappearance' of the bicarbonate daughter mineral occurs because it is being viewed in its approximate α-vibration direction. Bar = 20 μm.
Plate 6.3 Primary aqueous inclusions in apatite from ijolite (HC 476) from Home mountain.

(a) Apatite (Ap) containing large, tubular cavities aligned parallel to the c-axis of the apatite. Oil immersion (n = 1.54). Bar = 50 \mu m.

(b) Close-up of the left hand side of the larger tubular inclusion shown in (a) above. The daughter minerals present are: syltive (Sf), bicarbonate (B), a mildly birefringent solid (X) which is described as mineral number 6 in Table 6.1, a small, irregular, non-magnetic opaque speck (O) and a highly birefringent solid (Z) which shows a marked insolubility in the inclusion fluid at high temperatures (possibly a carbonate). Bar = 20 \mu m.

(c) Single tubular inclusion in apatite. Oil immersion (n = 1.53). Bar = 100 \mu m.

(d) Close-up of (c) above. The daughter minerals b, z, Sf and X are as described above in 6.3b. A small cube of halite (h) is also present. Also note the prismatic habit of (X). Bar = 20 \mu m.
plate 6·3
Plate 6.1  Inclusions in apatite from ijolite (HC 476) from Homa mountain.

(a) Small aqueous inclusion which has necked-down. Note the small "tail" protruding from the inclusion (arrowed). Bar = 10 \mu m.

(b) Aqueous inclusion containing a vapour bubble and some daughter minerals; a well-defined cube (c) of halite (?) is shown. The inclusion is attached to a large irregular crystal of calcite (CAL). Bar = 20 \mu m.

(c) Unusual complex inclusion containing an unidentified trapped mineral phase (UK) which has been caught-up in the inclusion fluid during the growth of the apatite crystal. The aqueous solution (Aq) is contained in both the larger portion of the inclusion and in the tubular tail which extends to a length of about 50 \mu m. The vapour bubble (V), partly shown in the photomicrograph, is entirely located in the "tail". Bar = 20 \mu m.

(d) Aqueous inclusion containing two captured mineral phases (UK). Bar = 20 \mu m.
FIG 6.1 HOMOGENISATION TEMPERATURES OF AQUEOUS INCLUSIONS IN APATITE FROM IJOLITES FROM HOMA MOUNTAIN.

HOMOGENISATION TEMPERATURE (°C).
CHAPTER 7
SODIUM : POTASSIUM RATIOS IN INCLUSIONS IN APATITE FROM SOME EAST AFRICAN CARBONATITIES AND IJOLITES

7.1. INTRODUCTION

There seems little doubt in the minds of most geologists that carbonatites are igneous rocks (Heinrich, 1966), but opinions still differ as to the exact nature of the carbonatitic fluid or magma. There is, however, ample evidence, as shown by the often extensive sodic and potassic fenitisation of country rocks surrounding the carbonatites and their associated alkalic rocks (ijolites etc.), that alkalis (Na⁺ and K⁺) must have been present in substantial quantities within the carbonatitic fluid.

Von Eckermann (1940b) was among the first to suggest that carbonatitic fluids must have been rich in alkalis, but it was not until 14 years later, following the discovery of natrocarbonatite lavas from Ol Doinyo Lengai (Dawson, 1962), that this idea became widely accepted.

The study of fluid inclusions in carbonatite apatites from some east African complexes, which are regarded as trapped portions of the actual carbonatitic fluid (Chapters 1, 2, 3, 5 and 6) has shown that such fluids are indeed rich in alkalis, as indicated by the widespread occurrence of alkali bicarbonate daughter minerals, predominately nahcolite (NaHCO₃), within the inclusions (Chapter 2). The sodium to potassium ratio has been determined by flame photometry for these unique portions of the crystallising medium present in these apatites. The results obtained indicate that soda is in excess of
potash which is in contrast to the chemistry of the rocks themselves
where potash invariably exceeds soda (Heinrich, 1966, p.221).
Similar results have also been obtained for inclusions in ijolite
apatites.

7.2. PREVIOUS WORK ON THE ANALYSIS OF SODIUM AND
POTASSIUM IN FLUID INCLUSIONS

Roedder (1972) has given an excellent account of the published
data on the composition of fluid inclusions together with a discussion
of the limitations of the various analytical methods employed.

The ubiquitous small size of fluid inclusions in minerals
(they seldom exceed 100 \( \mu \) ) means that the analysis of individual
inclusions is virtually impossible. Most reports of the analyses
of these fluids have been conducted on aqueous extracts leached from
crushed mineral grains or fragments, which contain numerous fluid-
filled cavities. Analyses are usually only qualitative and often
restricted solely to the determination of sodium and potassium within
the inclusion fluids (Sawkins, 1968; Roedder, 1972).

Only two published reports of the sodium to potassium ratios
in fluid inclusions from carbonatite minerals exist in the literature.
Wimmenauer (1963) observed large, tubular, fluid-filled cavities in
apatite from the Kaiserstuhl carbonatite, and from sketches which he
made of these cavities it was evident that they were of primary origin.
Apatite concentrates were crushed in an agate mortar and the alkalis
present in the aqueous extract leached from the crushed sample were
determined by flame photometry. The Na\(^+\) : K\(^+\) atomic ratio found by
Wimmenauer (op.cit.) was 2 : 1.
Yevzikova and Moskalyuk (1964) also obtained aqueous extracts from crushed calcite and dolomite from the Gula carbonatite of the northern Siberian platform, but found potash in excess of soda. Numerous inclusions were noted by these authors but because of the marked tendency for carbonate minerals to cleave very easily and to recrystallise, the inclusions were, in all probability, of secondary origin and not primary samples of the carbonatitic fluid.

7.3. **ANALYTICAL PROCEDURE FOR THE DETERMINATION OF SODIUM AND POTASSIUM IN INCLUSIONS IN APATITE FROM SOME EAST AFRICAN CARBONATITES AND IJOLITES**

7.3.1. Sample selection and preparation

Apatites from the Wasaki, Tororo, Homo and Ruri carbonatitic complexes of East Africa (King et al., 1972) often contain abundant, primary, fluid-filled cavities which represent unique samples of the crystallising medium. Fortunately, secondary inclusions are absent in most apatite crystals, and on those rare occasions where they have been observed, they are so minute and few in number in comparison to the large, abundant, primary inclusions that they can be disregarded.

Apatite concentrates were obtained from the carbonatites by digestion of the carbonate minerals using dilute acetic acid, followed by magnetic and heavy liquid separation. As it is essential to obtain apatite crystals as free as possible from other minerals (notably micas, nepheline, aegirine-augite) which may contribute to the sodium and potassium obtained by leaching the crushed apatites, the heavy liquid and magnetic separations were repeated until all traces of these minerals were removed and only the pure apatite grains remained.
The separation of apatite crystals from ijolitic rocks required a different procedure. The bulk rock sample was first crushed gently, using a stainless steel pestle and mortar, and the crushed sample sieved on nylon bolting cloth. Various grain-size fractions were obtained, but only that size fraction (normally -30, +120) where single apatite grains still contained abundant inclusions, unaffected by the crushing, were kept. Pure apatite grains were obtained from this fraction using heavy liquid and magnetic separation procedures.

The concentrated apatite grains from both the ijolites and carbonatites were then transferred to clean polythene beakers and treated once again with dilute, buffered acetic acid then washed several times in deionised water and twice in Analar acetone. Three final washings were then made using deionised water, and the pure apatite grains transferred to a previously cleaned P.T.F.E. bomb (Fig. 7.1). Deionised water was added, and the bomb plus contents placed in an oven and heated to temperatures between 100 and 120°C for periods of up to 4 hours. The bomb was then cooled and the washings removed and replaced by fresh deionised water. The procedure was repeated four or five times until the washings, when analysed on an EEL flame photometer, showed no significant amounts of alkalis present.

This method proved remarkably effective for cleansing the apatite grains prior to the analysis of sodium and potassium within the inclusions. It also served an additional function in that most secondary inclusions, which are located along weak healed fractures, are destroyed during heating. It should, however, be stressed that the homogenisation temperature of the primary inclusions should be known before heating, since inclusions which give low homogenisation
temperatures (< 150°C) may also be destroyed (that is, they would
decrepitate) at the heating temperatures used. The arbitrary heating
temperatures employed in the present study of between 100 and 120°C
are completely adequate, since homogenisation temperatures recorded
for inclusions in apatites from the iholites and carbonatites are
invariably in excess of 200°C (Chapters 3, 5, 6).

The cleaned apatite samples obtained were dried and stored in
scrupulously clean polythene beakers. Tables 7.1 and 7.2 list the
samples selected for study.

7.3.2. Preliminary studies

Zirkel (1870) was one of the earliest petrographers to study
fluid inclusions in minerals. By taking small grains of quartz
containing the inclusions and placing them in the hot part of a
colourless Bunsen flame, he obtained a series of minute explosions as
the inclusions decrepitated. Small flashes of yellow were observed
within the Bunsen flame accompanying this decrepitation which indicated
that there were significant amounts of sodium present within the
inclusions.

In an attempt to extend this method of yield more informative
results, a small direct-reading wavelength spectrometer (manufactured
by Bellingham and Stanley Ltd.) was used to analyse the spectrum of
the coloured flame. A small, coal gas/air flame provided by the fine
jet of a glass-blowing torch, and regulated to a height of 5cm and
width of 0.5cm was set up parallel to the spectrometer slit but 10cms
distance from it. A highly-polished parabolic mirror was placed around
the flame and served to focus the light emitted by this flame onto the
slit. The cleaned apatite grains were introduced on a clean platinum
loop to the base of the flame and decrепitation took place. The
flame was stoked 20 times with fresh apatite grains, and the emission
spectrum together with a blank on the flame were recorded on Ilford
Long Range Spectrum Photographic Plates (L.R.S.P.).

Apatite grains from the Tororo carbonatite (SUTO 100), Homa
carbonatite (HC249) and Wasaki carbonatites (U376, U735) were
decrепitated in the manner described above and the photographic plates
of the spectra obtained were analysed both visually and using a micro-
densitometer. All four spectra showed a relatively strong line at
5395 Å and two very weak lines at 7640 Å and 7665 Å units respectively.
No other lines were observed even when 50 stokes of the flame with
apatite grains were made. The spectra of helium (using a helium
discharge tube) and of pure sodium and potassium (using analar NaCl
and KCl) were also recorded on different parts of these plates in order
to calibrate the spectra obtained. The strong line at 5395 Å was
assigned to the sodium doublet (5396 and 5390 Å), which remained
unresolved because of the small dispersion of the spectrometer used.
The two weaker lines at 7640 Å and 7665 Å were assigned to potassium.

In an attempt to quantify these results (that is to determine
the Na⁺ : K⁺ ratio), standard solutions in which Na : K ranged from
1 : 10 to 100 : 1 were prepared and sprayed into the flame. The
spectra obtained on a number of photographic plates were analysed on
the microdensitometer and a calibration curve obtained in the manner
described by Ahrens and Taylor (1961) as a plot of Log \( \frac{c_{Na^+}}{c_{K^+}} \) versus

\[
\log \frac{I_{Na^+}}{I_{K^+}} = \text{The ratio of the concentration (mg/litre)}
\]
of sodium to the concentration of potassium (mg/litre) in the standard solutions, and \( \frac{I_{\text{Na}^+}}{I_{\text{K}^+}} \)

5895 Å to the intensity of the potassium line at 7670 Å (Fig. 7.2).

This calibration procedure is subject to serious limitations, particularly since every photographic plate has its own characteristics (that is, response to light) and must be calibrated individually. This is exemplified by the poor quality of the calibration graph obtained (Fig. 7.2).

When the results obtained from the decrpetitated samples were compared with the calibration graph it was found that sodium was always in excess of potassium by a factor of between about 2 and 10. Duplicate runs on the same sample, however, gave inconsistent results, and reproducibility of results within an acceptable margin of error (+100%) was not achieved. This method was therefore abandoned and a more accurate flame photometric procedure for the determination of sodium and potassium in leached aqueous extracts of crushed apatite grains, as described below, was adopted.

It should, however, be pointed out that the decrpetitation method is potentially well-suited to the analysis of alkalis in inclusions since only very small amounts of sample (less than 10mg of apatite grains were used in this study) are necessary, but in order to quantify the results a careful calibration procedure must be developed before meaningful and accurate values for the alkali ratios can be obtained.

The method has not proved totally futile. The results obtained at least indicate that significant amounts of sodium and potassium are present within the inclusions and that sodium is in excess of potassium. Lithium was not observed in any instance.
7.3.3. The determination by flame photometry of the sodium to potassium ratio in fluid inclusions

Between 0.5 and 1gm of previously cleaned apatite grains were placed in a clean agate mortar. About 5ml of pure deionised water was added, and the sample crushed with a clean agate pestle for approximately 5 minutes. In order to avoid the possibility of contaminating the resulting slurry with sweat from the hands, rubber gloves were worn throughout the crushing procedure. The resulting slurry was transferred to a clean polythene test-tube and centrifuged. The supernatant aqueous extract was then analysed for sodium and potassium using a previously calibrated EEL flame photometer. Lithium was absent in detectable amounts in all samples studied. As a check to see whether any contamination of the aqueous extract occurred during the crushing procedure, pure deionised water was added to the clean pestle and mortar. The crushing was performed, and this blank "solution" analysed for sodium and potassium. Neither element was found in detectable amounts (>1ppm) in the blank. However, after each determination the pestle and mortar must be scrupulously cleaned since soda and potash absorbed onto the surface of the agate mortar will contaminate the aqueous extracts from subsequent samples.

The actual weight of apatite used was limited by the amount of material available for study, and although Sawkins (1966) recommends sample sizes exceeding 100 grammes, adequate and reproducible results were obtained (Table 7.1) using as little as 0.3gm of separated apatite grains.
Table 7.1 Na : K WEIGHT RATIOS IN FLUID INCLUSIONS IN APATITES FROM SOME EAST AFRICAN CARBONATITES

<table>
<thead>
<tr>
<th>Locality</th>
<th>Sample Ref. Number</th>
<th>Sample Description</th>
<th>Na⁺ : K⁺ (Weight Ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wasaki</td>
<td>U876</td>
<td>Uyi Apatite-Sovite</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>U785</td>
<td>Sokolo Carbonatite</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>U693</td>
<td>Carbonatite Xenolith in Nyamaji Tuff</td>
<td>2.4</td>
</tr>
<tr>
<td>Tororo</td>
<td>SUTO 20</td>
<td>Aegerine-Apatite-Sovite from Limekiln Hill</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>SUTO 11?</td>
<td>Apatite-Magnetite-Carbonatite from Tororo Rock</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>SUTO 108</td>
<td>Apatite-Magnetite-Carbonatite from Tororo Rock</td>
<td>16.0</td>
</tr>
<tr>
<td>Homa Mountain</td>
<td>HC 249</td>
<td>Apatite-Carbonatite</td>
<td>4.2</td>
</tr>
<tr>
<td>North Ruri</td>
<td>N 43</td>
<td>Apatite-Aegerine-Sovite</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>N 314</td>
<td>Apatite-Carbonatite</td>
<td>6.0</td>
</tr>
<tr>
<td>Locality</td>
<td>Sample Ref. Number</td>
<td>Sample Description</td>
<td>$\text{Na}^+ : \text{K}^+$ (Weight Ratio)</td>
</tr>
<tr>
<td>------------------</td>
<td>--------------------</td>
<td>-------------------------------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>Wasaki</td>
<td>U1256</td>
<td>Usaki Pegmatite Ijolite</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>U849</td>
<td>Uyi Ijolite Invaded by Sovite</td>
<td>1.7</td>
</tr>
<tr>
<td>Homa Mountain</td>
<td>HC 476</td>
<td>Ijolite Fragment in Breccia</td>
<td>1.3</td>
</tr>
<tr>
<td>North Ruri</td>
<td>N 694</td>
<td>Micromelteigite</td>
<td>3.8</td>
</tr>
</tbody>
</table>
7.4. DISCUSSION OF RESULTS

The desirability of obtaining an estimate of the relative proportion of sodium to potassium in carbonatitic fluids has recently been restated by Wooley (1973), who suggests that such an estimate could provide an important key to our understanding of fenitisation processes.

The analysis of alkalies in fluid inclusions in carbonatite apatites has shown that sodium is in excess of potassium for all samples studied (Table 7.1). Since these inclusions are primary and represent trapped portions of the actual carbonatitic fluid, these results, which range from 2.8 - 16.0, give a direct measure of the relative proportion of sodium to potassium within this fluid. Except for the anomalously high ratio of 16.0 obtained for SUTO 100, the results from all four complexes studied are within the range 2.8 - 6.0.

The value of 16.0 obtained for SUTO 100 may be erroneous. Very little material was available for study and since the inclusions in apatite from this sample are generally small ( < 20μ ) and not very abundant, nearly all of the sample was used up in the first determination and a duplicate run was not possible. Furthermore, since a substantially lower value of 6.0 was obtained from a similar sample from the same complex (SUTO 112), it is concluded that the value of 16.0 obtained for SUTO 100 is erroneously high.

It is interesting to note that the Na⁺ : K⁺ ratios (3.43 and 4.03) for two samples of natrocarbonatite lavas from Oldoinyo Lengai (Dawson, 1966, p.163) are in the same range as the ratios obtained in this study (2.8 - 6.0, excluding SUTO 100), and although Deans et al. (1973) point out that it is unwise to assume that such lavas are...
typical carbonatite magmas, the $Na^+:K^+$ data shows that as far as alkali ratios are concerned, these lavas are typical of carbonatitic fluids.

Data on the $Na:K$ ratios in inclusions in apatite from a few ijolites have also been obtained (Table 7.2), and although the $Na^+:K^+$ ratio is once again greater than unity, it is doubtful whether these values represent the true $Na^+:K^+$ ratio in ijolitic magmas. The difficulty of obtaining a reliable estimate of this ratio from inclusions in ijolite apatites is two-fold. Firstly, the main inclusion-type present in the primary apatites are multisolid carbonate-rich inclusions (Ul256, N694). Crushing-stage studies in distilled water have shown (section 1.7.2.) that much of the crystalline contents of such inclusions are insoluble in water, hence any aqueous extract leached from crushed apatites from these two specimens only gives a value for the $Na^+:K^+$ ratio of the water-soluble fraction of the inclusions. Furthermore, other inclusion-types, such as silicate melt inclusions and occasional aqueous inclusions, may be present (section 1.7). These would also contribute to the alkalis leached from the apatites. Secondly, the apatites from HC1476 and U6b9 are probably derived from late-stage fluids (Chapters 3 and 6) and are not considered to be primary products of the ijolitic magma. Although the $Na^+:K^+$ ratios for these inclusions, which are predominately aqueous saline types, give a good indication of the relative proportion of sodium and potassium in the fluid responsible for the crystallisation of these apatites, this fluid is not a primary ijolitic fluid.
7.5. **SUMMARY AND CONCLUSIONS**

An analytical procedure has been described for the determination of the relative proportion of sodium to potassium in primary fluid inclusions in carbonatite apatites using an EEL flame photometer. The results obtained are considered to represent the actual sodium to potassium ratio in the carbonatitic fluid. The results show that the fluids responsible for the deposition of the East African carbonatites studied here, contain more sodium than potassium. The values obtained agree closely with the \( \text{Na}^+ : \text{K}^+ \) ratio found for the Oldoinyo Lengai natrocarbonatite lavas, and also with the ratio \( \text{Na}^+ : \text{K}^+ = 2 : 1 \) obtained by Wimmenauer (1963) for primary fluid inclusions in the Kaiserstuhl carbonatite apatites.

The \( \text{Na}^+ : \text{K}^+ \) values obtained for aqueous extracts leached from crushed ijolite apatites are not considered to be representative of the actual \( \text{Na}^+ : \text{K}^+ \) ratio of the primary ijolitic magma. However, these results are of some significance since they do give an indication of the relative proportion of sodium to potassium present in late-stage fluids associated with the ijolites (HCU76, U849).

It would seem desirable, in view of the frequent occurrence of inclusions in carbonatite apatites from other world-wide localities, (Chapter 1, Table 1.1), that similar \( \text{Na} : \text{K} \) ratios be obtained, in order to check whether all carbonatitic fluids indeed contain soda in excess of potash. It is believed that such results may prove particularly useful in the understanding of the chemistry of the fenitisation processes which are often associated with the emplacement of carbonatite and ijolites.
Fig. 7.1 Cross section of P.T.F.E. bomb used to clean the apatite crystals prior to the analysis of sodium and potassium within the inclusions.

- P.T.F.E inner casing and cap.
- Brass outer casing and cap.
- Viton O ring.
- H$_2$O Deionised water.
- C Hole for C-spanner.
FIG 7.2  Calibration graph for the determination of $\text{Na}^+:\text{K}^+$ ratios.
SUMMARY OF CONCLUSIONS

The apatites from rocks of the Wasaki complex of W.Kenya often contain well-formed, primary inclusions which are samples of the crystallising medium responsible for the deposition of the apatites. Many of these inclusions have necked-down or leaked during their history. However, these processes have been recognised and the study of primary, unaffected inclusions has allowed the following inferences to be drawn concerning the environment of deposition of the Wasaki rocks:

(a) Carbonatites

The apatites have crystallised from an aqueous CO$_2$-rich, alkali-rich fluid. The ability of this fluid to transport significant amounts of ore metals is demonstrated by the appearance of small, opaque, magnetic, daughter minerals within the inclusions. The existence of co-genetic solid calcite inclusions further shows that calcite has also precipitated in the presence of this fluid.

(b) Ijolites

The predominance of melt inclusions in apatites from the ijolites demonstrated that the apatites have crystallised from a melt. The nature of this melt was difficult to ascertain because of the complexity and diversity of the inclusions observed. However, the existence of carbonate-rich, multisolid inclusions in apatites from most of the ijolites studied, showed that carbonate-rich melts constituted at least part of the ijolitic magma. The presence of silicate melt inclusions, which were co-genetic with these multisolid, carbonate-rich inclusions in some specimens, further suggested that
a silicate melt and a carbonate-rich melt co-existed in the ijolitic magma. Aqueous, nahcolite-bearing, \( \text{CO}_2 \)-rich inclusions have been observed in some samples. Their presence indicates that aqueous, \( \text{CO}_2 \)-rich, saline solutions can also exist in the ijolitic fluid. The presence of carbonate-rich fluids in these melts shows that carbonatitic fluids can be derived from ijolitic fluids.

(c) Fenites

The fenite apatites contained low-pressure gaseous inclusions. Their presence indicates that fenitisation involved a low-pressure gas phase. Fenitising fluids or solutions (that is, highly mobile, alkali-rich aqueous fluids) could have been derived both from carbonatitic and ijolitic 'magmas'.

(d) Phonolites

The apatite from phonolite crystallised from a silicate melt which co-existed with a low-pressure gas phase. The apatites in "amygdales" from phonolite lava contained calcite-rich inclusions. It is tentatively suggested that these apatites may have crystallised from a carbonate-rich melt, present as an immiscible fraction within the silicate lava.

Nahcolite (\( \text{NaHCO}_3 \)) has been positively identified in the inclusions in apatite from the Wasaki carbonatites, and also in aqueous inclusions in apatites from two ijolite specimens (U366, U271). This is the first reported occurrence of nahcolite in igneous rocks. Its presence shows that alkalis occurred in greater amounts within carbonatitic and ijolitic magmas than the chemistry of the rocks.
themselves suggest. Nahcolite was also identified in aqueous inclusions in apatite from the Tororo, Homa and N.Ruri carbonatites.

Homogenisation temperature determinations on aqueous inclusions in apatites from the Wasaki carbonatites have shown that the minimum formation temperature of the apatites was in the following range:

(1) Uyi sovite (U876), 404-371°C
(2) Sokolo carbonatite (U785), 338-260°C
(3) Carbonatite xenolith in Nymaji phonolite (U693), 284-207°C

The manner in which homogenisation occurred in inclusions in apatites from the Uyi sovite (U876) has been interpreted to mean that the apatites in this sample have crystallised from a dense, super-critical fluid. A higher estimate of the formation temperature of these apatites (595-500°C) was determined from the 'solution' temperature of a transient phase (identified as a sodium carbonate melt) precipitated from the inclusion fluid at high temperatures.

Although the homogenisation temperature of melt inclusions in the Wasaki ijolite apatites could not be used as reliable indicators of the formation temperature of the apatites, a minimum crystallisation temperature has been deduced from the melting temperature of the inclusion contents. The temperatures obtained were 630-950°C.

Liquid immiscibility between silicate and carbonate-rich melts has been observed within the inclusions from the Usaki ijolite pegmatite (U1256) at high temperatures ( > 800°C) produced during heating-runs. This is positive evidence that immiscibility between carbonate-rich and silicate melts can occur in natural ijolitic magmas. It is concluded that carbonatitic fluids can be derived from ijolitic melts
by a process of liquid immiscibility.

The Tororo carbonatite apatites contain aqueous inclusions similar to those observed in the Wasaki carbonatite apatites. It is similarly concluded that the Tororo apatites have crystallised from an aqueous CO$_2$-rich, alkali-rich fluid. The minimum temperature of formation of these apatites, as determined from homogenisation temperatures, were as follows:

- Tororo Rock, 436-208°C
- Limekiln Hill, 466-230°C

Apatites from rocks of the Homa mountain carbonatitic complex were noticeably devoid of inclusions. Those observed in the carbonatite apatites had necked so extensively that detailed studies were not possible. Nevertheless, the inclusions once again indicated that the apatites had crystallised from an alkali-rich, CO$_2$-bearing, aqueous fluid. A value for the mean minimum temperature of formation (299°C) was determined from heating-stage studies.

The apatites from the Homa ijolites contained a predominance of aqueous, CO$_2$-poor alkali-rich inclusions. This was in contrast to the Wasaki ijolite apatites which contained predominately melt inclusions. The minimum formation temperature range for these apatites was 458-232°C. It is concluded that the Homa ijolite apatites here studied (HC476, HC934) have crystallised from a late-stage, aqueous, CO$_2$-poor saline fluid.

A method has been described for the determination of the Na$^+$ : K$^+$ ratios in aqueous inclusions. Since the aqueous inclusions in the carbonatite apatites are trapped portions of the carbonatitic fluid, the values obtained give a direct estimate of the actual
Na$^+$ : K$^+$ ratio of this fluid. The range obtained was 2.4 - 16.0. These results were compared with the Na$^+$ : K$^+$ ratio for the natrocarbonatite lavas of Oldoinyo L'Engai (3.5 - 4.0), and were found to be in close agreement with this value. This demonstrates that the Na$^+$ : K$^+$ ratio for these lavas are typical of carbonatitic fluids.
APPENDIX A

CALIBRATION OF THE MICROSCOPE HEATING-STAGE

The Leitz 1350 microscope heating-stage, used throughout this study, consists of a water-cooled heating compartment supporting a small, flat sapphire object carrier. A platinum-rhodium heating coil, connected to a low voltage finely adjustable transformer, supplies heat to the sample. The temperature is measured with a Pt Rh-Pt thermocouple in contact with the object carrier. A comprehensive account of this heating-stage and its operation has been given by Harker (1971). The temperature measured by the thermocouple is recorded on a "0.5 quality" standardised galvonometer which has a temperature range up to 1600°C graduated in 10°C intervals, and a separate range up to 700°C graduated in 5°C intervals. The cold junction of the thermocouple is at room temperature, so the zero of the galvonometer is set to the usual room temperature of 23°C. Should the room temperature vary from this zero setting allowance has to be made in the calculation of the actual temperature recorded by the thermocouple (EQUATION 1)

\[ T_{\text{therm}} = T_{\text{galvo}} + T_{\text{room}} + \Delta T_{\text{room}} \quad \ldots (1) \]

where

- \( T_{\text{therm}} \) = Temperature at the thermocouple hot junction
- \( T_{\text{galvo}} \) = Temperature recorded on the galvonometer
- \( T_{\text{room}} \) = Arbitrary room temperature at which galvonometer is set to zero, in this case 23°C
- \( \Delta T_{\text{room}} \) = The difference in temperature between the actual room temperature and the arbitrary room temperature of 23°C.
As the hot junction of the thermocouple does not come directly into contact with the sample but only touches the sapphire object carrier, a difference between the temperature recorded by the thermocouple and the true temperature within the sample might be expected (Harker, 1971). Roedder (1972) also states that large static thermal gradients are present in air conduction heating-stages and that suitable temperature corrections are necessary to allow for the thermal lag between specimen and thermocouple.

To evaluate these temperature gradients it is essential to calibrate the heating-stage with known melting points of pure organic and inorganic substances. Harker (1971) has shown that the thermal gradients for the heating-stage used in this study are negligible up to 593°C (the melting point of BaNO₃) and that the observed melting points of the standards used were in agreement to within ± 2°C of the actual melting points. The slight discrepancy of ± 2°C was attributed to experimental error in the reading of the galvonometer and in the purity of the calibration standards. It was therefore concluded that homogenisation temperatures of inclusions up to about 600°C are not subject to any correction factors. Similar calibration runs were performed throughout this study and it was confirmed that temperature gradients are negligible up to about 600°C, although an experimental error of ± 1°C is more realistic for temperatures between 400 and 600°C. Additional calibration runs were performed for temperatures up to and slightly in excess of 1000°C, using the galvonometer scale range 0 - 1600°C. It was found that a definite thermal lag between thermocouple and sample exists at these elevated temperatures becoming increasingly noticeable as the
temperature increases. Calibration was performed in the range 593-1063°C using the following "spec. pure" substances:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>1063</td>
</tr>
<tr>
<td>Silver</td>
<td>961</td>
</tr>
<tr>
<td>LiF</td>
<td>842</td>
</tr>
<tr>
<td>NaCl</td>
<td>801</td>
</tr>
<tr>
<td>KCl</td>
<td>776</td>
</tr>
<tr>
<td>RbCl</td>
<td>715</td>
</tr>
<tr>
<td>Ba(NO₃)₂</td>
<td>593</td>
</tr>
</tbody>
</table>

Four sets of values were obtained for the apparent melting points of these substances and average values obtained. These figures are subject to an experimental error of not more than ± 0°C; this error being in part due to difficulty in assessing the exact moment of melting, and to the innaccuracy in reading the galvonometer (which, on the range used, is graduated in 10° intervals).

Fig. A.I shows the calibration chart for the heating stage in the range 500-1200°C and its deviation from the true temperature. The correction factor (C.F.) which must be subtracted from the observed temperature to obtain the true temperature of the sample can be calculated for any temperature from this calibration chart. The correction factor increases in magnitude rapidly beyond 900°C reaching a value of 55°C at 1100°C. Above about 1150°C the correction factor is exceptionally large and difficult to assess, and it has been inadvisable to proceed with homogenisation runs beyond this temperature.

The corrected temperature for inclusions homogenising up to temperatures of 1100°C can be derived from the following expression (EQUATION 2):
\[ T_h = \text{Therm.} - \text{C.F.} + \text{ERROR} \] 

Where \( T_h \) = Actual homogenisation temperature
\( \text{Therm.} \) = Thermocouple temperature
\( \text{C.F.} \) = Correction factor for any value of \( \text{Therm.} \)
\( \text{ERROR} \) = The experimental error.

Combining Equations (1) and (2) the following overall expression for \( T_h \) is produced:

\[ T_h = T_{galvo} + T_{room} + \Delta T_{room} - \text{C.F.} + \text{ERROR} \]

for inclusions homogenising in the range 0 - 400°C
\( \text{C.F.} = 0 \) and \( \text{ERROR} = 2°C \)

for inclusions homogenising in the range 400 - 600°C
\( \text{C.F.} = 0 \) and \( \text{ERROR} = 4°C \)

for inclusions homogenising above 600°C
\( \text{C.F.} \neq 0 \) and \( \text{ERROR} = 8°C \)
**Fig. A.1.** The calibration chart for the Leitz 1350 heating stage.

**A** = Theoretical line if no thermal lag exists between sample and thermocouple

**E** = Experimental line obtained from the melting points of pure inorganic substances showing deviation from the theoretical line

**C.f.** = Correction factor

**T_{obs}** = Observed temperature (°C)

**T_{act}** = Actual temperature (°C)
Fig A-1 Calibration chart for the Leitz 1350 heating stage.
APPENDIX B

CRITICAL PHENOMENA IN FLUID SYSTEMS; SOME DEFINITIONS

Smith (1963, p. 22) states that "... There is a considerable amount of confusion in geological literature over critical phenomena in magmas and hydrothermal fluids, which has not been clarified by attempts of physical chemists to explain the relations to geologists". Roedder and Coombs (1967), who also noted this apparent confusion, have found it necessary to explain the meaning of terms such as 'boiling', gas, liquid and critical temperature when discussing liquid immiscibility in granitic melts.

In order to explain the physical meaning of terms such as critical temperature, density and pressure, supercritical fluids and critical phenomenon used in this thesis, and particularly in Chapter 3, some definitions will be given below. For a more detailed account of critical phenomena the reader is referred to an excellent article on the critical region by Sengers and Sengers (1968).

(1) CRITICAL TEMPERATURE

Is defined as that single temperature above which a fluid cannot be liquified by pressure alone (Weast, 1965, p.F.57). Above this temperature, only one single fluid phase can exist. This fluid is defined as a SUPERCRITICAL FLUID. Below the critical temperature two fluid phases, vapour and liquid, can co-exist.

(2) CRITICAL PRESSURE

Is defined as the pressure under which a substance may exist as
A gas (that is SUPERCRITICAL FLUID) in equilibrium with the liquid at the critical temperature (Weast, op.cit.). In simpler terms, the critical pressure may also be defined as the pressure at the critical point.

(3) CRITICAL DENSITY

Is defined as the density of the fluid at its critical temperature and pressure.

(4) CRITICAL POINT

According to Sengers and Sengers (1963) this point marks the highest temperature of the co-existence curve which separates the two-phase region (liquid and vapour) from the single-phase region (gas, liquid or supercritical fluid). The temperature, pressure and density of the fluid at this point are its critical values, i.e. critical temperature, critical pressure and critical density.

(5) CRITICAL PHENOMENON

This term has often been used in fluid inclusion studies (Roedder, 1972, p.716) to denote the type of homogenisation, which is very occasionally observed when a gas/liquid inclusion homogenises, upon progressive heating, by the gradual fading of the meniscus which separates the gas phase from the liquid phase within the inclusion. The temperature at which homogenisation takes place, that is when the meniscus fades completely so that the gas and liquid homogenise to a single homogeneous phase, is actually the critical temperature of the inclusion fluid. Homogenisation is said to occur at the CRITICAL
POINT, and inclusions which homogenise at this point are said to have a CRITICAL DEGREE OF FILLING. The critical degree of filling is simply a measure of the percentage of the total volume of the inclusion occupied by the vapour phase at room temperature, and is directly related to the critical density of the fluid.

Roedder (1962) presents a PV T plot for water above and below its critical point, and has superimposed the behaviour of an inclusion which homogenises at the critical point on to this curve. In order to demonstrate this type of homogenisation, a short 16mm colour cine-film, available from the Geology Department, Leicester University, was made of the behaviour of FREON 115 (CCLF₂ - CF₃) as it passes through its critical point. The critical values for this freon compound are as follows:

\[
\begin{align*}
T_c &= 30.0^\circ C \\
P_c &= 30.3 \text{ atm.} \\
V_c &= 1.679 \text{ ml./g} \\
D_c &= \frac{1}{1.679} \text{ g/ml.}
\end{align*}
\]

A commercially produced freon-filled cell (manufactured by Leybold-Heraeus of W.Germany) was used for this study. The cell is filled with freon 115 at its critical density so that when the cell is heated, the meniscus, which separates the liquid from vapour, fades gradually up until the critical temperature, at which point the liquid and vapour phase merge completely into a single homogeneous fluid.

The behaviour upon heating this freon-filled cell, which can be considered as an "artificial fluid inclusion", is shown in Plate B.1.
The cell at 35°C shows a distinct meniscus separating the liquid (l) and the vapour (v). As the temperature is increased the meniscus fades gradually. At 79°C the meniscus is exceedingly faint and at 80°C (the critical temperature for Freon 115) the meniscus has disappeared completely. The darkening of the contents of the cell at or near to the critical point (80°C) is known as critical opalescence. (Schmidt and Tompson, 1968, p.33). This opalescence disappears at 81°C at which temperature the cell contains a colourless, homogeneous, supercritical fluid.
APPENDIX C  The volcanic and intrusive complexes of E. Uganda and W. Kenya.
APPENDIX D  The Ruri hills and Wasaki peninsula.

GEOLOGICAL SKETCH MAP OF THE RURI HILLS AND WASAKI PENINSULA

- Alluvium
- Phonolitic dykes
- Phonolitic plugs
- Phonolitic lavas
- Melanephelinite lavas
- Agglomerate & tuffs

1 KILOMETER 1 MILE

- Coarse-grained carbonate
- Medium & fine grained carbonate
- Phonolitic breccias & agglomerates
- Wollastonite-urtilite
- Lizardite & nepheline-syenite
- Fenite

Nyonzian basement
Preliminary Evidence on the Nature and Composition of Carbonatite Magma

Carbonatites are igneous rocks but the exact nature of carbonatite magma has not been established. Silicate magmas, both extrusive and intrusive, are molten and normally carry a low-pressure gas phase. Carbonatite magmas appear also to be molten when extrusive but there is evidence, in the form of brecciation and fenitization, that a gaseous phase plays a dominant role in carbonatite intrusions (see also ref. 3). We now report that a fluid medium capable of transporting carbonatitic material can exist, not as a molten liquid but as a gaseous and mobile supercritical fluid from which carbonates can crystallize directly. Such a system is a strong contrast with the usual notion of an igneous magma.

A gas extraction line has been constructed for the analysis of the small volumes of gas observed in the uniform and primary fluid inclusions within crystals of apatite from carbonatites, using samples from intrusive sövite complexes near Homa Bay in western Kenya. The extracted gases were analysed by fractional freezing and by mass spectrometry. Dissolved and crystalline phases were semi-quantitatively analysed by flame emission micro-techniques, and the fluid inclusions as a whole have been examined by heating-, freezing-, and crushing-stage methods as well as by standard optical determinative techniques.

The inclusions within the apatites of the sövite carbonatites differ in composition from those in apatites of ijolitic intrusive complexes. The apatites in the sövites contain both aqueous gas-bearing inclusions (with crystalline daughter phases) and separate solid calcite inclusions. The crystalline daughter phases are chiefly composed of a sodium carbonate together with some calcium carbonate, and the accompanying gas phase is chiefly carbon dioxide held at a pressure of 100 to 200 bars at room temperature. The apatites in the ijolites nearby contain glasses and a variety of optically isotropic and anisotropic crystalline solids, as well as aqueous phase inclusions which differ in composition from those in the sövitic apatites.
The temperatures of homogenization recorded during heating-state experiments indicate that the minimum temperature of crystallization of the sövite is roughly 550° C. The mode of homogenization shows that, at these temperatures, carbon dioxide and water were present as a super-critical fluid, and that this fluid is capable of dissolving all the solid carbonate present—up to about 10% by volume of the inclusion. Because the inclusions are primary, they represent trapped portions of the medium in which the apatites were crystallizing. This medium constitutes a fluid carbonatite magma.

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Received June 8, 1972.

5 Roedder, E., in Geochemistry of Hydrothermal Ore Deposits (edit. by Barnes, H. L.), 515 (Holt, Rinehart, New York, 1967).
Preliminary Evidence on the Nature and Composition of Carbonatite Magma

Carbonatites are igneous rocks but the exact nature of carbonatite magma has not been established. Silicate magmas, both extrusive and intrusive, are molten and normally carry a low-pressure gas phase. Carbonatite magmas appear also to be molten when extrusive but there is evidence, in the form of brecciation and fenitization, that a gaseous phase plays a dominant role in carbonatite intrusions (see also ref. 3). We now report that a fluid medium capable of transporting carbonatic material can exist, not as a molten liquid but as a gaseous and mobile supercritical fluid from which carbonates can crystallize directly. Such a system is a strong contrast with the usual notion of an igneous magma.

A gas extraction line has been constructed for the analysis of the small volumes of gas observed in the uniform and primary fluid inclusions within crystals of apatite from carbonatites, using samples from intrusive sővitic complexes near Homa Bay in western Kenya. The extracted gases were analysed by fractional freezing and by mass spectrometry. Dissolved and crystalline phases were semi-quantitatively analysed by flame emission micro-techniques, and the fluid inclusions as a whole have been examined by heating-, freezing-, and crushing-stage methods as well as by standard optical determinative techniques.

The inclusions within the apatites of the sővite carbonatites differ in composition from those in apatites of ijolitic intrusive complexes. The apatites in the sővites contain both aqueous gas-bearing inclusions (with crystalline daughter phases) and separate solid calcite inclusions. The crystalline daughter phases are chiefly composed of a sodium carbonate together with some calcium carbonate, and the accompanying gas phase is chiefly carbon dioxide held at a pressure of 100 to 200 bars at room temperature. The apatites in the ijolites nearby contain glasses and a variety of optically isotropic and anisotropic crystalline solids, as well as aqueous phase inclusions which differ in composition from those in the sővitic apatites.
The temperatures of homogenization recorded during heating-state experiments indicate that the minimum temperature of crystallization of the sövite is roughly 550° C. The mode of homogenization shows that, at these temperatures, carbon dioxide and water were present as a super-critical fluid, and that this fluid is capable of dissolving all the solid carbonate present—up to about 10% by volume of the inclusion. Because the inclusions are primary, they represent trapped portions of the medium in which the apatites were crystallizing. This medium constitutes a fluid carbonatite magma.

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Abundant fluid inclusions are present in apatites from several E African carbonatites and ijolites. Aqueous CO$_2$-rich inclusions in apatites from most carbonatites contain soluble carbonate daughters. The aqueous CO$_2$-poor inclusions in ijolites also contain carbonate daughter phases but other soluble cubic and rectangular daughter phases predominate. Glassy and crystallized inclusions, whilst totally absent from carbonatitic apatites, are common in ijolitic apatites.

Homogenization temperatures obtained range from 300–650°C for ijolite and 250–480°C for carbonatite apatites; these represent minimum crystallization temperatures. Glassy and crystallized inclusions homogenize between about 750°C and 1150°C and may be samples of a melt. These inclusions maintain their fluidity down to temperatures of approximately 500°C.

The mode of homogenization of apatite inclusions from an apatite sovite suggests trapping of a homogeneous supercritical fluid and critical phenomena have been observed in some of these inclusions. The solution temperatures of the carbonate daughters is independent of mode of homogenization. A second solid phase precipitated from these inclusions at temperatures between about 350°C and 500°C, 'redissolved' at about 500–600°C, thus permitting a higher crystallization temperature to be placed on this rock type. Again this 'solution' temperature is independent of mode of homogenization.

Hot supercritical fluids rich in CO$_2$, H$_2$O and alkalis are envisaged as being responsible in part for the crystallization of carbonatites, whilst ijolites show evidence of crystallization from a melt co-existing with an aqueous CO$_2$-poor alkaline fluid. Preliminary results for Na:K ratios in these fluids range from 1.3–3.8 for ijolites and 3.1–16.0 for carbonatites.
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Primary inclusions are present in apatites from carbonatites and ijolites of the Wasaki, Homa and Tororo complexes of E. Africa. These unique portions of crystallising fluids give valuable information about the nature of carbonatite and ijolite magmas.

CO$_2$ - rich, aqueous inclusions, which contain substantial amounts of alkalis, predominate in apatites from these carbonatites. The Na$^+$/K$^+$ weight ratio was found to be in the range 2.4-16.0. Significant amounts of ore metals are also present, as shown by the occurrence of minute, magnetic, crystalline specks within the inclusion fluid. It is concluded that the carbonatitic fluid from which the apatites crystallised, consisted of a highly mobile, CO$_2$ - rich, aqueous saline fluid.

Homogenisation temperatures, which represent the minimum formation temperature of the apatites, ranged from about 200$^\circ$C to 485$^\circ$C. The mode of homogenisation of one sample, the Uyi carbonatite, indicated that this fluid was supercritical. A higher estimate of the formation temperature (500-590$^\circ$C) of the apatites from this sample was obtained from the solution temperature of a transient phase (probably Na$_2$CO$_3$) precipitated from the inclusion fluid at high temperatures during heating-runs.

Melt inclusions predominate in apatites from the Wasaki ijolites. Carbonate-rich and silicate-rich inclusions are co-genetic in the apatites from some samples. Heating studies have shown that liquid immiscibility between carbonate-rich and silicate melts can occur in ijolitic magmas.
Aqueous, CO₂-rich, saline fluids may also occur in these magmas. Carbonatitic fluids can be derived from ijolitic magmas. The minimum formation temperature of the Wasaki ijolite apatites was in the range 680°C-950°C.

Inclusion studies in apatites from the Koma ijolites showed that the apatites crystallised from a highly saline, aqueous fluid. The minimum formation temperature was in the range 453°C-232°C.

Nahcolite (NaHCO₃) is described in these aqueous inclusions. This is the first reported occurrence of this mineral in igneous rocks.