Fluid-inclusion evidence for the formation conditions of apatite from the Tororo carbonatite complex of eastern Uganda

ANDREW H. RANKIN

Division of Mining Geology, Royal School of Mines, Imperial College, London S.W. 7

SUMMARY. Portions of the carbonatitic fluids responsible for the deposition of apatite from the Tororo carbonatite complex are trapped and preserved as minute ($<$ 100 μm) inclusions within the apatites. These fluids consist predominantly of alkali-carbonate-bearing brines and demonstrate that water and alkalis played an important role in the formation of the carbonatites from this complex. Furthermore, the opinion that carbonatite 'magmas' are richer in alkalis and water than the chemistry of the carbonatites themselves reveal is clearly substantiated. The mean minimum formation temperature of the apatites from five separate carbonatite samples were determined from the homogenization temperatures of 200 primary aqueous inclusions. The results from Limekiln Hill samples (328 °C, 321 °C, 359 °C) are similar to those from samples of the separate carbonatite mass at Tororo Rock (353 °C, 365 °C).

PREVIOUS studies on fluid inclusions in minerals from carbonatites have shown that carbonatitic fluids can exist either as carbonate melts (Romanchev, 1972) or as highly mobile, alkali-carbonate brines (Rankin, 1975). Apart from recent results on the Wasaki complex of western Kenya, and a few results in the Russian literature (summarized by Rankin, 1975), little information is available on fluid-inclusion geothermometry of carbonatites. This paper supplements previous studies and reports an optical and thermometric study of primary inclusions in apatite from the Tororo Rock and Limekiln Hill carbonatites of eastern Uganda (King and Sutherland, 1966). The study allows limits to be placed on their minimum formation temperatures and permits further discussion of the properties of carbonatitic fluids.

Preliminary examination of thin sections of the Tororo carbonatites showed that the abundant calcite of these rocks lacks definitely primary fluid inclusions, and those present are either too small for study ($<$ 3 μm) or secondary in origin. Conversely, apatite, a common accessory mineral that is earlier than, or cogenetic with, most of the calcite, and occurs as stubby prisms or ovoid grains, often contains relatively large primary inclusions. Acicular or skeletal (hollow) crystals of apatite, thought to be indicative of rapid growth from a melt (Wyllie et al., 1962) are not observed.

Five separate carbonatite samples (Table I) that contained sufficiently large ($>$0·1 mm) and abundant apatite crystals were selected for detailed inclusion studies. Apatite concentrates were obtained from the five bulk-rock samples by conventional separation techniques and their inclusions studied at high magnification using oil immersion. These inclusions are dominantly aqueous saline types but small numbers of solid inclusions also occur.

Primary aqueous inclusions and their subsequent alteration

Primary aqueous inclusions usually occur as uniform spheroidal or negative crystal-shaped, elongate cavities (fig. 1) and are remarkably similar in morphology and composition to those present in apatite from some other E. African carbonatites (Rankin, 1975). On the basis of their common occurrence as elongate cavities, parallel to the c-axis of the apatite, they are assigned a primary origin (trapped during primary growth of the crystal). They contain an aqueous

solution, a mobile vapour bubble, and often one or more daughter phases (phases precipitated from the trapped inclusion fluid as it cooled). The size and abundance of the inclusions is variable. Most (> 85 % of all those present) are smaller than 20 μm and the remainder range in size up to a maximum of about 100 μm. Table I gives an indication of the abundance of primary aqueous inclusions in the apatites and shows that, except for sample 112, most apatites contain at least one inclusion and that it is uncommon to find more than ten inclusions in the

TABLE I. *The abundance of primary aqueous inclusions in apatites from five separate carbonatites of the Tororo complex*

Locality & Sample Ref. No.*	Rock-Type	Percentage of apatite crystals containing indicated number of inclusions**			
		NONE	1–3	4–10	11 or more
Limekiln Hill 20	Apatite-Sovite	12	52	39	7
Limekiln Hill 22	Aegirine-Apatite-Sovite	17	40	35	8
Limekiln Hill 26	Aegirine-Apatite-Sovite	34	43	26	7
Tororo Rock 108	Apatite-Magnetite-Carbonatite	33	53	12	2
Tororo Rock 112	Apatite-Magnetite-Carbonatite	63	29	8	0

* Samples were selected from the Reference collection of the Geology Dept., Leicester University. All sample numbers are prefixed by SUTO.
** These percentages were determined by counting the number of inclusions in 200 apatite crystals selected at random from each sample. Inclusions less than 1–2 μ in size were not considered.

Errata: Col. 3, *for* 34 *read* 24; col. 4, *for* 52 *read* 42.

same crystal. The mechanisms of inclusion formation are complex (Roedder, 1967) and it is beyond the scope of this present study to account for this variation in size, distribution, and abundance.

Many inclusions have been affected by necking down processes (Roedder, 1967) and, in consequence, may contain abnormally high proportions of aqueous solution or vapour (fig. 2c, d, e).

The apatites from Limekiln Hill samples are often fractured. When these traverse a primary aqueous inclusion leakage occurs and anomalous 'gas-filled' inclusions are produced (actually air, Rankin, 1975) (fig. 2a, c). Sometimes these emptied inclusions are later infilled with secondary calcite or brownish/red ferruginous material (fig. 2b). Inclusions altered by necking down or leakage do not provide information on the formation conditions of the apatites and great care was taken in this study to consider only those inclusions unaffected by these processes.

Phases present in unaltered primary aqueous inclusions. The vapour bubble occupies approximately 20 to 30% of the volume of the cavity and shows a small volume expansion when the inclusions are opened in liquid paraffin under the microscope at room temperatures. This shows that the bubble is held under a significant positive pressure and must, therefore, contain volatiles other than water vapour. Carbon dioxide is most likely in view of the chemistry of the host rock and the positive recognition of liquefied CO_2 in aqueous inclusions in apatite from other carbonatites (Rankin, 1973 and 1975).

The most common daughter phases in aqueous inclusions in apatite from Limekiln Hill samples are nahcolite ($NaHCO_3$) (Rankin and LeBas, 1974), which may occupy up to 30% of the volume of the cavity (fig. 1b, f), and an unidentified, opaque, apparently non-magnetic phase, occupying less than 1 % of the volume of the cavity. Small amounts of other highly birefringent solids, possibly carbonates, are occasionally present (Table II).

The daughter phases in inclusions in the Tororo Rock apatites are more variable. Nahcolite is again common in those from sample 112 but is rare in those from the other Tororo Rock
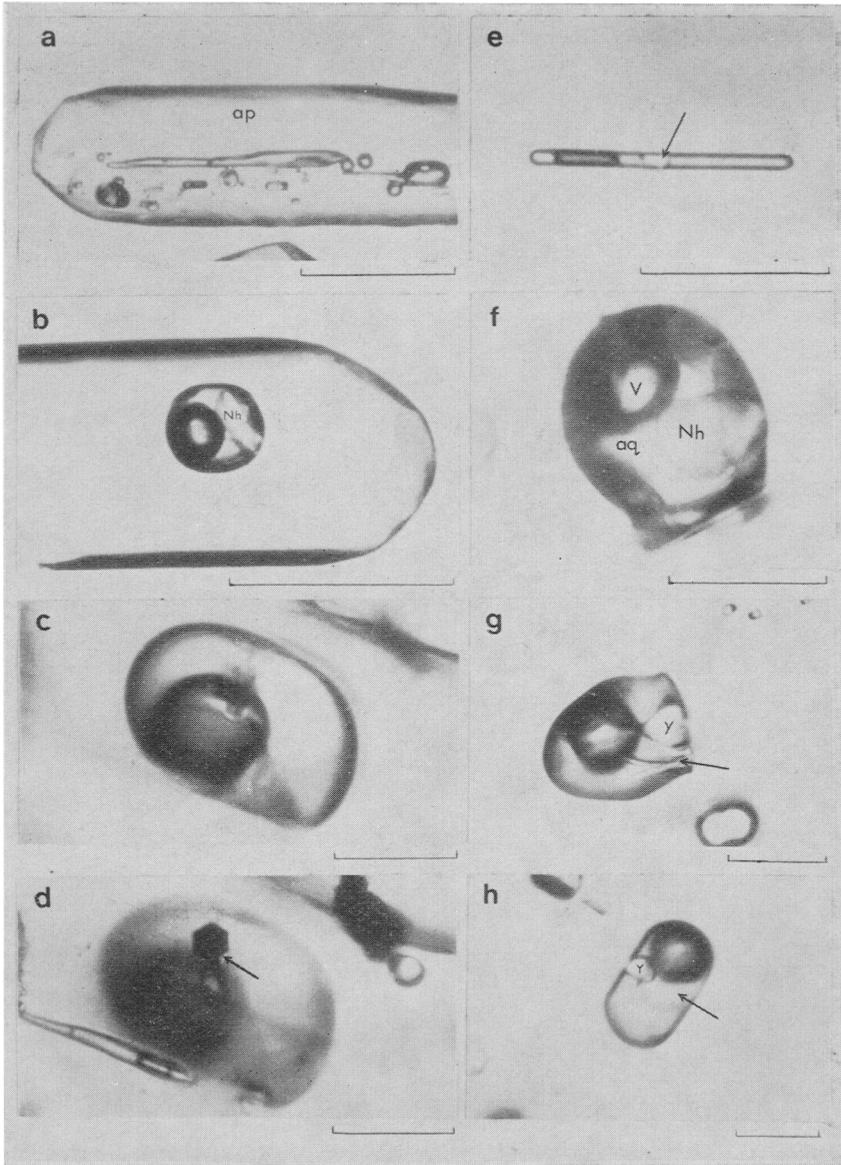
FIG. 1. Aqueous inclusions in apatite from Tororo carbonatites. (a) Elongate apatite crystal (ap) containing a large, tubular inclusion. Partial necking-down has taken place. Oil immersion ($n = 1.56$), Bar = 50 μm. (b) Large, spheroidal inclusion containing a nahcolite daughter mineral (Nh). Note the absence of any other inclusions. Solitary inclusions such as these are particularly useful for thermometric studies since necking-down processes could not possibly have taken place. Oil immersion ($n = 1.56$), Bar = 50μm. (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 μm. (d) As (c) above, but focused this time on the top of the inclusion. A hexagonal platelet of pyrrhotine (arrowed) is seen within the inclusion. Bar = 20 μm. (e) Tubular inclusion aligned parallel with the c-axis of the apatite host. A small nahcolite daughter (arrowed) is clearly visible. Bar = 20 μm. (f) Inclusion containing an aqueous solution (aq), a vapour bubble (v) and a nahcolite daughter mineral (Nh). Bar = 20 μm. (g) Inclusion containing an anisotropic, pale yellow daughter mineral (y) and several acicular daughters (arrowed) showing curved habit. Bar = 20 μm. (h) Regular-shaped inclusion containing a pale yellow daughter mineral (y). Nahcolite is also present in this inclusion but because the refractive index of the inclusion fluid almost exactly matches the refractive index of the nahcolite in this orientation, it is invisible. Bar = 20 μm.

(a), (b), (g), (h) are from SUTO 108; (c), (d), (e) are from SUTO 112; (f) is from SUTO 20.
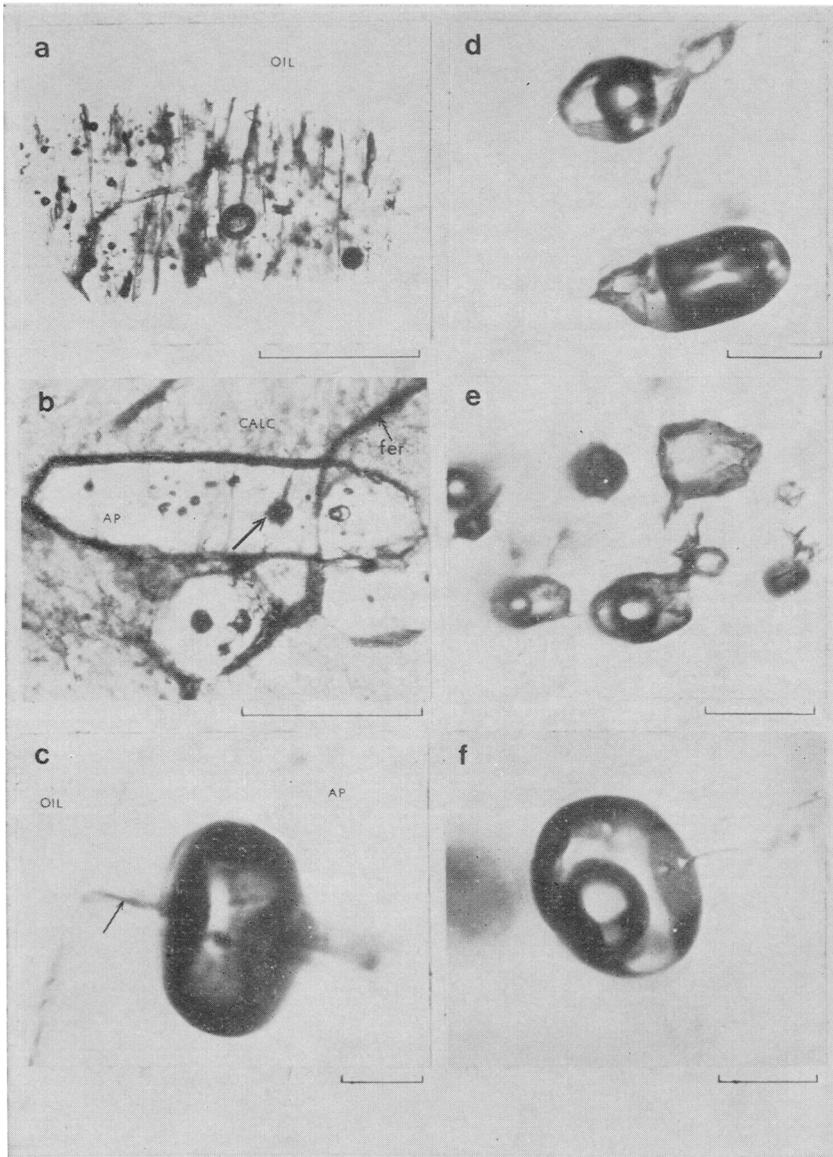
FIG. 2. Leakage and necking-down of aqueous inclusions in apatite. (a) Apatite crystal, in immersion oil ($n = 1·63$), showing innumerable fractures and planes of secondary inclusions. Bar = 50 μm. (b) Thin section showing a ferruginous veinlet (fer) cutting apatite (ap) and calcite (calc). The ferruginous material also coats the surface of the apatite crystal. A small inclusion (arrowed) has been infilled by this material. Bar = 100 μm. (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 small fracture (arrowed) leading to the surface of the crystal. Bar = 20 μm. (d) and (e) Necked-down aqueous inclusions. Bar = 20 μm. (f) Rounded, aqueous inclusion showing small tail protruding from the inclusion wall. Such tails are indicative of inclusions that have necked. Bar = 20 μm.

　　(a) is from SUTO 26; (b), (c), (e), (f) are from SUTO 20; (d) is from SUTO 22.

sample (108). Small, opaque solid phases occur in many inclusions in apatite from both samples but, unlike those observed in inclusions from the Limekiln Hill samples, these often exist as distinct hexagonal platelets and are markedly magnetic. They have, therefore, been identified as pyrrhotine. Pyrrhotine has also been recorded as a daughter phase in aqueous inclusions in apatite from one of the carbonatites of the Wasaki area of western Kenya (Rankin, 1975).

Two further daughter minerals, both unidentified, are present only in the inclusions from sample 108. One, a pale yellow, water-soluble, anisotropic phase, predominates. The other shows a distinctive acicular habit, is strongly birefringent (carbonate phase?) and usually occurs as a cluster of closely spaced needles (fig. 1g, e).

Other primary inclusions. Single crystals of calcite are sometimes present as rounded, slightly elongate, mineral inclusions completely sealed within the apatites, and are thought to result from the trapping of already precipitated crystals of calcite. They often occur side-by-side with primary aqueous inclusions (fig. 3a, b) in the same apatite crystal but occasionally a small portion of aqueous fluid is actually trapped together with these calcite crystals and complex inclusions of gas, liquid and captured calcite result. It is concluded from these observations that these calcites coexisted with the aqueous fluid (now preserved as aqueous inclusions) during the growth of the apatites. Monocrystalline inclusions of calcite have also been described in apatite from the Oka carbonatite (Girault, 1966) and by Rankin (1975) in the Wasaki carbonatite apatites.

An unidentified mineral phase (denoted by U in fig. 3c, d) with low to moderate birefringence and straight extinction sometimes occurs as solid inclusions in apatite from sample 108. Small portions of aqueous fluid may be trapped together with these solids in the same inclusion. A similar origin to the calcite inclusions described above can be assigned to these inclusions.

Thermometric studies

The temperature at which the gas and liquid phases in a primary aqueous inclusion become homogeneous (the homogenization temperature, T_h) during progressive heating of the sample represents the minimum formation temperature of the host material, provided that leakage or necking down has not taken place (Roedder, 1967). These temperatures, ± 5 °C, were recorded for 200 relatively large ($> 20 \mu$m) primary aqueous inclusions in about 70 apatite grains using a previously calibrated Leitz 1350 microscope heating stage; 195 of the inclusions homogenized to the liquid phase (208–425 °C) and one inclusion from each of the five samples homogenized to the gas phase (408–466 °C), (Table III, Fig. 4).

All the daughter phases, apart from the opaque minerals, dissolved completely in the inclusion fluid below the homogenization temperature. The failure of the opaque phases to dissolve, even after prolonged heating of the sample, may simply mean that equilibrium was not attained between this phase and the inclusion fluid during the time taken for the heating runs. Alternatively, it may imply that these phases are not true daughter minerals but captured mineral phases.

Two of the inclusions used for homogenization temperature determinations contained captured calcite crystals and five contained the captured mineral phase denoted by U in the photomicrographs. Homogenization of the gas and liquid phases in these inclusions occurred without noticeable solution of the captive phases. Continued heating past the homogenization temperature caused slight corrosion of the calcite, but not of the unidentified phase U, before the inclusions finally decrepitated.

Heating of 'normal' aqueous inclusions above their homogenization temperatures also resulted in decrepitation. None of these runs above homogenization showed phase changes in

the fluid similar to those previously described (Rankin, 1975) in inclusions in apatite from the Wasaki sovite (i.e., growth and subsequent solution of a Na_2CO_3 phase), possibly because they decrepitated before a high enough temperature could be obtained.

There appears to be no correlation between the homogenization temperature of an inclusion and its bulk composition, i.e., presence or absence of the various daughter and captured mineral phases.

TABLE II. *Frequency of occurrence of daughter minerals in primary aqueous inclusions in apatite from the Tororo carbonatites*

Sample Ref. Number	20	22	26	108	112
Daughter Mineral	Percentage of inclusions containing indicated daughter mineral				
Nahcolite (Nh)	42	40	20	2	19
Non-magnetic opaques	11	30	36	0	0
Pyrrhotite platelets	0	0	0	4	24
Acicular needles	0	0	0	6	0
Yellow, anisotropic phase (Y)	0	0	0	27	0
Small specks of other birefringent solids	12	2	1	2	8
Percentage of inclusions which do not contain daughter phases	31	30	36	48	52

Errata: Col. 1, *add below last line:* or captured mineral phases.

TABLE III. *Summary of homogenization temperatures recorded for aqueous inclusions in apatite from the Tororo carbonatites*

Sample Ref. number	20	22	26	108	112
Number of determinations	47	36	34	46	37
Maximum Temperature (°C)	408*	466*	432*	436*	427*
	(407)	(412)	(418)	(418)	(425)
Minimum Temperature (°C)	230	246	241	266	208
Standard Deviation	41.9	44.8	43.9	32.3	39.7
Mean Temperature (°C)	328	321	359	353	365
Confidence limits of mean (at 95% level)	12.3	15.2	15.3	9.6	13.2

*Homogenisation was to the gas phase in these five inclusions. It is believed that these inclusions have necked and, therefore, the figure in parentheses represents true maximum homogenisation temperatures (to liquid).

Discussion of homogenization temperature data. The temperature range obtained for all samples is relatively large. Inclusions that have necked often give anomalously high or low T_h values, which represent incorrect minimum formation temperatures (Roedder, 1967). Great care was taken to avoid studying necked inclusions. Therefore, the wide spread of data is, for the most part, real and reflects true variations in the minimum formation temperatures. However, the five inclusions that atypically homogenized to the gas phase at anomalously high temperatures are considered to have necked.

With the exception of sample 26, the T_h values for the Tororo rock samples are slightly lower than for the Limekiln Hill samples. Student's *t* tests show that the T_h results for sample 26 are significantly different at the 95% confidence level from the T_h data for the other two samples (20 and 22). In fact, the distribution and means of the T_h values for this sample are closely comparable with those for the Tororo Rock specimens (Table III, fig. 4). Consequently,

it is not possible to make generalizations about the similarity or dissimilarity of the T_h data from the two separate complexes.

Positive temperature corrections, often referred to as 'pressure corrections', need to be added to the T_h data to obtain actual formation temperatures (Roedder, 1967). This requires an independent estimate of the pressure prevailing during crystallization and knowledge of the compressibility of CO_2-rich, alkali-carbonate fluids. Because neither of these are currently
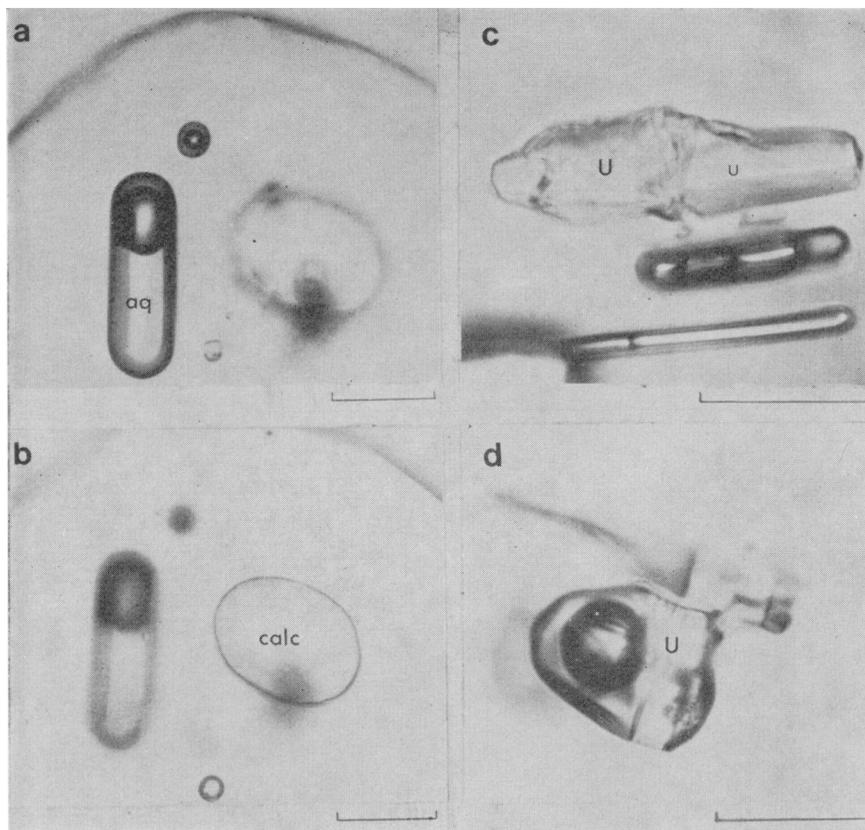
FIG. 3. Other primary inclusions in apatite from the Tororo carbonatites. (a) and (b) Cogenetic aqueous inclusion (aq) and spheroidal, monocrystalline inclusion of calcite (calc). Bar = 20 μm. (c) Monocrystalline inclusion of an unidentified solid (U). Bar = 20 μm. (d) Complex inclusion containing crystals 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) are from SUTO 108; (d) is from SUTO 112.

available, the magnitude of these corrections cannot be evaluated. They could be as high as 250 °C or as low as 25 °C. The T_h data, therefore, only give the minimum formation temperature ranges of the apatites.

Previous estimates of the formation temperatures of carbonatites using geothermometers based on isotopic and chemical equilibria and mineral stabilities are generally within the late magmatic to hydrothermal temperature range, 300 °C to 700 °C (summarized by Heinrich, 1966, and by Mitchell and Krouse, 1975). A similar temperature range for minerals from carbonatites has also been reported on the basis of fluid inclusion geothermometry (summarized by Rankin, 1975). The mean minimum formation temperatures of the Tororo carbonatite
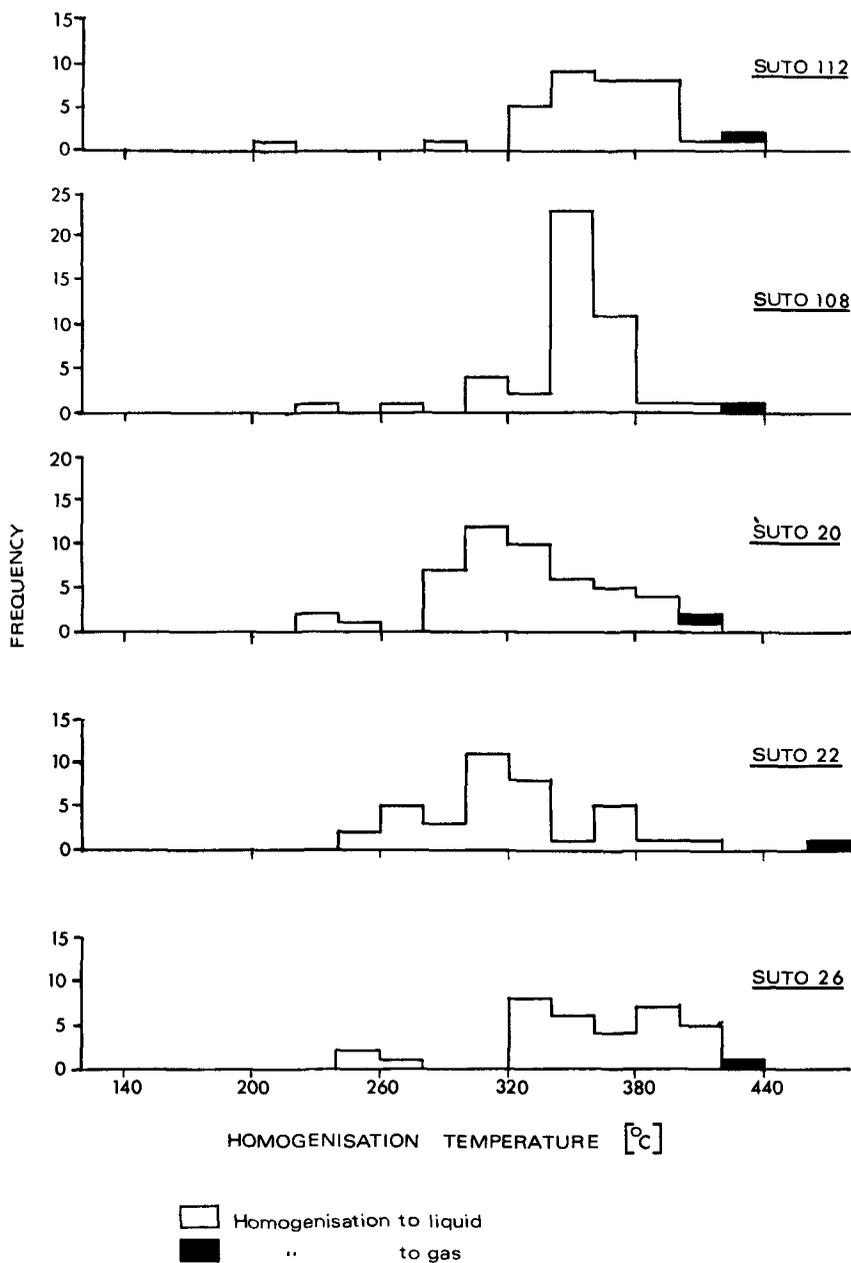
FIG. 4. Homogenization temperatures of aqueous inclusions in apatites from the Tororo carbonatites.

apatites (mean T_h for the five samples; 321 °C to 365 °C) obtained in this study are, therefore, well in accordance with previous thermometric data even allowing for a few hundreds of °C pressure correction.

Conclusions

Sutherland (1966) has previously recognized hydration as an important process associated with the emplacement of the Tororo carbonatites. Recent isotope (Pineau *et al.*, 1973; Lancelot

and Allegre, 1974) and rare earth data (Loubet *et al.*, 1972) on these carbonatites also indicate that CO_2-bearing aqueous fluids played a significant role in the formation of these carbonatites. This present study clearly shows that such fluids, trapped and preserved as primary fluid inclusions within the apatites, are indeed important. The predominance of nahcolite as a daughter mineral in the inclusions in apatite from four of the samples studied (all except sample 108) further shows that these fluids are essentially alkali-carbonate brines and once again (Rankin, 1975) confirms that carbonatitic fluids can contain considerable amounts of alkalis as originally suggested by von Eckermann (1948) and recently restated by Gittins *et al.* (1975).

There is little doubt that the apatites from these four samples crystallized directly from this fluid. The possibility that they may have formed from a melt and that the aqueous inclusions merely represent a coexisting aqueous phase is unlikely because melt inclusions, a common phenomenon in naturally-occurring and synthetic melt-grown apatites (Wyllie *et al.*, 1962; Kogarko, 1971; Eysel and Roy, 1973; Rankin, 1975) have never been observed in the Tororo carbonatite apatites, and because acicular apatite crystals, thought to be indicative of the former presence of a melt in a rock (Wyllie *et al.*, 1962), are absent from the Tororo carbonatites.

Aqueous inclusions in apatite from one of the Tororo Rock samples (108) differ somewhat in composition from the aqueous inclusions in apatite from other samples as shown by the predominance of two additional unidentified, water-soluble daughter minerals over the less common nahcolite. Solid inclusions of an unidentified captive mineral phase are also present in these apatites and further show that the chemical composition of the fluids from which these apatites crystallized, though still essentially aqueous, CO_2-bearing solutions, are more complex than simple alkali carbonate brines.

The common occurrence of primary calcite inclusions cogenetic with aqueous inclusions in apatite shows that some early calcite was present in the aqueous fluid as a precipitated phase at the time the apatites crystallized. Unfortunately, it was not possible to obtain direct fluid inclusion evidence for the formation conditions of calcite from the carbonatites. However, these indirect observations indicate that alkali-carbonate fluids may also be responsible for the transport and deposition of at least some of the calcite. This contention is substantiated by recent experimental studies of Malinin and Dernov-Pegarev (1974) who showed that appreciable quantities of calcite (up to 24g $CaCO_3$/1000 g of solution) can indeed be transported by alkali-carbonate solutions, even at low temperatures (200–350 °C).

The fluid inclusion evidence that carbonatitic material (apatite and at least some calcite) can be precipitated directly from aqueous alkali carbonate solutions at relatively low temperatures is not at variance with the consensus of opinion that carbonatites are igneous rocks. The field relationships of the Tororo carbonatites (King and Sutherland, 1966) certainly indicate a magmatic origin, but as shown by the experimental studies of Wyllie and his co-workers (Wyllie, 1966), carbonatite magmas can exhibit continuous transitions from true carbonate melts to dilute hydrothermal fluids or so-called 'carbothermal solutions'. In the light of fluid inclusion data it is apparent that carbothermal processes are more important in these and other carbonatites (Rankin, 1973 and 1975) whilst in others the fluid-inclusion evidence points to formation from a classical carbonate melt at relatively high temperatures (Romanchev, 1972).

REFERENCES

Eckermann (H. von), 1948. *Sveriges geol. Unders.* no. 36.
Eysel (W.) and Roy (D. M.), 1973. *J. Crystal Growth*, 20, 245.
Girault (J.), 1966. *Bull. Soc. fr. Minéral. Cristallogr.* 89, 496.

Gittins (J.), Allen (C. R.), and Cooper (A. F.), 1975. *Geol. Mag.* **112**, 503.
Heinrich (E. W.), 1966. *The Geology of Carbonatites*. Rand, McNally and Co., N.Y.
King (B. C.) and Sutherland (D. S.), 1966. In: *Carbonatites* (O. F. Tuttle and J. Gittins, eds.) Interscience.
Kogarko (L. N.), 1971. *Geochem. Int.* **8**, 90 (Translated from Russian).
Lancelot (J. R.) and Allegre (C. J.), 1974. *Earth Planet. Sci. Lett.* **22**, 233.
Loubet (M.), Bernat (M.), Javoy (M.), and Allegre (C. J.), 1972. Ibid. **14**, 226.
Malinin (S. D.) and Dernov-Pegarev (V. F.), 1974. *Geokhimiya,* **3**, 454.
Mitchell (R. H.) and Krouse (H. R.), 1975. *Geochim. Cosmochim. Acta* **39**, 1505.
Pineau (F.), Javoy (M.), and Allegre (C. J.), 1973. Ibid. **37**, 2363.
Rankin (A. H.), 1973. Ph.D. Thesis, Univ. Leicester.
—— 1975. *Lithos,* **8**, 123.
—— and LeBas (M. J.), 1974. *Mineral. Mag.* **39**, 564.
Roedder (E.), 1967. In: *Geochemistry of Hydrothermal Ore Deposits* (H. L. Barnes ed.) Holt, Rinehart and Winston.
Romanchev (B. P.), 1972. *Geochem. Int.* **9**, 115 (Translated from Russian).
Sutherland (D. S.), 1966. Ph.D. Thesis, Univ. London.
Wyllie (P. J.), 1966. In: *Carbonatites* (O. F. Tuttle and J. Gittins, eds.) Interscience.
—— Cox (K. G.) and Biggar (G. M.), 1962. *J. Petr.* **3**, 238.

[Manuscript received 20 May 1976, revised 27 August 1976]