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The composition of solid inclusions and the occurrence of shortite in apatites from the Tororo carbonatite complex of eastern Uganda

J. A. ASPDEN

Institute of Geological Sciences, Keyworth, Nottingham, England

ABSTRACT. Apatite concentrates obtained from a carbonatite of the Tororo complex contain cogenetic fluid and solid primary inclusions. The solid inclusions are commonly composed of calcite and shortite and these minerals, together with the host apatite, were deposited from aqueous fluids at approximately 400 °C.

IN his study of primary inclusions in apatites from the Tororo carbonatite complex of eastern Uganda, Rankin (1977) recognized the presence of cogenetic aqueous and solid inclusions. The aqueous inclusions, which represent trapped portions of the 'carbonatitic fluid', consist of a vapour bubble, an aqueous solution, and varying amounts of daughter minerals. The solid inclusions, which are formed by the trapping of pre-existing solids, are usually monomineralic but occasionally contain more than one crystalline phase together with minor amounts of aqueous fluid. As pointed out by Rankin (1977), neither melt inclusions, which are common in naturally occurring and synthetic melt-grown apatites, nor acicular apatites, which are believed to indicate the former presence of a melt, have been observed in the Tororo samples.

This paper complements the earlier work of Rankin in that, by using a combination of optical and microchemical tests, as well as electron-microprobe analysis (EMPA), it confirms the presence of calcite and identifies shortite ($Ca_2Na_2(CO_3)_3$—phase 'U' of Rankin), pyrrhotine, and magnetite as solid-inclusion phases in sample S108. Individual grains of apatite which contained suitable inclusions were mounted in araldite and polished using 5 μm diamond paste and an oil-based lubricating fluid. During polishing the apatites were examined in reflected light and, in order to avoid excessive plucking out of material, immediately the inclusion contents were exposed polishing was stopped. The specimens were then cleaned with a paper tissue dampened with carbon tetrachloride and re-examined in transmitted light before probing.

Composition of the solid inclusions

Calcite. Inclusions consisting of rounded crystals of a highly birefringent mineral (> 0.15) are common within the apatites. This mineral was identified as calcite by Rankin (1977) and the identification confirmed by EMPA, using X-ray scanning photographs (e.g. fig. 2). Monocrystalline inclusions of calcite are relatively common in carbonatitic apatites (e.g. Rankin, 1975; Girault, 1966) and they have also been recognized in apatites from both Alnö and Usaki ijolites (Aspden, 1980, 1977).

Shortite ($Ca_2Na_2(CO_3)_3$). Although calcite forms the most conspicuous solid inclusion phase, similar, but often smaller, inclusions which are composed of a colourless to pale-yellow mineral are widespread. Several such inclusions may occur within a single grain of apatite and they often occur alongside crystals of calcite (fig. 1A). Occasionally both minerals are observed within the same inclusion (fig. 1B). The second mineral is believed to be shortite for the reasons outlined below.

Individual crystals are usually slightly prismatic to rectangular in shape. The mineral is length-fast and has a straight extinction. It has a low to moderate birefringence (approximately 0.04) but it is identified as a carbonate by its positive reaction with cold dilute HCl. A total of twelve of these inclusions have been analysed qualitatively using the probe and in each case they were found to consist of Ca/Na carbonates.

Several such carbonates are known to occur naturally and these include the following: shortite, nyerereite ($CaNa_2(CO_3)_2$), pirssonite ($CaNa_2(CO_3)_2.2H_2O$), and gaylussite ($CaNa_2(CO_3)_2.5H_2O$). Of these minerals, shortite, which is orthorhombic and has a birefringence of 0.039 (Fahey, 1939), has the optical properties which best fit the observations recorded from the solid inclusions. The birefringence values of both pirssonite and gaylussite (0.0694 and 0.0798 respectively, Winchell and Winchell, 1964) are considerably higher than that calculated for the solid inclusions. Furthermore, these minerals break down well below 353 °C (Milton and Evans, 1973), which is the mean minimum formation-temperature recorded for the apatites in this sample (Rankin, 1977). Similarly, although naturally occurring nyerereite which is found in the carbonatite lavas of the Tanzanian volcano Oldoinyo Lengai (Dawson, 1962*a*, 1962*b*) is orthorhombic (McKie and Frankis, 1977), it has a maximum birefringence of 0.0232 and characteristically shows cross-hatched twinning in basal sections. Since such twinning has not been observed, and in view of the rather low birefringence value of the natural mineral (c.f. Cooper *et al.*, 1975), it appears unlikely that the Ca-Na carbonate recognized within the Tororo apatites can be nyerereite.

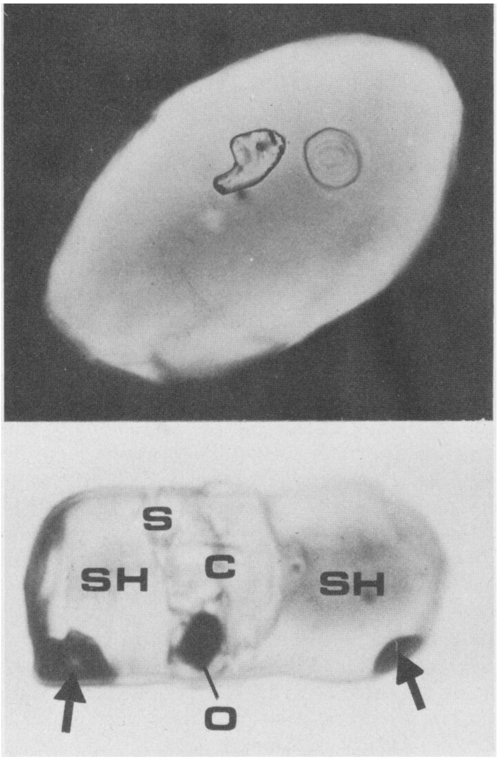

FIG. 1A (*top*). A single crystal of apatite containing a rounded solid inclusion of calcite and a more irregular-shaped inclusion of shortite. Magnification × 300. FIG. 1B (*lower*). A solid inclusion consisting of shortite (SH), calcite (C), an unidentified silicate speck (S), and an opaque phase (O). Small amounts of vapour are also present (arrowed). This inclusion is unusually complex, but the crystal of calcite and the silicate and opaque specks are themselves regarded as solid inclusions which were captured during the growth of the shortite crystal prior to its entrapment by apatite. Magnification × 1000.

In an attempt to determine more closely the composition of the carbonate, several solid inclusions were analysed quantitatively and the Ca and Na contents, determined as oxides, converted to carbonates by assuming stoichiometry. Phosphorus was run at the end of each analysis in order to avoid possible interference from the host apatite, but because of the difficulties of sample preparation, particularly in the case of the smaller inclusions, some of the specimens have rather irregular surfaces and consequently low totals are often

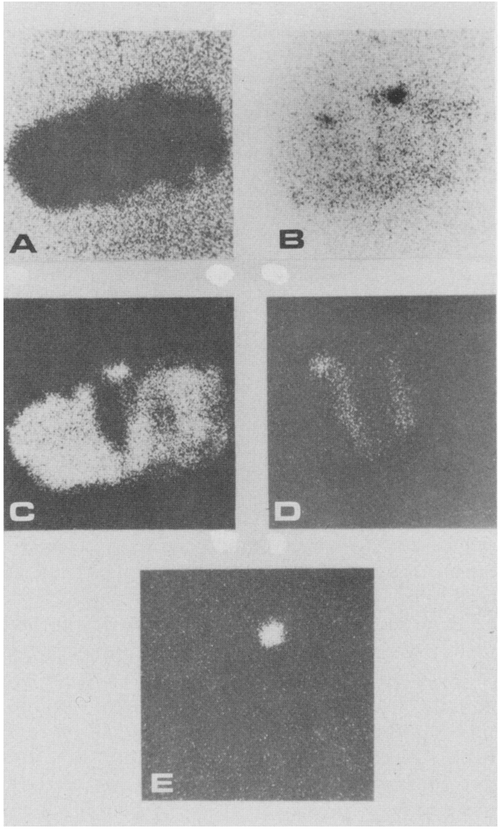

FIG. 2. Series of electron-probe scanning photographs obtained from the inclusion shown in fig. 1B. The inclusion is dominated by the Ca-Na carbonate, shortite, but also contains a centrally placed crystal of calcite and an unidentified silicate. The opaque phase visible in fig. 1B was plucked out during polishing. A narrow zone of K enrichment is present within the shortite at its junction with the calcite. The nature of this zone remains uncertain. The quantitative analyses from this inclusion are given in Table I. A = P; B = Ca; C = Na; D = K; E = Si. Magnification × 500. (Note that the optical image is the reverse of the scanning image and hence the silicate appears on the rhs of the calcite crystal and not the lhs as in fig. 1B.

recorded (Table I). In spite of these shortcomings, when the analyses are recalculated to 100% and plotted in the $CaCO_3$-Na_2CO_3 binary (fig. 3), all but two of them show a good clustering around shortite and this, together with the optical observations, indicates the presence of the mineral within the Tororo apatites.

TABLE I. *Electron microprobe analyses (wt%) of the solid inclusions.*

$CaCO_3$	Na_2CO_3	Total
*62.5	38.3	100.8
*62.4	38.3	100.7
*99.3	0.0	99.3
61.2	33.2	94.4
66.9	33.7	100.6
68.2	26.4	94.6
65.2	34.9	100.1
54.7	38.0	92.7
57.6	37.1	94.7
15.8	84.2	100.0
5.7	81.6	87.3

* See figs. 1A and 2.

Mixed inclusions of shortite and Na-rich carbonate. Although the majority of inclusions consist of discrete, optically uniform crystals, occasionally shortite occurs intimately mixed with a poorly crystalline mineral which shows pale high-order interference colours and has been identified as a Na-rich carbonate. Quantitative analysis of this phase proved to be difficult, largely because of its small size and irregular shape, but two analyses obtained from a single specimen confirm the Na-rich nature of this mineral (Table I and fig. 3).

Opaque inclusions. The Tororo apatites contain both pyrrhotine and magnetite as solid inclusions. Pyrrhotine, which is also present in the aqueous inclusions (Rankin, 1977), forms distinctive black hexagonal plates and EMPA indicates an Fe/S ratio of approximately 1 : 1. Inclusions of magnetite are less common but this mineral is identified on the basis of its cubic outline and because it is a common accessory in the host rock from which the apatites were extracted.

Silicate inclusions. Inclusions composed entirely of silicates seem to be absent, but small (< 5 μm) silicate specks have been detected within four solid inclusions (e.g. fig. 2). Quantitative analyses are not available, but in each case they were found to contain Mg and lesser amounts of Fe. Al and Ca were not present.

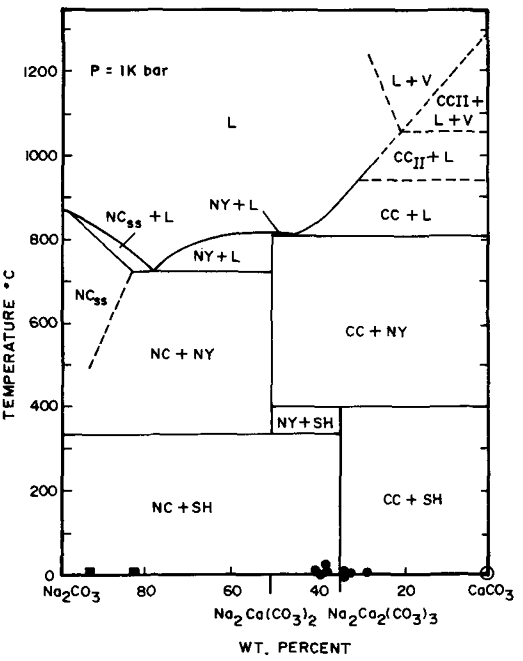

FIG. 3. $CaCO_3$-Na_2CO_3 binary after Cooper *et al.*, 1975, showing the position of the analyses in Table I. V = vapour; L = liquid; NC = Na_2CO_3; CC = $CaCO_3$; NC_{ss} = Na_2CO_{3ss}; NY = $Na_2Ca(CO_3)_2$; SH = $Na_2Ca_2(CO_3)_3$.

Discussion

Although pyrrhotine and magnetite, as well as minor silicates, are found within the Tororo apatites these phases are relatively minor compared to both calcite and shortite. Shortite, which occurs as an authigenic mineral in the Green River Formation, Wyoming (Fahey, 1939), has not been previously reported in carbonatites but it has been recorded in kimberlite (Watkinson and Chao, 1973), where it is thought to form as a result of the subsolidus breakdown of nyerereite (Gittins and Cooper, 1974). However, since the *majority* of shortite inclusions within the Tororo apatites consist of optically uniform single crystals, there can be little doubt that this mineral, along with calcite, was present as a stable phase within the carbonatitic fluid.

Several workers have independently noted the importance of an aqueous phase in the development of the Tororo carbonatite complex (Sutherland, 1966; Loubet *et al.*, 1972; Lancelot and Allegre, 1974; Rankin, 1977). These data are also supported by the present study because, as shown in fig. 3, in the system $CaCO_3$-Na_2CO_3 the assemblage calcite + shortite (CC + SH) does not appear on the liquidus and could not therefore crystallize directly from an anhydrous 'carbonatite' melt.

In view of the high-level nature of the present outcrop in the Tororo complex (Heinrich, 1966), it seems unlikely that the apatites could have formed much in excess of 1 kb. Under these conditions shortite will have an upper-temperature stability of approximately 400 °C (Frankis and McKie, 1973), but above this temperature it is replaced by nyerereite as the stable double carbonate. Although mixed inclusions of shortite and Na-rich carbonate are present, inclusions consisting *entirely* of Na-rich carbonate have not been recorded either optically or by EMPA. The absence of such inclusions is interpreted as indicating that sodium carbonate did not exist as a solid phase and the mixed inclusions are considered to represent the product of the subsolidus breakdown of nyerereite.

As noted above, the common occurrence of shortite and calcite indicates that the bulk composition of the carbonatitic fluid must, for the most part, have lain within the CC + SH field. However, relatively small changes in either the composition and (or) temperature of this fluid would be sufficient to bring about the formation of nyerereite. In synthetic 'carbonatite' systems apatite has a wide temperature interval of crystallization (Wyllie, 1966). It therefore seems likely that, during the early stages of inclusion formation, a small amount of nyerereite could have existed, but as the temperature (or Na content) decreased then this would be replaced by shortite. Hence the solid inclusions are thought to have formed over a range of temperature, the precise limits of which are unknown, but probably close to 400 °C, i.e. the upper temperature limit of stability of shortite.

Published estimates, based on homogenization studies carried out on the aqueous inclusions present in this sample, range from 266–418 °C (mean 353 °C) (Rankin, 1977). These values are uncorrected for pressure and represent the minimum formation temperatures for the apatites. Based on the information provided by the solid inclusions, a mean temperature correction of approximately 50 °C would appear appropriate.

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