Calzirtite and the mineralogy of residual soils from the Bukusu carbonatite complex, south-eastern Uganda

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Summary. Calzirtite, essentially $CaTiZr_3O_9$, has been identified in residual soils from the Bukusu carbonatite complex in Uganda. A satisfactory ultrasonic technique was developed for cleaning the samples prior to studying their mineralogy. Other heavy minerals present include ilmenite, perovskite, melanite, apatite, zircon, and baddeleyite. The properties and composition of calzirtite are compared with the available data from occurrences in the U.S.S.R. The mineral has a metasomatic paragenesis and probably indicates the presence of carbonatized rocks at depth.

THE rare calcium titano-zirconate calzirtite has been discovered in eluvial soils derived from the Bukusu carbonatite complex in south-eastern Uganda. Calzirtite has previously been described from at least three localities in the U.S.S.R. and from a complex in Brazil, but its occurrence at Bukusu seems to represent the first reported discovery of the mineral anywhere in Africa (Baldock, 1967). The mineral was identified at several localities within the complex during a detailed reinvestigation of Bukusu undertaken for the Geological Survey of Uganda and later as a research project at Leeds University. As part of the economic reappraisal and to aid the sub-soil 'mapping' of Bukusu, a comprehensive study of the mineralogy of the residual *terra rossa* deposits overlying much of the centre has been carried out in conjunction with, *inter alia,* the delineation of the secondary geochemical dispersion patterns of trace elements characteristic of ultrabasic or carbonatite complexes.

Sample treatment. The residual mineral constituents of typical tropical soils are so coated with iron oxides and admixed with a clay fraction that treatment is needed before the samples can be examined. The method found to be most suitable for cleaning the soils was a modification of a technique suggested by Dr. T. Deans of the Institute of Geological Sciences, London. The process is carried out in glass beakers suspended with a wetting agent in a water-filled 20 kc ultrasonic tank and yields cleaner, better-preserved concentrates of the distinctive crystalline minerals than does a method employing an ultrasonic probe. Two 25 g soil samples can be thoroughly but gently cleaned in about one hour, during most of which time they need no attention. However, a two-stage procedure is necessary to avoid solidification of the fine clays with consequent stagnation of the sample; using a tank of higher frequency merely intensifies this undesired effect. Four samples can be treated simultaneously by suspending the two pairs of beakers in a frame above the tank. The soil is first subjected to ultrasonic cleaning above a 300-mesh nylon sieve, which is held in a 'Perspex' frame near the top of a one-litre beaker. The liberated clays and iron oxides sink through the sieve to collect as a sludge in the bottom of the beaker, while resistates of a size $> 50\ \mu$ (+300 mesh) are retained above. Complete cleaning is achieved by transferring the sample to another (600 ml) beaker for direct exposure to ultrasonic agitation. The thick iron oxide coating of the mineral grains is soon removed and limonitic nodules are easily broken down in this way. The cleaned residua were subsequently separated into heavy, light, and magnetic fractions using heavy liquids and a strong hand magnet; the constituent minerals were identified by optical and X-ray powder photographic means.

Soil mineralogy. In the light fractions quartz and feldspar were found to be the only important constituents, but even in soils almost certainly overlying alkaline undersaturated and ultrabasic rocks at depth both these minerals are common. In the eluvial *terra rossa* at Bukusu the dominant non-magnetic heavy resistates are ilmenite and perovskite with ubiquitous leucoxenic anatase. Zircon is common in many samples, being dominantly pink to red and of prismatic habit when derived from the Basement granitoid gneisses but colourless to pale pink and usually bipyramidal in soils overlying the complex itself. All samples carry traces of crystalline apatite, but large concentrations of ellipsoidal apatite are restricted to particular areas at Bukusu and thus assist in delineating the subsoil distribution of the carbonatite itself. Baddeleyite, schorlomite (titaniferous andradite), diopside, tremolite, and hornblende are locally plentiful but the last three, with vermiculite, only become major constituents in deeper soil horizons 20 to 40 ft below the surface.

Octahedral pyrochlore, which is the most distinctive and characteristic mineral in residual deposits at many other carbonatite complexes, such as Sukulu, Lueshe, and Chilwa, occurs extremely rarely in the soils overlying Bukusu. Dark red to brown octahedra are in fact very common, but these have, in all cases, been confirmed by X-ray powder photographs to be perovskite. Qualitative X-ray fluorescent and electron microprobe analyses have shown that they contain minor or trace amounts of niobium, although this element was not originally detected in the rare-earth bearing perovskite (knopite) samples from the Surumbusa area of Bukusu (Broughton *et al.*, 1950).

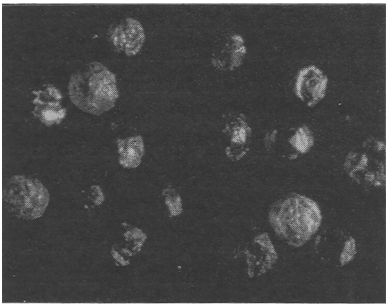

FIG. 1. Calzirtite from Nambara, E. Bukusu. Polyhedral and rounded grains of pale to deep wine-red calzirtite from cleaned soil sample; idiomorphic crystal faces and zoning show in some grains. ×15.

The *calzirtite* found at Bukusu is usually pale to deep wine-red in colour, although a pale yellow-green variety occurs much more rarely. Minor concentrations of the mineral occur at two localities, but it is not abundant in any of the samples studied. Typical rounded, reddish crystals with partially preserved polyhedral outlines closely resemble garnets at first sight but are also very similar to the deep red-brown calzirtite from the type area in the Aldan province of south-east Siberia (Zdorik *et al.*, 1961). Rare idiomorphic crystals have distinctive habits (fig. 1), resembling those of the calzirtite from the Gula ultrabasic complex in polar Siberia (Zhabin *et al.*, 1962). The greenish variety is anhedral and more like that described from the only other reported occurrence outside the U.S.S.R., at Tapira, Brazil (van der Veen, 1965).

Identification of the mineral by X-ray powder photography confirms that the pattern is very similar to that of pyrochlore but for the absence of the lowest-angle strong pyrochlore line and a slightly wider line-spacing (fig. 2), indicating a smaller cell size. The crystal structure thus also resembles that of uraninite and has been shown to be pseudo-cubic, a derivative of the CaF_2–CeO_2 structural type (Pyatenko and Pudovkina, 1961). Optically the calzirtite from Bukusu has very high refractive indices but low birefringence and is uniaxial positive, with other properties apparently identical to the tetragonal Siberian type. Its distinctive habit, brighter red colour and adamantine lustre enable calzirtite to be distinguished from the much more common red-brown perovskites or garnets.

Semi-quantitative analyses obtained by comparing individual crystals with those of the type Siberian material (loaned by Dr. T. Deans) on the electron microprobe indicate that the calzirtite from Bukusu is relatively enriched in calcium and titanium at the expense of zirconium while the iron content may either be much lower or slightly higher. These differences have been confirmed by a chemical analysis carried out by Dr. von Knorring on a pure hand-picked sample of 0·10 g, but nevertheless show that this calzirtite bears a fairly close relationship to the theoretical composition of $CaTiZr_3O_9$—equivalent to $CaTiO_3+3ZrO_2$ or one part perovskite and three parts baddeleyite. Nb_2O_5 was not determined, but a qualitative X-ray fluorescence analysis shows it to be present.

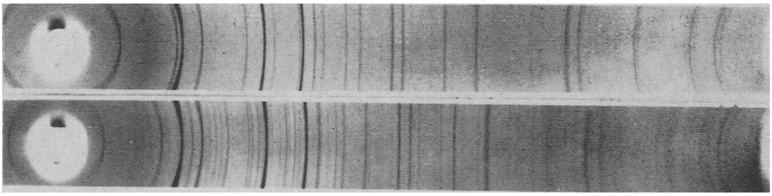

FIG. 2. X-ray powder photographs of pyrochlore from Sukulu (above), and calzirtite from Bukusu (below). (11·46 cm camera Cu-$K\alpha$ radiation, nickel filter.)

ZrO_2 66·2, TiO_2 18·1, CaO 13·3, Fe_2O_3 0·4, SiO_2 0·8, Nb_2O_5 n.d., ign. loss 0·6, H_2O −0·1, total 99·5 %

Paragenesis. The type material from Aldan, Siberia, occurs in metasomatic calcite–forsterite–magnetite rocks of an alkaline ultrabasic massif (Zdorik *et al.*, 1961); it probably occurs in the same environment in the Sebel–Järvi alkaline complex, Kola Peninsula, but has been obtained from carbonatite itself in the Gula massif (Zhabin *et al.*, 1962). Distinct concentrations of the mineral at two localities (Nambara and Nakupa) within Bukusu suggest that it has a similar (metasomatic) paragenesis at this complex. Calzirtite does, however, occur in the soil with perovskite, baddeleyite, and zircon so that the stability conditions under which it would form are not known. However, it seems probable that this mineral is confined mainly to metasomatically carbonatized rocks, such as phoscorite (apatite–magnetite–forsterite–carbonate rock) or in some cases to carbonatite itself. Identification of calzirtite in soil samples from unexposed areas is therefore thought to indicate the possible presence of carbonatized rocks at depth. Investigation of the soil mineralogy at other carbonatite complexes might disclose further occurrences of calzirtite and confirm the conclusions reached from this first discovery of the mineral at any alkaline complex in Africa.

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