The occurrence of rutile, brookite, and anatase on Dartmoor.[1]

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[Read January 9, 1923.]

Modes of Occurrence and Distribution.

THE occurrence of brookite and anatase within the limits of the Dartmoor granite exposure was first indicated by a sample of stream-sand taken two years ago below the bridge at Dartmeet—a locality which is noteworthy for sands rich in these and other accessory minerals of the Dartmoor granite.

Anatase, either alone or associated with brookite in small amounts, was found in a majority of the sands taken the following year at selected points along (1) the Plym River, between Cadover Bridge and Harter Tor, (2) the East Dart and the West Dart, upstream from Dartmeet, (3) the West Webburn, upstream from Ponsworthy, (4) the East Webburn, upstream from Lizwell Meet, and (5) minor streams in the Hamel Down-Bonehill Down area. Rutile proved to be a rare mineral, liable to be overlooked in a residue containing brown cassiterite, from which it cannot readily be distinguished except by microchemical means.

Concentrates from crushed samples of sound grey granites have yielded neither brookite nor anatase; and rutile grains, in almost negligible amount, have been verified in only five samples: a garnetiferous variety of the so-called 'giant granite' from Chinkwell Tor, more normal varieties of this type from Saddle Tor and Tunhill Rocks, a fine-grained type from The Nutcrackers, Rippon Tor, and a Pudsham Down boulder.

[1] This is the first of a series of papers on the Dartmoor granite, of which a preliminary account was read before the Society on June 27, 1922.

The source of the stream-sand occurrences remained in doubt until anatase and brookite were found to be abundant in the pinkish sand taken from the pit on pneumatolysed granite at Lock Gate Cross, near Ponsworthy. An examination of this granite and of similar types from other localities brought to light both brookite and anatase, which were associated in approximately the same relative proportions as those previously noted. The yield of these minerals from the crushed rock was out of all proportion to the amount anticipated from the evidence of thin sections alone.

Noteworthy localities for red granite with a brookite-anatase content include the following: Blackaton Down (near the ford); Challacombe; Hamel Down (above Widecombe); Rowden Down (small quarry on the road to Lower Cator); Ponsworthy (immediately south of the bridge); Lock Gate Cross; Sharp Tor, &c.

Apart from its occurrence in red granite, anatase, either alone or in association with brookite, has been found in 39 out of 53 sands representative of stream beds, sand pits, warrens, and sub-soils at various localities between Manaton, Haytor, and Cold East Cross on the east and a N.–S. line through Princetown on the west. With three exceptions the barren samples were high-level warren-sands and sub-soils, though the samples containing anatase alone include four warren-sands and seven sub-soils. The presence of anatase in high-level sands, &c., may be an index to red granite at little depth below the surface (e.g. on the col between Chinkwell and Honeybag Tors) or in the immediate neighbourhood (e.g. below the north face of Rippon Tor); but the possibility of there being another mode of origin for this mineral is discussed in a later section of this paper. The presence of brookite in such sands proves to be a much more certain index (e.g. at Lock Gate Cross and pits on Sherberton Common); occasionally it is of similar significance in low-level pits, e.g. below and east of Rowden Down.

Genesis.

On the basis of texture, &c., the various types of normal grey granite can be ranged in parallel series with the red pneumatolysed types. In the unaltered grey types the total content of minerals which sink in bromoform shows a distinct tendency to rise with degree of coarseness in grain and with content of felspar phenocrysts. The most abundant of the heavy minerals is biotite containing up to 2·04 % of titania, and with it are associated, in varying amounts, ilmenite (usually in excess of magnetite), apatite, zircon, monazite, sphene, pyrrhotite, pyrites, garnet, and some others in insignificant amount. Adopting the percentage by weight of these heavy minerals as the 'index figure' for a rock type, it is found that the index figures for a red granite and its presumed original are usually of about the same order; but the mineral assemblages differ: in the severely pneumatolysed types the assemblage comprises anatase, brookite, tourmaline, non-sulphidic ore, together with zircon, often monazite, and sometimes fluor, topaz, and cassiterite. It is clear that apatite, biotite, sphene, and to a less extent ilmenite, &c., tend to be destroyed during pneumatolysis, and that their constituent oxides become contributory to the tourmaline-brookite-anatase association. As regards mass change, the net effect is probably to add material to the rock, which may nevertheless become somewhat drusy. But increment is not opposed to the conclusion arrived at that the tourmaline-brookite-anatase-ilmenite assemblage is roughly equivalent in mass to the original biotite-ilmenite-sphene assemblage.

The breakdown and reconstitution of titaniferous species during pneumatolysis appears to be the main mode of genesis for the Dartmoor brookite and anatase—probably the only mode for the brookite. Whether, and to what extent, titania is present in water of deep-seated origin which may gain access to the rock during the process remains a speculation. The possibility, however, that anatase may arise in another way is suggested by the following considerations:

Stream-sands from the East Dart, the Plym, and the West Webburn have yielded grains of ilmenite encrusted with granules of anatase, but no grains comparable to these have been observed in concentrates from crushed grey granite. On the other hand, recorded occurrences of anatase as an alteration product of ilmenite are numerous. Moreover, in three cases at least, high-level sands, &c., on Dartmoor have yielded anatase without brookite though there is no evidence that pneumatolysed granite occurs either just below or in the immediate locality. Further data were provided by the results of a chemical investigation of the Dartmoor biotite.

By prolonged boiling with strong hydrochloric acid the biotite is bleached to the silvery white, flaky substance 'bauerite'[1] closely resembling muscovite in appearance; this substance floats in bromoform. Samples of (*a*) the biotite, and of (*b*) the partially bleached and (*c*) the

[1] F. Rinne, 1911 [Min. Mag., vol. 16, p. 355]; O. Dreibrodt, 1912 [Journ. Chem. Soc., 1913, Abstr. ii, p. 868]; V. M. Goldschmidt and E. Johnson, 1922 [Min. Abstr., vol. 2, p. 32].

completely bleached residues were prepared and analysed. The biotite used was isolated from the granite of Haytor east quarry.

	(a) Biotite.	(b) Residue—partially bleached.	(c) Residue—completely bleached.
SiO_2	34·65	76·37	80·69 %
Al_2O_3	20·37	6·19	3·62
Fe_2O_3	3·49	0·86	0·49
FeO	18·48	nil	nil
MgO	5·25	0·30	nil
CaO	0·76	0·87	0·51
Na_2O	0·53	2·53	0·64
K_2O	8·31	3·24	1·40
Li_2O	0·32	n.d.	n.d.
TiO_2	1·77	1·23	0·61
H_2O (below 110° C.)	1·00	0·86	6·96
H_2O (above 110° C.)	4·52	7·07	5·10
MnO	0·48	n.d.	n.d.
BaO	trace	,,	,,
Cr_2O_3	trace	,,	,,
ZrO_2	? trace	,,	,,
V_2O_3	0·04	,,	,,
F	0·68	,,	,,
	100·65		
Less O for F	0·29		
	100·36	99·52	100·02

Analysis (a) and (c): by Dr. H. F. Harwood.
Analysis (b): by Mr. G. M. Stockley, A.R.C.S., A.I.C.

It is to be observed that the titania content of the bleached residues is quite appreciable. Essentially the whole of this titania was readily extracted by a 2 % solution of salicylic acid, and a solution of sodium carbonate extracted a large proportion of the silica. It is concluded that both silica and titania are present in a hydrated form in these residues: the titania may be rather firmly held, or adsorbed at least, by the silica.

This experimental evidence favours the view that a titano-silicic acid is formed when the biotite is attacked by the boiling mineral acid; it further suggests an analogy between the destructive process described and that conceivably initiated by fluoboric vapours during the pneumatolysis of a granite rich in biotite. In the latter case, the hydrous titania and silica produced may respectively contribute to the formation of anatase, &c., and quartz (or chalcedony, which has been repeatedly noted); the ferromagnesian radicles may be accommodated in secondary tourmaline (which is frequently zoned—typically blue and brown) or in a system of destabilized felspar, from which may arise the chloritic pseudomorphs so commonly observed in the red granites. Some alumina may contribute to the formation of secondary muscovite, or to topaz, or to both these, and lime may enter fluor. Specular haematite has occasionally been observed in this association.

Under more normal conditions, such as those of weathering, biotite alters to chlorite. When it enters a sediment it rapidly loses its identity and merges into the obscure substance which may be described vaguely as chloritic matter. Biotite altering beneath a capping of turf and in a sour-water environment is likely to undergo complete disintegration, and it appears at least possible that (*a*) its decomposition products include a more or less colloidal complex of titania and silica, and that (*b*) the silica and titania may slowly disengage themselves and become crystalline: the silica may expend its potential energy in repairing and extending quartz grains, or in initiating new ones; in a similar way, titania may apply itself to anatase. It is also possible that the alteration of ilmenite to granular anatase proceeds via a complex of hydrated ferric oxide and hydrated titania, and anatase nuclei thus authigenically produced could receive extensions in the manner suggested above.

Recorded experiments whereby rutile, brookite, and anatase have been formed artificially do not provide any very close parallel between the experimental conditions and those conceivably set up during pneumatolysis of the Dartmoor granite. So far as the experiments go they indicate that, for these minerals, the respective conditioning temperatures stand related as the specific gravities: rutile > brookite > anatase. The Dartmoor occurrences, and inferences drawn from them, are at least in accord with this indication.

The discussion has some bearing on the genesis of clay-slate needles, but this subject is outside the scope of the present paper.

Form and habit of crystals.

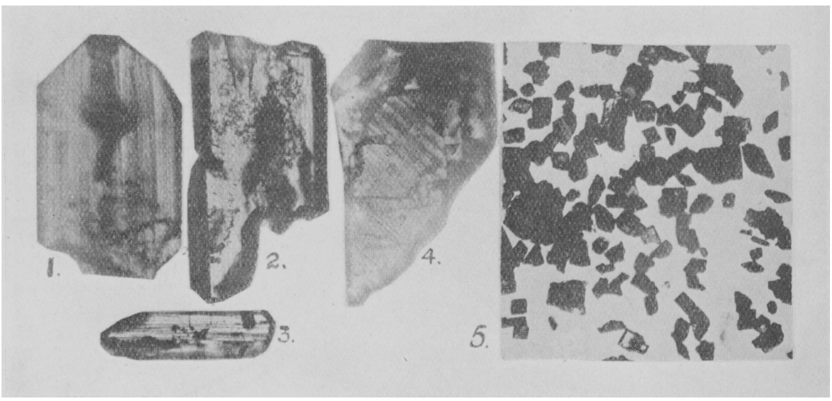
Rutile.—Occurs as yellow-brown needles embedded in quartz, and as minute irregular grains of a deeper brown. Very rarely observed.

Brookite.—Typically reddish-yellow, sometimes deep brown. Euhedral grains are fairly common; doubly-terminated crystals are rather rare. Tabular parallel to *a*(100),[1] which is invariably striated vertically; *m*(110), subordinate; *b*(010), poorly developed; *c*(001), with a brachy-

[1] Dana's letters and indices for forms are used throughout.

dome, fairly common; bipyramidal facets have been observed. The curious optical behaviour of this mineral affords a ready means of identification without the delay involved in verifying the crossed axial planes. A tabular fragment rarely extinguishes completely, and when it is examined between crossed nicols its interference-colour changes in quality as the stage is rotated through 90°: the tints observed may compass an order.

Anatase.—Colour highly variable: in approximate order of frequency —yellow to brown, deep or pale; blue, blue-green to olive-green and



Photomicrographs of crystals of brookite and anatase derived from pneumatolysed (red) granite, Dartmoor.

FIG. 1. ×110. Brookite from sand pit, Lock Gate Cross; tabular parallel to *a*(100), showing strong vertical striations and feeble development of *m*(110).

" 2. ×110. Brookite from sand pit, road side, at the foot of the north-east slope of Rowden Down; showing feeble striations and strong development of *m*(110).

" 3. × 85. Brookite, from sand pit, Lock Gate Cross, doubly terminated.

" 4. × 56. Anatase from stream-sand, Dartmeet Bridge; tabular parallel to *c*(001), and showing the characteristic diagonal striations.

" 5. × 15. Concentrate of anatase from stream-sand, Dartmeet Bridge; composed of tabular crystals mainly; a few crystals of the bipyramidal variety (octahedrite) also occur.

almost opaque; pale lilac and slate-grey. Blotchy colouring, in browns and blues, is very common. Anhedral grains are the exception. It presents two habits: tabular and bipyramidal. Tabular parallel to *c*(001), combined with *p*(111), subordinate. The basal plane often shows two sets of striae at right angles, and diagonal. Elongation in the direction of a lateral axis, resulting in oblong tablets, is very common. The conjunction of large and small tablets in parallel position is also common. Crystals of tabular habit greatly outnumber those of the bipyramidal (octahedrite) type. The latter are simple bipyramids, $p(111)$; strong horizontal striae are commonly observed.
