The temperature-range of formation for tourmaline, rutile, brookite, and anatase in the Dartmoor granite.

(With Plates IV and V.)

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THE range of temperature within which tourmaline can arise in nature has not hitherto been determined. No synthesis of this mineral is on record, and experimental data are therefore lacking. On the other hand, rutile, brookite, and anatase have all been prepared synthetically, and the experimental data suggest that rutile is formed at the highest temperatures, brookite at temperatures considerably lower, and anatase at a point still lower on the scale. It is generally conceded that for rutile a pyrogenic origin is possible, and that brookite and anatase appear only as secondary minerals. The status of tourmaline as a possible pyrogenic mineral is regarded as doubtful by Clarke,[1] who states that 'in igneous rocks tourmaline seems to have been produced by fumarole action, and not as a direct separation from the magma'.

Within the Dartmoor area tourmaline is so widespread, and its modes of occurrence are so varied, that it invites an attempt to date its birth relative to that of associated minerals, and thus to determine its status as a possible pyrogenic mineral.

For such investigations Wright and Larsen[2] indicate the utility of quartz as a 'geological thermometer', and they established some important generalizations to which appeal may be made in determining the

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[1] F. W. Clarke, 'The data of geochemistry', 1924, p. 417.

[2] F. E. Wright and E. S. Larsen, 'Quartz as a geologic thermometer'. Amer. Journ. Sci., 1909, ser. 4, vol. 27, pp. 421–447.

stability-ranges of associated minerals—in the present case tourmaline, rutile, brookite, and anatase. For the purposes of this discussion the range of the 'thermometer' will be extended to include temperatures fixed for tridymite and cristobalite. Each of these three crystalline forms of silica exists in two modifications (α and β), but for present purposes discrimination is necessary between the α and β forms of quartz only. The thermometric scale shown diagrammatically in fig. 1 is based mainly on results recorded by Quensel,[1] Day and Shepherd,[2] Wright and Larsen (loc. cit.), Rinne and Kolb,[3] Koenigsberger,[4] and White.[5]

The Modifications of Quartz: Generalizations established by Wright and Larsen.

At ordinary temperatures all quartz is α-quartz, which at 575° C. undergoes enantiotropic inversion to β-quartz, the inversion being heralded through an interval of about 400° by continuously increasing rates of expansion and by changes in optical properties. On both rising and falling temperature the inversion is sharp and prompt.

Idiomorphic crystals of α-quartz tend to be prismatic in habit, to display unequal development of the terminal planes, and to develop trigonal trapezohedra. The symmetry class is trapezohedral-tetartohedral (trigonal holoaxial). Right- and left-handed forms are more frequent and are more readily compounded as twins in the α-phase than in the β-phase, α-quartz being merely a distortion of the β-structure.[6] Vein-quartzes, geode-quartzes, and the quartz of certain pegmatites originated as the α-phase, or low-temperature form.

Idiomorphic crystals of β-quartz tend to be bipyramidal in habit, and to display equal development of the terminal planes, trigonal trapezohedra being absent. The symmetry class is trapezohedral-hemihedral (hexagonal holoaxial).[7] The quartz of granite-pegmatites, graphic peg-

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[1] P. Quensel, Centralblatt Min., 1906, p. 728.

[2] A. L. Day and E. S. Shepherd, Amer. Journ. Sci., 1906, ser. 4, vol. 22, p. 276.

[3] F. Rinne and R. Kolb, Neues Jahrb. Min., 1910, vol. ii, p. 138.

[4] J. Koenigsberger and W. J. Müller, Centralblatt Min., 1906, p. 371.

[5] W. P. White, Amer. Journ. Sci., 1919, ser. 4, vol. 47, p. 1.

[6] R. E. Gibbs, 'The polymorphism of silicon dioxide and the structure of tridymite'. Proc. Roy. Soc. London, Ser. A, 1926, vol. 113, pp. 351–368.

[7] R. W. G. Wyckoff, 'The crystal structure of the high temperature (β-) modification of quartz'. Amer. Journ. Sci., 1926, ser. 5, vol. 11, pp. 101–112. [Min. Abstr., vol. 3, p. 183.]

matites, granites, and porphyries originated as the β-phase, or high-temperature form.

On the passage of either phase through the inversion-point, the original external form tends to persist, but internal molecular rearrangement occurs. The consequences entailed by the crystallographic relations between the two phases include internal effects which serve to indicate whether quartz has ever passed through the inversion-point. These effects are (1) intricate actual or potential fracturing, brought to light by etching a basal plate with cold hydrofluoric acid for $1\frac{1}{4}$ hours, and (2) intricate and irregular twinning. Basal plates of quartz are of rare occurrence in granite sections. The etch-test applied by us to several of the granular aggregates to be described has yielded only indecisive results.

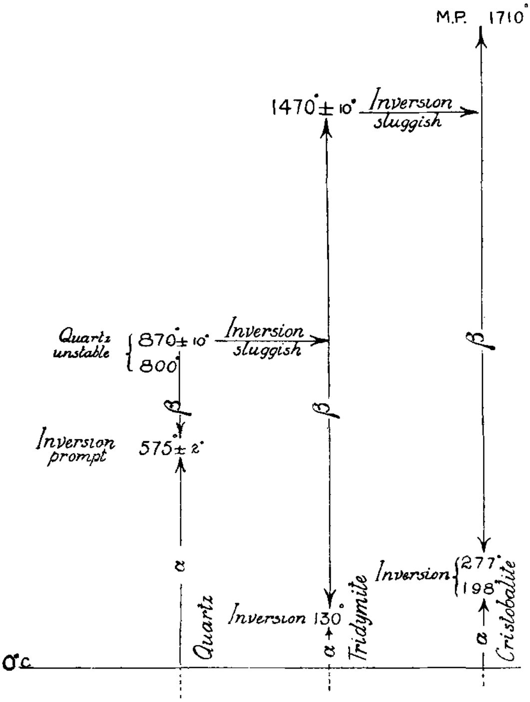

FIG. 1. Geological thermometer.

(See foot-note 3, p. 218.)

Syntheses of crystalline silica and titanic oxides: their significance.

Methods of synthesizing the various forms of silica fall into three main groups involving respectively (1) simple ignition or dry fusion, (2) the use of dry fluxes, and (3) the use of aqueous fluxes under pressure.[1]

Syntheses effected by the simple ignition of silica glass, quartz crystals, quartz sand, or the simple dry fusion of quartzose rock resulted in the production of tridymite or cristobalite at temperatures which are in general agreement with the stability-range indicated by the scale. So also are the products of processes involving the use of 'dry' fluxes.

On the other hand, K. Chrustschoff's experiments[2] showed that by the use of aqueous fluxes the high-temperature forms cristobalite and tridymite can be produced at temperatures well within the stability-range of the low-temperature form α-quartz: cristobalite at 180°-228°, quartz at 240°-300°, tridymite at 310°-360°, tridymite and quartz together at 300°-520° (approx.).

Thus though quartz has been produced artificially only at temperatures below 800°, tridymite and cristobalite, which in dry melts would not ordinarily form below 800°, have been produced artificially in aqueous fluxes at much lower temperatures. Similarly, the crystallization of felspars from aqueous melts is known to be possible at temperatures considerably lower than those at which they would ordinarily crystallize out from relatively 'dry' melts.

This effect of aqueous-flux conditions is also suggested by the known temperature relations between rutile, brookite, and anatase. Experimental data[3] suggest for these three species a 'high', 'low', and 'lower' temperature-range of formation respectively, but the three arise together in some of the reddened and tourmalinized varieties of the Dartmoor granite. In artificial syntheses[4] rutile has been produced either by ignition at high temperatures or by the use of anhydrous fluxes engaging neither fluorides nor chlorides; whereas in every case (with one possible exception[5]) in which either brookite or anatase was identified among

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[1] Cited by F. W. Clarke, loc. cit., pp. 361-366.

[2] K. Chrustschoff, Amer. Chemist, 1873, vol. 3, p. 281; Compt. Rend. Acad. Sci. Paris, 1887, vol. 104, p. 602; Neues Jahrb. Min., 1897, vol. i, p. 240.

[3] Summarized by F. W. Clarke, loc. cit., p. 355.

[4] Described and discussed by F. W. Clarke, loc. cit., pp. 354-356.

[5] B. Doss (Neues Jahrb. Min., 1894, vol. ii, p. 147) fused titanic oxide in beads of either microcosmic salt or borax in a loop of platinum wire. Anatase was produced only in the beads of microcosmic salt; borax beads yielded only rutile. The crystals of anatase were too minute (0·1 mm.) for accurate gonio-

the products, synthesis engaged water or compounds of fluorine or chlorine. It is a significant fact that a typical environment in which brookite and anatase may originate together is that produced by pneumatolysis accompanied by the production of tourmaline and quartz with or without gilbertite, fluorite, topaz, and chalcedony.

The foregoing data will now be co-ordinated and applied.

Tourmaline : the range of its crystallization-temperature.

A convenient starting-point is afforded by the somewhat rare geodes occurring in the normal granite, e. g. that quarried at Merrivale. The structure of the Merrivale geodes comprises something more than the mere crystal-infilling of an irregular cavity.[1] The cavity wall is only the inner surface of a distinct wall-zone in which the geode crystals may be more or less deeply rooted. The geode structure as a whole may be regarded as beginning at the outer surface of the wall-zone in contact with the normal biotitic granite. The crystals infilling the cavity comprise :

(*a*) Euhedrons of orthoclase, the faces of which are often encrusted with minute flakes and rosette-clusters of gilbertite inshot with slender needles of tourmaline—often very pale in colour (blue, lilac, brown, greenish-brown), sometimes almost colourless.

(*b*) Large crystals of clear quartz occasionally showing the characteristic development of the α-phase. These quartz crystals commonly enclose numerous needles and prisms of tourmaline orientated indiscriminately and often projecting beyond the limits of the quartz crystals.

(*c*) Gilbertite as irregular masses, or rosette-clusters up to one inch in diameter. These clusters are sessile on quartz, felspar, and tourmaline indifferently. The gilbertite (K_2O 10·35, Na_2O 1·26, H_2O 4·34 %) is in obvious reaction relation[2] to the perthitic orthoclase.

(*d*) Deep purple fluorite, as irregular masses, often intimately intergrown with gilbertite, felspar, quartz, and tourmaline.

(*e*) Long stout prisms of dark-coloured tourmaline. The voids between large crystals of quartz, felspar, gilbertite, &c., are often bridged by these tourmaline prisms, the ends of which are embedded in the crystals flanking the voids.

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metric measurement, and were identified on the evidence of chemical tests and of angles measured by means of the microscope.

[1] When a liquid (e. g. water, critical temperature 374°) containing a dissolved salt is heated above its critical temperature the salt is also volatilized. (J. H. L. Vogt, Econ. Geol., 1926, vol. 21, p. 218.)

[2] N. L. Bowen, 'The reaction relation in petrogenesis'. Journ. Geol., 1922, vol. 30, pp. 177–198.

(*f*) Thin square micaceous tablets of emerald-green torbernite, lying on the felspar or on the aggregates of gilbertite. These were apparently the last crystals to form.

(*g*) Very rare and minute flakes of gold.

From the fact that quartz crystals which project into the cavity occasionally display the characteristic features of the α-phase, it may be inferred that the quartz, and therefore also its inclusions of tourmaline, crystallized at a temperature below 575°.

The wall-zone is essentially free from biotite. Texturally, it may be pegmatite, graphic granite, granite, or even microgranite. Its constituent minerals are those found in the cavity itself: felspar, quartz, tourmaline, fluorite, and gilbertite. Long euhedral prisms of tourmaline showing the characteristic cross-sections are common. Flakes of torbernite have been detected in minute drusy cavities.

The outer part of this wall-zone merges into the biotitic groundmass of the granite, the quartz of which, according to Wright and Larsen, originated as the β-phase, and therefore at a temperature above 575°. Hence this wall-zone connotes the temperature-interval $575° \pm x°$, with 575° as a mean.

Tourmaline occurs in the Merrivale granite itself, in the closely allied Foggintor and Sweltor types, and in the Dartmoor granite generally. Thin sections of the granite often show anhedral tourmaline in such textural relationship to quartz, felspar, and mica as to indicate for it a genesis approximately contemporaneous with that of one or other of these major constituents. The selected cases described below will serve to illustrate this fact.

Plate IV, fig. 1, shows greenish-brown tourmaline in a granite composed of albite, perthitic orthoclase, perthitic microcline, pinitized cordierite, and a little biotite. A few irregular masses of tourmaline are partly or wholly surrounded by felspar, but in the main the tourmaline is interstitial to quartz, and the two minerals appear to be almost contemporaneous products of a highly siliceous residual flux. The textural role of quartz thus associated with tourmaline does not differ appreciably from that of the quartz in the tourmaline-free portions of the rock-slice figured, and if for the quartz a pyrogenic origin is conceded, the tourmaline with which it is associated has a claim to the same status. According to Wright and Larsen, quartz in granites crystallized at some temperature above 575° and below 800°, and hence for the tourmaline in this particular case a temperature of formation $575° + x°$ is implied.

Plate IV, fig. 2, shows similar tourmaline in quasi-eutectic intergrowth with quartz in a thin layer of pegmatite lying parallel to a pseudo-bedding-plane in the granite at the Merrivale quarry. Attempts to determine, by Wright and Larsen's etch-test, whether the quartz originated in the α- or the β-phase resulted in wholly indecisive results, but the genesis of the tourmaline was certainly contemporaneous with that of the quartz.

Plate IV, fig. 3, shows a similar quasi-eutectic of quartz and tourmaline around a porphyritic felspar in a garnetiferous graphic granite. Blebs of 'graphic' quartz are enclosed in the felspars shown and some of these blebs contain tourmaline. According to Wright and Larsen, the quartz in graphic granites originated as the β-phase or high-temperature form, and hence the tourmaline (in part at least) originated at the temperature $575^\circ + x^\circ$. The figure illustrates the penetrative power of a residual and highly siliceous borosilicate flux which retained some of the constituents of tourmaline until a comparatively late stage in the process of crystallization.

The penetrative power and the reactivity of such a residual flux is clearly revealed also in figs. 4 and 5 (Plate IV), showing garnetiferous cordierite-biotite-granite in which both biotite[1] and felspar have undergone tourmalinization around relatively large 'pools' of clear quartz. Texturally these quartz 'pools', within and around which tourmalinization has occurred, are in marked contrast to the normal groundmass quartz, and their origin is referred by the authors to a late stage in the process of crystallization, a step which is warranted by two significant facts:

(1) Steel-blue anatase of tabular habit has replaced certain inclusions (probably apatite) in the original biotite. Two such replacements occur in the tourmaline shown in the centre of each of figs. 4 and 5 (Plate IV). The larger of the two in fig. 5 is shown in detail in fig. 6.

(2) Secondary tourmaline showing finger-like outgrowths penetrating adjacent felspars is not uncommon. A similar habit is displayed even more emphatically by occurrences of muscovite in granite from the Haytor quarry and elsewhere. In some cases this habit in muscovite is closely imitated by quartz, the locus of the two minerals being intimately related to quartz 'pools'. The mica has the aspect and general properties of true muscovite, as distinct from the yellowish gilbertite occurring in the Merrivale geode-structures. The 'reaction relation' between muscovite and orthoclase has its analogue in the described relation of tourmaline to felspar and biotite together: both the muscovite and the

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[1] Dartmoor biotite contains up to 1·9 % of titanic oxide.

tourmaline originated from reaction of residual flux with previously crystallized minerals. If for the muscovite a pyrogenic status is claimed the same status may be accorded to the tourmaline, and therefore also in this particular case to the by-product of tourmalinization, namely, the anatase replacing apatite. The necessity for distinguishing between 'pyrogenic primary' and 'pyrogenic secondary' minerals is evident.

In the more heavily biotitic granites the biotite often presents to adjacent quartz an irregular margin fringed with minute finger-like projections (Plate IV, fig. 7 *a*) the tips of which are sometimes converted to tourmaline. Such occurrences of tourmaline imply that constituents of tourmaline such as boric acid were retained in a residual flux until quartz had almost completed its crystallization, when their concentration attained the degree necessary for reaction with biotite to form secondary tourmaline. Figs. 7 *b* and 7 *c* show tourmaline developed in quartz 'pools' between biotite crystals. In fig. 7 *b* the growth of the irregular masses of tourmaline probably began before that of the biotite finished. In fig. 7 *c* the minute euhedral hemimorph of tourmaline completely enclosed in biotite suggests that the tourmaline was actually in existence before biotite completed its growth. The same fact is indicated by the relationship of tourmaline to ilmenite and biotite in fig. 7 *d*: here ilmenite occurs as a marginal precipitation in biotite; but the tourmaline figured was actually in place before biotite-growth ceased, for at least two of the ilmenite grains are moulded on the tourmaline.

The evidence so far adduced shows that the genesis of tourmaline may occur within the temperature-range $575° \pm x°$, the lower limit of this range being the temperature at which the Merrivale geodes were infilled, the upper limit that at which biotite was completing its growth.

On the further evidence described below this range may be extended upwards. The minute tourmaline euhedron occurring as an inclusion in biotite (Plate IV, fig. 7 *c*) is not unique: similar euhedrons have been noted among the minute zircons in the insoluble residue after the baueritization[1] of biotite in bulk. Similar euhedrons occasionally occur as inclusions in porphyritic felspar, which may also completely enclose nests of tourmaline prisms. Moreover, tourmaline has been observed in sector-twinned cordierite which, though originating usually as a groundmass constituent, may itself be porphyritic and has often been noted among the inclusions in porphyritic felspar.

The temperature-range of formation for tourmaline may thus be

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[1] A. Brammall and H. F. Harwood, 'The occurrence of rutile, brookite, and anatase on Dartmoor'. Min. Mag., 1923, vol. 20, p. 22, foot-note references.

extended to cover the range for biotite-growth and to overlap that of porphyritic constituents. A similar inference may be drawn from a study of the peripheral features of certain types of quartz-tourmaline nodes; these have already been described in some detail.[1] The upper limit of the range thus extended is uncertain; but as quartz often occurs as an inclusion in porphyritic felspar a temperature higher than 800° cannot be assumed: $575^\circ + x^\circ$ is probably below 800°.

Reference may here be made to the abundance of tourmaline in many granitic veins and sheet-intercalates which the authors class broadly as 'elvans'. Occasionally aplitic in facies, they are essentially granites, but of relatively fine grain. As Wright and Larsen established the fact that the quartz in porphyries originated as the β-phase or high-temperature form, it is probable that the quartz in these elvan-types originated in the same phase. The genesis of tourmaline in these types presents no special features not covered by the cases already described.

Reference has also been made to the reaction effects produced by residual aqueous and borosilicate fluxes at a late stage in the crystallization processes. Confinement of these residuals under pressure inhibited the escape of their more volatile constituents, and reaction between them and solid mineral-phases in their environment proceeded to completion where the residuals accumulated.

The release and escape of these volatile constituents from fluid granitic material injected along fissures is well illustrated by an occurrence on the south side of Mel Tor. Near the base of the tor a nearly vertical vein of microgranite containing a little tourmaline is traceable upwards for several yards until its outcrop is lost under turf and granite blocks. Near the top of the tor a nearly vertical vein consisting essentially of quartz and schorl is traceable downwards to the level of the turf and blocks. As the two veins appeared to lie in the same plane they were traced out beneath the moor-surface, and with the kindly help of Professor A. M. Davies the continuity of the one with the other was proved: the low-level microgranite merged into the high-level quartz-schorl rock through an intermediate facies of pinkish quartzose tourmaline-microgranite. Thus the upper parts of a vein-intrusion which consolidated at depth as a biotitic microgranite (with a little tourmaline) became enriched in those volatile components which promote the formation of tourmaline.

The abundant development of tourmaline in quartzose veins, in granites reddened or otherwise altered by post-solidification pneumatolysis, and in

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[1] A. Brammall and H. F. Harwood, 'Tourmalinization in the Dartmoor granite'. Min. Mag., 1925, vol. 20, pp. 319–330.

country-rock affected by emanations from the granite suggests that the most favourable conditions for the genesis of tourmaline are attained at temperatures below that connoted by the Merrivale geodes. Tourmaline arising under these conditions is commonly associated with secondary rutile, brookite, and anatase (singly or in association). In the following sections these titanium-minerals and tourmaline will be examined together.

Rutile, Brookite, and Anatase : Temperatures of Formation.

Rutile, in the form of granules and stout prisms, has been noted as an inclusion in apparently unaltered biotite, but more frequently as an obvious by-product of reactions occurring at magma temperatures and resulting in the production of tourmaline from systems involving biotite. Plate V, fig. 1 *a*, shows granular rutile in tourmaline, some of the granules being moulded on apatite. Fig. 1 *b* illustrates both the granular and the prismatic habit of such rutile.

Similar rutile has apparently arisen from reactions due to fluxes residual at relatively lower temperatures and now appears in an environment indistinguishable from that shown in Plate IV, figs. 4 and 5.

Secondary rutile (with very rare anatase and no brookite) is unusually abundant in a severely pneumatolysed dike-granite exposed in the disused quarry below the reservoir dam on Holne Moor. In hand-specimens (Plate V, fig. 2 *a*) this rock somewhat resembles the typical Cornish luxulyanite, from which, however, it differs considerably in thin sections (Plate V, fig. 2 *b*). Like the Cornish rock, it is composed of corroded felspars embedded in a groundmass of quartz enclosing tourmaline, but in the Holne Moor type the delicate schorl-needles characteristic of the Cornish rock are quite subordinate to stout euhedral and beautifully zoned prisms. The tourmaline contains 0·56 % TiO_2. Accessory minerals include ilmenite, sphene, fluorite, zircon, and rutile. The habit and relative amount of zircon, the amount of the rutile, and the size of the felspar relics link the original rock with the biotite-rich porphyritic granites. Fluxing precedent to tourmalinization appears to have been more complete and to have occurred at a higher temperature than was the case with typical luxulyanite, from which Mr. J. G. C. Leech informs us he has isolated both brookite and anatase.

Thin delicate needles of rutile have been observed in the groundmass quartz of biotite-granites from several localities ; in quartz associated with anatase around tourmalinization-foci in such granites ; in reddened and pneumatolysed types in which rutile is associated with brookite, or anatase, or both; and characteristically in the chloritized biotite of granites showing feeble hydrothermal alteration.[1]

Brookite has been isolated from many reddened granites. Few of these occurrences lend themselves to the problem in hand, but the two described below are significant.

Foliated, veined, and tourmalinized granite exposed for several yards on the south wall of the entrance to the disused Foggintor quarry shows a series of sharp complex folds traced out by quartz-schorl veins $\frac{1}{2}$ to $1\frac{1}{2}$ inches apart (Plate V, fig. 3). These veins alternate with bands of pinkish felspars lying with their broad surfaces in the foliation planes, which strike roughly east-west.

Plate V, fig. 3 (re-drawn from a field sketch), shows the structure over a portion of the wall. A thrust-plane truncating relatively early folds is clearly traceable, but the regularity of the folds is repeatedly broken by minor shear planes and brecciated patches (Plate V, fig. 4). The folds were certainly produced when the mass was plastic enough to permit the felspars to orientate themselves at right angles to pressure, which was directed roughly north-south and probably from the south. The structure creates the illusion that the folding and the veining are contemporary effects, but this possibility is dispelled by a study of thin sections, which show the veining to be of post-consolidation date. Nevertheless, the foliation-planes were potentially 'open', and favoured penetration by pneumatolytic agents the arteries for which are seen in the immediate vicinity.

The crushed material yields abundant brookite, together with tabular anatase. Biotite is absent, though it is abundant in the normal quarry-rock. The tourmaline (containing 1·05 % TiO_2) occurs mainly as delicate needles massed about the margins of the altered felspars. The etch-test, with hydrofluoric acid, applied to a polished slab of the rock yielded wholly indecisive evidence as to the phase in which the quartz originated, but it revealed the presence of abundant yellow gilbertite developed mainly along the cleavage planes of the felspars. The same test applied to the Holne Moor rock proved the presence of gilbertite in only negligible amount. As this secondary mica is a conspicuous mineral in the Merrivale geodes but dies out beyond the geode-wall in contact with the normal granite, it probably connotes a temperature-range of formation

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[1] Such rutile needles in chloritized biotite are also described (with an excellent figure) by E. E. Lowe, 'The igneous rocks of the Mountsorrel district'. Leicester Lit. Phil. Soc., 1926, p. 10, fig. 3.

having its upper limit round about 575°. The features of this tourmalinized granite (yielding brookite and anatase) indicate that in this case tourmalinization was conditioned by a lower degree of fluxing and a lower temperature than in the case of the Holne Moor rock characterized by rutile.

In a feebly reddened and moderately schorlaceous microgranite, containing rutile needles together with scanty brookite and anatase, the quartz shows evidence of having originated as either chalcedony or opal (Plate V, fig. 7). Concerning the stability-range of opal and chalcedony precise data are lacking, but Koenigsberger and Müller (loc. cit.) produced opal in experiments which do not appear to have engaged any temperature higher than 360°. The rock itself records a much lower degree of pneumatolysis than the Holne Moor or Foggintor tourmalinized granites described above, and it is probable that the original rock was modified at temperatures much nearer the lower limit for effective tourmalinization.

Anatase, both tabular and pyramidal, often accompanies brookite, and both varieties of the mineral vary in colour—from deep green, blue, or brown, and almost black through varying shades of green, blue, and brown to pale green, blue, yellow, or almost colourless; particoloured crystals are not uncommon. The relation which doubtless exists between crystal habit and temperature of formation presents a problem still unsolved.

Steel-blue and distinctly pleochroic tabular anatase has replaced apatite in biotite tourmalinized by the reactivity of residual flux at a late stage in the crystallization of the magma (Plate IV, figs. 4 and 5). Such anatase is sometimes accompanied by granular rutile or rutile needles enclosed in quartz. These occurrences suggest for the stability-range of anatase an upper limit which, by analogy with geode-phenomena, is probably round about 575°.

The anatase-brookite association is common in rocks reddened and tourmalinized after consolidation. Examples have already been described.

Significant developments of anatase occur in a facies of the Holne Moor microgranite which is only feebly tourmalinized and contains biotite showing every stage of alteration to chlorite. Flakes of altered biotite are often dense with clusters of rutile needles associated with anatase, the latter forming aggregates of steel-blue pleochroic tablets with the aspect shown in Plate V, fig. 5. In the same rock occasional flakes of apparently fresh biotite contain extremely thin and very minute tablets of pale anatase (Plate V, fig. 6) lying parallel to the biotite cleavages.

These developments of anatase (unaccompanied by brookite) appear to have arisen under simple hydrothermal conditions which involved no fluxing, and little or no tourmalinization. They connote for this mineral the lowest part of the temperature-range of formation so far as this range is determinable from rock in situ.

Summary and Conclusions.

To determine the approximate temperature-range of formation for Dartmoor tourmaline and associated rutile, brookite, and anatase, the authors have applied the work and conclusions of Wright and Larsen, who define two restricted groups of siliceous rocks the quartz in which may be assumed to have originated as the α-phase (i. e. below 575°) and the β-phase (i. e. above 575°) respectively.

Tourmaline-bearing geodes in the Dartmoor granite afford a convenient starting-point. The geode quartz originated as the α-phase; hence tourmaline, demonstrably contemporary in origin with this quartz, originated at a temperature below 575°.

The geode-walls, which also contain tourmaline, merge into tourmaliniferous biotite-granite, in which the normal groundmass quartz originated as the β-phase, i.e. above 575°. Tourmaline which arose in the geode-walls therefore connotes a growth-temperature having 575° as a mean. This range is extended upwards to $575^\circ + x^\circ$ on the evidence of tourmaline-growth (1) demonstrably contemporary in origin with quartz in the normal groundmass, or with biotite, (2) euhedrally developed and appearing as inclusions in biotite, or in porphyritic felspar, (3) developed in certain types of quartz-tourmaline nodes, (4) in quasi-graphic intergrowth with quartz in graphic granites, and (5) in 'reaction relation' to felspar and biotite as a product of reactions for which temperatures of residual magma are indicated. This upper limit, $575^\circ + x^\circ$, may conceivably approach 800°, the point above which the crystallization of quartz direct from the magma would not occur.

The temperature-interval between 575° and the low temperature connoted by simple hydrothermal action accompanied by little or no tourmalinization is bridged by tourmaline-growth (1) in granites reddened and often profoundly altered by post-solidification pneumatolysis, (2) in quartz-tourmaline veins, (3) in granite tourmalinized under conditions favourable to the genesis of opal or chalcedony, which subsequently inverts to quartz, and (4) in country-rock affected by emanations from the granite.

How far this temperature-range of tourmaline-growth may be extended downwards to include possible authigenic tourmaline is uncertain.[1]

Parallel observations on the genesis of rutile, brookite, and anatase lead to conclusions applicable solely to occurrences of these minerals in this granite. The fact that the biotite in the granite is titaniferous and is associated with ilmenite and, to a less extent, with sphene, is a factor favourable to the genesis of rutile, &c., as secondary minerals.

Hautefeuille[2] synthesized anatase by decomposing titanic fluoride with aqueous vapour at about the boiling-point of cadmium (770°), and brookite by the action of hydrofluoric acid on titanic chloride at a temperature not higher than the boiling-point of zinc (920°). Hence anatase has been produced at a temperature only 30 degrees below that at which quartz becomes unstable,[3] and brookite, at a temperature approaching that at which quartz would invert to either tridymite or cristobalite. Both syntheses were therefore effected at temperatures consistent with crystallization direct from magma, but neither brookite nor anatase occurs as a direct separation from the magma. Hautefeuille's syntheses engaged only simple systems offering for the liberated titanic oxide no claimants in the form of other oxides such as lime, ferrous oxide, magnesia, silica, &c. In the complex magma-system such oxides were available, and their combinations with titanic oxide achieved titaniferous biotite, titaniferous tourmaline, ilmenite, and sphene.

Rutile originated (1) as a primary or as a secondary mineral at temperatures above that at which crystallization from the magma attained completion, (2) as a secondary mineral in high-temperature borosilicate fluxes involving biotite, felspar, and ilmenite, (3) as delicate needles over a temperature-range approximately co-extensive with the stability-range of tourmaline, and especially at the relatively low temperatures consistent with the simple hydrothermal alteration of biotite.

The upper limit of the stability-range for anatase is lower than that for rutile, but higher than that for brookite, and is located within the

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[1] Such tourmaline, in the form of extremely minute pale greenish hemimorphic prisms, has been observed in the Skiddaw Slate and in certain Bolivian phyllites. A. Brammall, 'Reconstitution processes in shales, slates, and phyllites'. Min. Mag., 1921, vol. 19, pp. 211-224.

[2] P. Hautefeuille (1865), cited by Clarke, loc. cit., pp. 354-355.

[3] Quartz is unstable at all temperatures above 800° (Day and Shepherd, loc. cit.), is metastable above 870° (White, loc. cit., p. 30), is transformed to tridymite at 870° ± 10° (C. N. Fenner, Amer. Journ. Sci., 1913, ser. 4, vol. 36, p. 331), tridymite passing over to cristobalite at 1470° ± 10° (Fenner).

temperature-range for crystallization from residual magma yielding quartz and tourmaline to the groundmass. The lower limit of the stability range for brookite is higher than that for anatase and rutile. The range for brookite seems to lie within that for anatase.

The temperature-range of formation thus approximately defined for each of these titanium minerals is that determinable from observations of modes of genesis in a particular granite affected by pneumatolytic agents at a late stage in its cooling history.

Taking into consideration occurrences of the three species developed authigenically in sedimentary rocks, as distinct from metamorphic rocks, the temperature-range of formation for all three species must be extended downwards to points as yet undetermined.

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Description of Plates IV and V.

Letters on the figures: F (Felspar), Q (Quartz), T (Tourmaline), B (Biotite), Ru (Rutile), An (Anatase), Ap (Apatite), I (Ilmenite), Z (Zircon).

Plate IV.

Fig. 1. Tourmaline almost contemporaneous with quartz in a medium-grained granite composed of microperthite, microcline, albite, biotite, pinite, and the common accessories. Hollow Tor. (×9.)

Fig. 2. Quasi-eutectic intergrowth of quartz and tourmaline in pegmatite. Merrivale quarry. (About one-half actual size.)

Fig. 3. A similar intergrowth around and penetrating orthoclase in a garnetiferous graphic granite. The graphic quartz carries tourmaline. Widdecombe. (About actual size.)

Figs. 4 *and* 5. Secondary brown tourmaline in reaction relation to biotite and felspar, and accompanied by much quartz. Tourmaline has invaded the biotite at right angles and parallel to cleavage. The forked body in the tourmaline of fig. 4, and the two cigar-shaped bodies in the tourmaline of fig. 5 are replacements of apatite by steel-blue anatase. Biotite-cordierite-garnet-granite. Sweltor quarry. (×16.)

Fig. 6. The larger of the two cigar-shaped bodies in the tourmaline of fig. 5. Anatase and fluorite replacing apatite.

Fig. 7. (*a*) Fringe-like outgrowth from biotite; sometimes tourmalinized at contact with quartz.

(*b*) Irregular tourmaline-growth in a quartz 'pool' flanked by biotite. The growth-periods for biotite and tourmaline overlap.

(*c*) A minute euhedron of brown tourmaline occurring, like zircon, apatite, and monazite, as an inclusion in biotite.

(*d*) Showing overlap of the growth-periods of biotite, ilmenite, and tourmaline.

Highly biotitic vein-granite, Widdecombe. (×30.)

Plate V.

Fig. 1. Secondary particoloured tourmaline produced mainly at the expense of biotite, with the development of yellow-brown rutile as granules (fig. 1 *a*), as granules and prisms (fig. 1 *b*). Granite, Wittabarrow. (×15.)

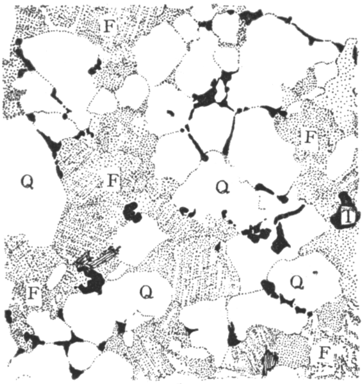
Fig. 2. Tourmalinized dike-granite. Hand-specimens (fig. 2 *a*) recall luxulyanite, but thin sections (fig. 2 *b*) show euhedral zoned prisms dominant over the acicular schorl characteristic of luxulyanite. The rock figured contains abundant rutile, with very rare anatase and no brookite. Holne Moor reservoir quarry. (Fig. 2 *b*, ×18.)

Fig. 3. Quartz-schorl veins tracing out pressure-folds and thrust-planes in tourmalinized granite yielding brookite, anatase, and rutile needles. Foggintor quarry.

Fig. 4. A polished block of the granite described above. Thrust-planes break the continuity of the folds.

Figs. 5 and 6. Aggregates of steel-blue anatase, and pale-yellow tablets of anatase associated with rutile needles in chloritized biotite (diameters, 0·3–0·9 mm.). Microgranite, Holne Moor.

Fig. 7. Schorl needles associated with anatase, brookite, and rutile needles in secondary quartz which originated as either opal or chalcedony. Reddened granite, Top Tor. (×28.)



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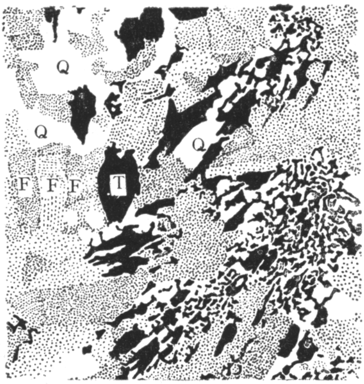

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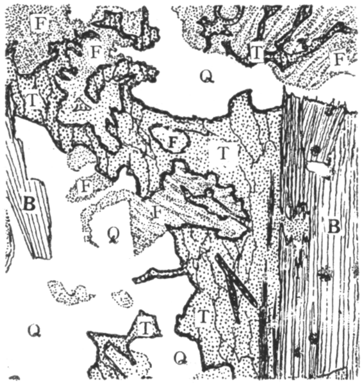

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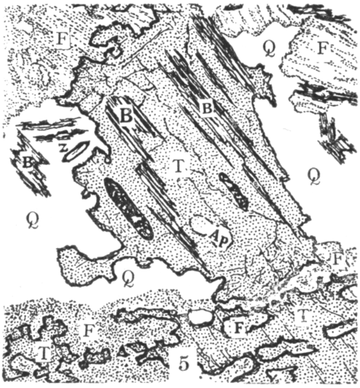

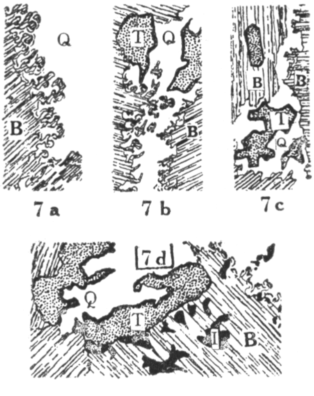

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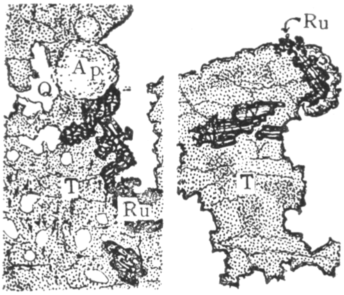

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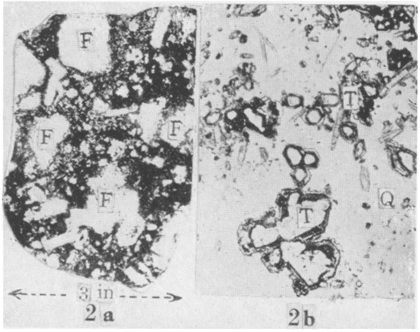

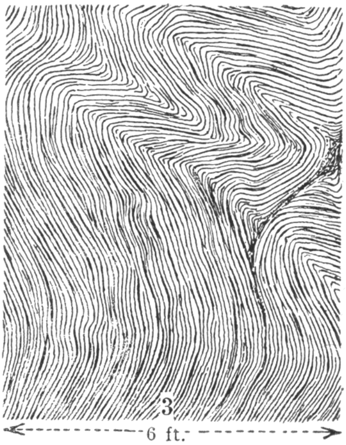

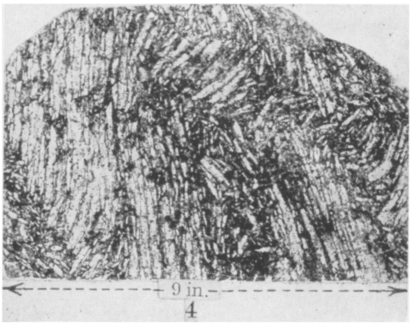

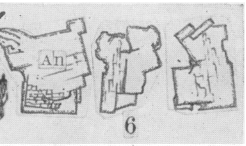

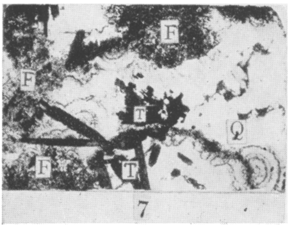

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