Chemical weathering on the Carnmenellis granite

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SUMMARY. The behaviour of 25 major and trace elements, together with mineral changes, has been examined in a deep weathering profile on the Carnmenellis granite, Cornwall. The bulk chemical and mineralogical composition of the regolith shows only minor changes from the parent rock indicating a low degree of chemical weathering. However, within the regolith marked differences occur between the fine fractions from the various horizons. Chlorite and degraded muscovite characterize the fines of horizons $A+B$ and C whereas gibbsite and kaolinite characterize horizon D. Secondary minerals becoming base deficient with depth is the reverse of normal behaviour and two possible theories are advanced to explain this anomaly. Most of the trace elements are concentrated in the $< 10\ \mu m$ fraction of the various horizons, in part by an association with degraded muscovite. Tin and Zr occur in resistates and Be, Sr, and Co are mainly lost during weathering.

A CONSIDERABLE amount of work has been done in an attempt to elucidate the nature of the weathering process and the controls upon it but relatively little of it has been from the geochemical point of view. Some of the more notable contributions in this respect have been Butler (1953, 1954), Short (1961), and Harris and Adams (1966). Consequently a deep weathering profile located in the Bosahan quarry on the Carnmenellis granite, Cornwall, was selected for such a study. The geology of the Carnmenellis granite has been described by Ghosh (1934) and a sketch map after Ghosh is shown in fig. 1. This map shows that the Bosahan quarry lies on the border of an area covered by type 2 granite, although other workers, e.g. Austin (1960) consider that there is no difference between types 1 and 2.

FIG. 1. The Carnmenellis granite, simplified after Ghosh (1934)

The salient features of the rock in this quarry are that it is generally fresh and contains large and abundant porphyritic crystals of microcline perthite in a coarse groundmass of quartz, oligoclase, biotite, and muscovite, with biotite the dominant mica. Tourmaline, andalusite, ilmenite, pyrite, apatite, zircon, and monazite are accessories. Hydrothermal alteration is patchily developed and occurs as partial sericitization and kaolinization of oligoclase, as the development of muscovite at the
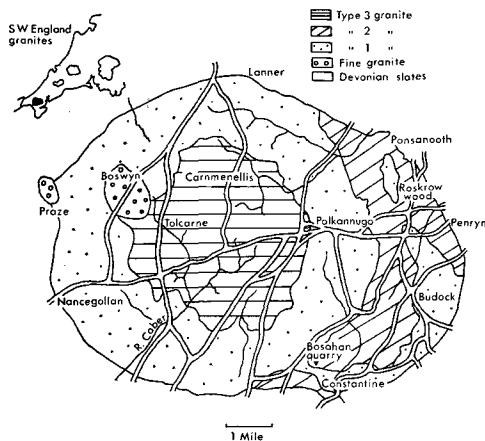
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expense of both feldspars, andalusite and, rarely, biotite, and as the chloritization and kaolinization of biotite. Tourmaline and fluorite are also deposited along some joint planes. Flow structure is well developed and defined by the parallelism of the perthite phenocrysts.

A diagram and description of the profile that has been exposed at the top of a quarry face by overburden stripping is given in fig. 2. The profile is typical of the soils developed on the Carnmenellis and other Cornish granites (Brunsden, 1964, and Clayden, 1967). The head layer is separated from the underlying growan (deeply rotted granite) by an irregular erosion surface; the upper part of the profile is therefore not *in situ*. This was not considered to be sufficient grounds for rejecting this profile since in the quarry itself and the immediate upslope areas the mineralogy and texture of the granite is reasonably uniform. Large samples, about 5 kg, were collected in each case.

It was expected that the greatest chemical and mineralogical changes would occur in the finest fractions of the profile and so these were separated from samples 1, 2, 5, and 7 by settling after removal of sesquioxides (dithionite leach) and organic matter (Na hypochlorite) (Brewer, 1964). Samples 1, 2, and 5 were selected as documenting the obvious horizons ($A+B$, C, and D) in the profile; sample 7 was collected from a sub-horizon within the D horizon, apparently showing an unusually high degree of weathering. The following fractions were separated: < 2 μm, 2–10 μm, 10–20 μm, 20–30 μm, 30–50 μm, and 50–211 μm.

The major and minor elements in the bulk samples and selected elements in the size fractions were determined mainly by wet chemical methods as originally outlined by Shapiro and Brannock (1955) and modified by Riley (1958). Colorimetric measurements were carried out on a Unicam SP 500 spectrophotometer. Fluorine was determined using the method of Huang and Johns (1967). The weight loss over the range 110°–375 °C was attributed to organic matter (Keeling, 1962). Aluminium, Ca, Mg, and Mn in the size fractions were determined on a Perkin-Elmer atomic absorption spectrophotometer model 303.

The X-ray studies were carried out on a Phillips PW 1050 diffractometer using Cu-$K\alpha$ radiation with a Ni filter. Semi-quantitative data for quartz and feldspars were obtained by calibrating the peak intensities of fresh rock samples with optically determined modes after ascertaining that the relationship between mineral concentration and peak intensity was linear. It was hoped this method would minimize matrix errors.

The trace element analyses were carried out using a Hilger and Watts automatic large quartz and glass spectrograph, model E. 478, with an enclosed arc stand. The procedure of dividing the elements into two groups, involatiles and volatiles, as recommended by Ahrens and Taylor (1961), was followed. Working curves were constructed from the rock standards G–1, W–1, T–1, G–2, GSP–1, AGV–1, PCC–1, DTS–1, and BCR–1 using preferred values taken from Flanagan (1967), Fleischer (1965), and the Tanzanian Geological Survey publication on the Msusule Tonalite (1963). Standard errors for each element were calculated from 6 repeat arcings of each standard and are comparable with those usually obtained in spectrographic analysis. Further experimental details are given in Rice (1970). The raw data has been deposited with the Institute of Geological Sciences Library, Exhibition Road, London S.W. 7, and is available on request in the following form:

Table 1. Major and minor element analyses of the fresh and weathered bulk rock samples.
Table 2. Trace element analyses (ppm) of the fresh and weathered bulk rock samples.

Depth (inches)

Sample nos.

Depth scale labeled at -0, -10, 20, -30, 40, 50, 60, -70 with horizons A+B, C, D marked on the left.

Acid brown earth

◄ 1

Medium brown, slightly stony, non-humose (< 13 % organic matter) sandy loam; fine crumb structure, crumbly and very friable, fine plant roots.

◄ 2

Head

◄ 3

Yellow brown, stony loamy sand with cobbles of reddened granite, no obvious crumb structure, fine roots; rests unconformably on the growan.

Erosion surface

Growan

◄ 4

Pale yellow-buff sand, which retains the granite texture but has lost intergranular cohesion.

◄ 5

Iron-stained granite with numerous horizontal joints.

◄ 6

Lenses of strong iron-stained sand designated sub-horizon D7.

◄ 7
◄ 8

◄ 9

◄ 10

Granite

◄ 11-15

Iron stained granite with less common horizontal joints, passes fairly rapidly (within several inches) into fresh granite.
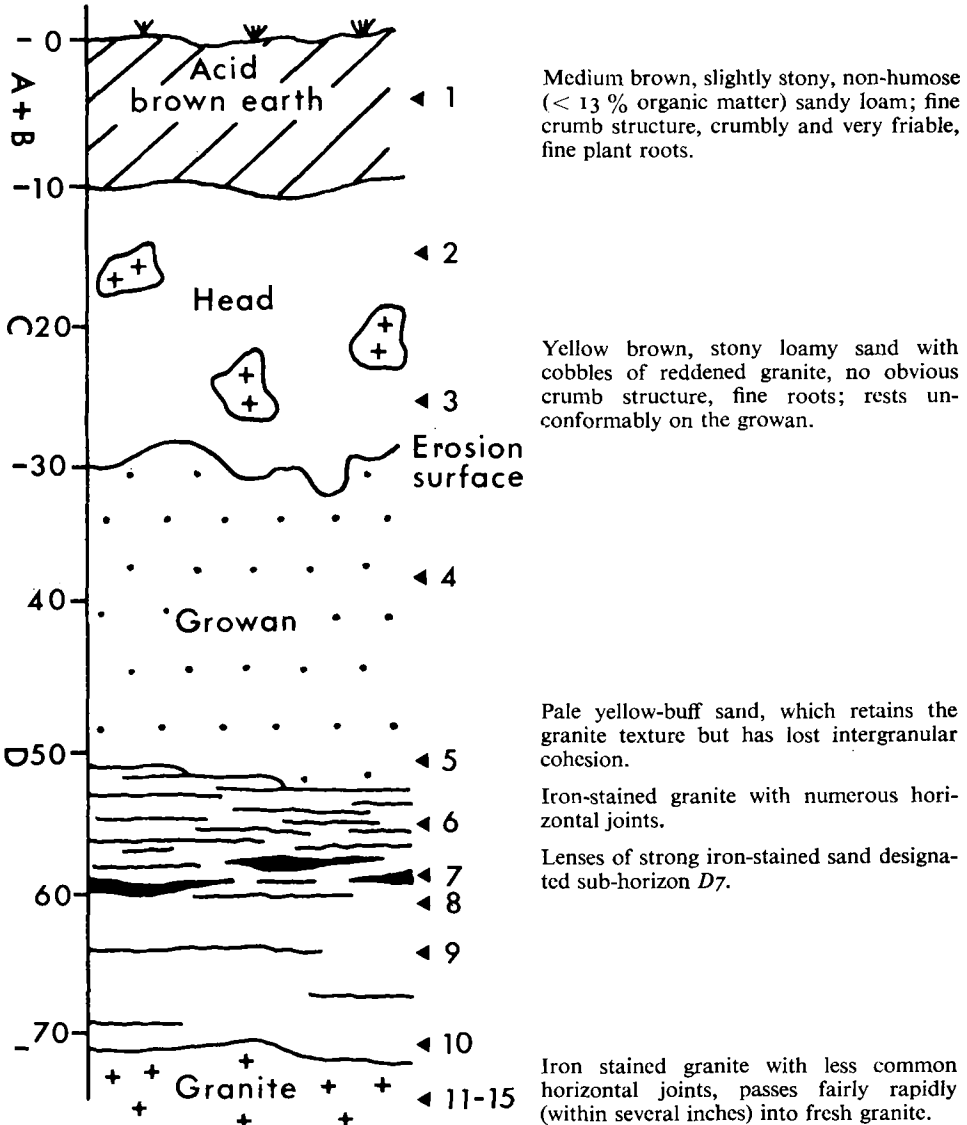
FIG. 2. Profile description: Locality: Bosahan quarry, Cornwall. Grid reference: 190SW 734304. Elevation: 450 ft. Slope and aspect: 5°, near crest of SW facing slope. Drainage class: free. Vegetation: heathland with gorse, agricultural grassland nearby. Profile horizons are lettered $A+B$, C, and D. Fresh granite samples are numbered 11 to 15. Sample 15 was collected from another quarry 100 yds to the E.

Table 3. Partial mineralogical analyses for the bulk rock samples and fine fractions.
Table 4. Trace element analyses (ppm) of the fine fractions from horizons $A+B$, C, D, and sub-horizon $D7$.
Table 5. Major and minor element analyses of the fine fractions from horizons $A+B$, C, D, and sub-horizon $D7$.
Table 6. Major and minor element analyses of fresh and weathered muscovites and biotites. Selected biotite analyses are also located in Rice (C. M.), 1969, *Min. Mag.* **37**, 210–215. [M.A. 69–2295]

Bulk chemistry of the profile. It was found that significant chemical changes have occurred during weathering for all the major elements (except Mn) but only one, Zr (and perhaps Cr), of the trace elements (fig. 3). Generally speaking the three obvious horizons and a sub-horizon that can be distinguished in the field are also distinct chemically. For example, within the regolith Si is depleted in horizon C and sub-horizon $D7$, total iron is enriched in horizon C and Al depleted in horizon $A+B$. Ferrous iron, Ca, Na, and F are generally depleted in horizons $A+B$, C, D, and sub-horizon $D7$. Sub-horizon $D7$ differs from the rest of horizon D in that Fe^{2+} and Na are more strongly depleted. The obvious limonitic staining of the profile shows that Fe^{2+} is unstable and accounts for its depletion. The breakdown of oligoclase releases most of the Ca and Na in the rock and these elements together with F, which is largely derived from mica breakdown, are washed out of the profile. Extensive feldspar destruction in the upper horizons is probably responsible for the Al depletion in these horizons.

The data in Table I show that the enrichment in horizons $A+B$, C, and sub-horizon $D7$ of H_2O^- and H_2O^+ must be due largely to iron sesquioxides together with, in horizon $A+B$, organic matter. Most of the weight loss between 110° and 375 °C in horizons C, D, and sub-horizon $D7$ and a significant proportion in horizon $A+B$ is probably due to the partial dehydration of the sesquioxides.

The remaining elements exhibit more complex behaviour depending on the horizon. Phosphorus is enriched in sub-horizon $D7$ relative to the fresh rock and depleted in horizons $A+B$ and C; little change occurs in D. The main source of this element is apatite, which petrographic evidence indicates to be unstable during weathering. The mechanism of enrichment in sub-horizon $D7$ is unknown but P fixation by sesquioxides is a well-known feature of soils.

Potassium is depleted in horizons $A+B$ and C, which is partly at variance with the modal data for microcline perthite, the main source. This anomaly is probably related to the poor precision (error at 1 $\hat{\sigma}$ = 14 %) associated with the X-ray data. The slight enrichment in the D horizons is also difficult to explain but it may be due to an inadequate assessment of fresh rock variation, which is difficult for potassium since most of it occurs in large phenocrysts of microcline perthite.

Magnesium is depleted in horizons $A+B$ and C, and Ti enriched. The bulk of these elements is located in biotite, which is particularly unstable in these two horizons. Some of the Mg is fixed in chlorite after biotite destruction but the majority is lost. Rutile occurs as inclusions in biotite and probably accounts for the bulk of the Ti. Below sub-horizon $D7$ both elements show variation outside that estimated for the
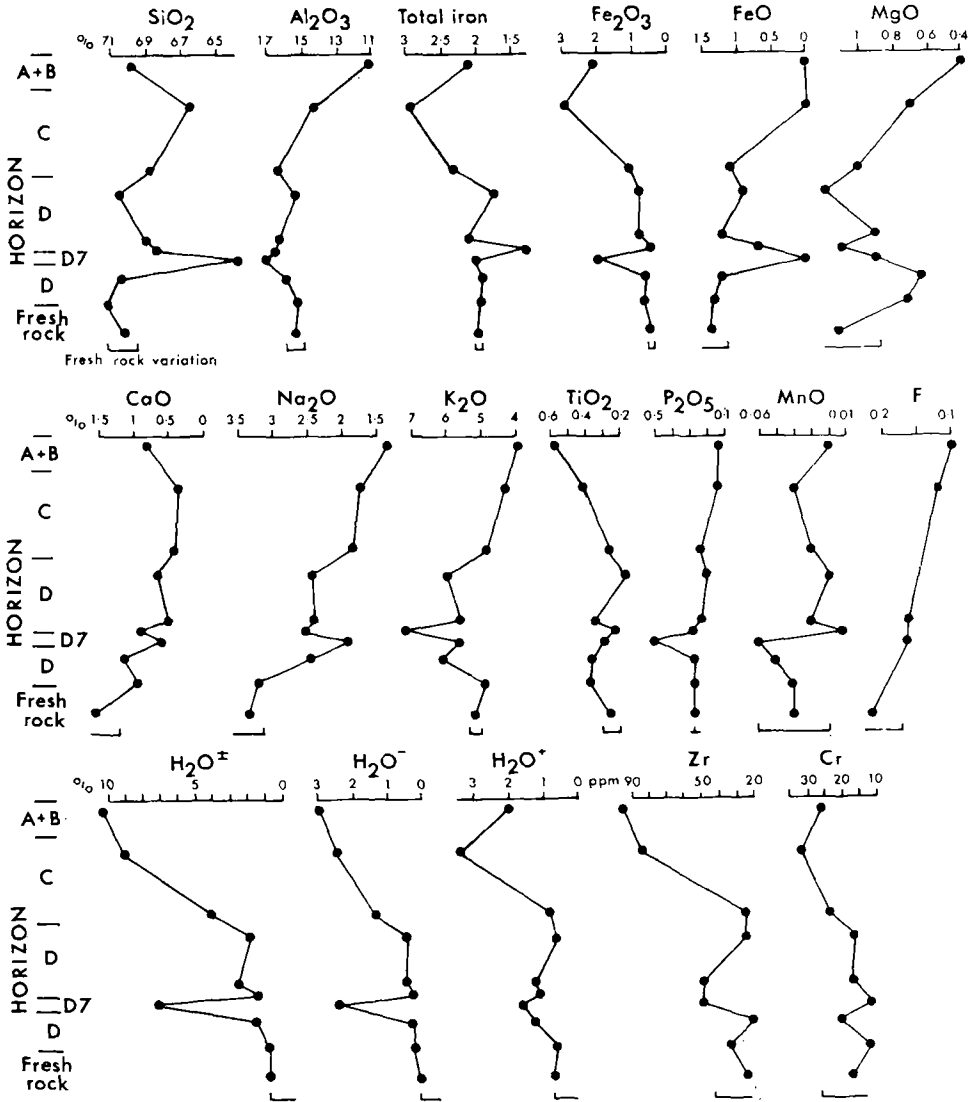
Fig. 3. Variation in bulk rock chemistry with depth; the limits of fresh rock variation are marked by bars, which represent the mean and one standard deviation of four fresh rock samples.

fresh rock. Since this is a relatively unweathered part of the profile the most likely explanation is that the estimate of fresh rock variation is in error.

Magnesium, Ca, Na, K, P, and F are therefore depleted in horizons $A+B$ and C relative to the fresh rock. In general the greatest depletion of bases is from horizon $A+B$. The chemistry of sub-horizon $D7$ differs from horizons $A+B$ and C in that Na and Ca only are lost relative to the fresh rock. This suggests a degree of weathering

TABLE I. *Size analysis of the fine fractions from the A+B, C, and D horizons and sub-horizon D7*

Fraction (μm)	D7	D	C	A+B
> 211	57·9	87·0	47·4	50·3
50–211	12·8	6·6	11·0	12·0
30–50	3·1	0·6	7·7	6·8
20–30	2·6	0·1	3·7	3·0
10–20	3·2	0·6	5·5	4·2
2–10	4·2	0·9	8·9	6·4
< 2	1·8	2·4	0·8	2·5
Organic matter taken as wt. loss 110 °C/375 °C	3·4	1·0	3·4	5·6
Sesquioxides removed by the dithionite leach, by difference	[11·0]	[0·8]	[11·6]	[9·2]
	100·0	100·0	100·0	100·0

for sub-horizon D7 intermediate between horizons (*A+B* and *C*) and *D*. The latter is least different from the fresh rock for all elements. In fact relative to the fresh rock most changes in the profile are small and this together with the low organic matter and clay content (compared to a mature podzol or brown earth) indicates a juvenile soil.

The absence of significant change for the majority of the rare elements is also consistent with this observation. The Zr enrichment can be attributed to the mechanical accumulation of zircon—a common accessory mineral in the rock. The data for Cr is of doubtful significance since it depends on a single result, which is only just outside the fresh rock variation.

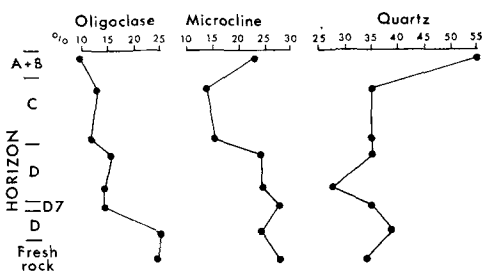*Bulk mineralogy of the profile.* The distribution patterns for quartz and feldspar reflect (like the chemical data) the horizons distinguished in the field (fig. 4). The quartz maximum in horizon *A+B* is consistent with weathering in a temperate climate. Oligoclase was found to be one of the most unstable of the primary minerals in that approximately 50 % of it is destroyed once it enters the weathering zone. As expected the behaviour of oligoclase is similar to that of Ca. Microcline, however, remains constant in the *D* horizon

FIG. 4. Variation in bulk-rock quartz and feldspar with depth.

relative to the parent rock but decreases by about 50 % in the *C* horizon, which is in broad agreement with the trend shown by K. However, the enrichment of microcline in the *A+B* relative to the *C* horizon is at variance with the chemical data and is probably due to the poor precision of the X-ray method.

Despite the highly weathered appearance of sub-horizon D7, the quartz and feldspar

contents are remarkably similar to other D horizons. On the microscopic scale, however, all feldspar is pseudomorphed by a fine grained iron-stained apparently isotropic material. It would seem likely that the feldspars still maintain their structural identity on a sub-microscopic scale, in the coarser particles at least.

The behaviour of the micas in the bulk rock samples was only superficially studied. An optical and X-ray diffraction examination suggested that biotite is absent from horizons $A+B$ and C and present in reduced quantities in sub-horizon $D7$. The high level of sesquioxides in these three horizons also supports this conclusion. Muscovite, on the other hand, occurs in all horizons and alteration seems restricted to edge effects. Mica levels in horizon D are comparable with the fresh rock.

Chemical change between horizons is small, whereas the high sesquioxide content of certain horizons and the marked depletion of oligoclase and biotite show there has been considerable within-horizon redistribution of some elements, but not quite to the stage of alumino-silicate formation.

Gibbsite was detected in bulk samples from horizon D and sub-horizon $D7$ but not in the $A+B$ or C horizons or the fresh rock (Table II). Its absence in the fresh rock indicates it is formed by weathering. This mineral is a typical product of tropical weathering and is a major constituent of lateritic soils; it is uncommon in temperate climates and has only rarely been reported in Britain (Ball, 1964; Wilson, 1969; Green and Eden, 1971). Its occurrence in the D horizon is unexpected since soil solutions should become more base-rich with depth and minerals precipitating from them should obviously reflect this trend.

Kaolinite occurs in all horizons but chlorite only in horizons $A+B$ and C (Table II) and both are present in the fresh rock.

In conclusion, the bulk mineralogy and chemistry and field data indicate a juvenile acid brown earth (sol brun lessivé) with possible incipient laterization in the D horizon. This situation, where the lower part of the profile has been affected by a more intensive chemical weathering than the upper part, is unusual and is discussed in a later section together with the origin of sub-horizon $D7$.

Mineralogy of the fine fractions. In the $A+B$ and C horizons little change occurs in the primary phase assemblage as the grain size decreases except for the replacement of biotite by chlorite in the fraction < 50 μm and the appearance of gibbsite (Table II). The latter mineral occurs in all the fractions examined in horizon C but only the < 2 μm fraction of horizon $A+B$; it was not detected in the bulk samples. In the D horizon the assemblage again shows little change except that quartz and microcline are absent from the < 2 μm fraction and chlorite accompanies biotite in the 10–20 μm fraction. Substantial changes occur, however, in the primary assemblage in the various fractions of sub-horizon $D7$. Only biotite persists into the < 2 μm fraction and quartz is restricted to the fraction > 50 μm. Gibbsite occurs in all fractions of the D horizons and K-mica in all fractions throughout the profile except the finest fractions of sub-horizon $D7$. Indeed the finest fraction (< 2 μm) of the latter horizon is composed essentially of gibbsite and kaolinite. Analyses of weathered muscovites demonstrate that the species designated K-mica is a K-deficient muscovite with additional H_2O^+.

The presence of all major primary phases (with the exception of biotite) in the finest fraction of horizons $A+B$ and C shows that weathering is more advanced here than in the D horizons, where only oligoclase and a 10 Å phase occur in the finest fraction; no definite primary phases were identified in the same fraction of sub-horizon $D7$. From the above data the relative stabilities of the major phases are, in order of decreasing stability: quartz ≈ microcline ≈ muscovite > oligoclase > biotite.

TABLE II. *Qualitative mineralogical analysis by X-ray diffraction of the bulk rock samples and fine fractions from horizons $A+B$, C, and D and sub-horizon $D7$. Fresh rock sample 11 is also included*

Horizon A+B	Bulk rock	50-211 μm	30-50 μm	20-30 μm	10-20 μm	2-10 μm	<2 μm	Horizon D	Bulk rock	50-211 μm	30-50 μm	20-30 μm	10-20 μm	2-10 μm	<2 μm	Fresh rock 11
Quartz	+	+	+	+	+	+	+		+	+	+	+	+	+	−	+
Microcline	+	+	+	+	+	+	+		+	+	+	+	+	+	−	+
Oligoclase	+	+	+	+	+	+	+		+	+	+	+	+	+	+	+
Biotite	−	+	−	−	−	−	−		+	+	+	+	+	+	M	+
Muscovite	+	+	+	+	+	+	+		+	+	+	+	+	+	M	+
Kaolinite	−	+	+	+	+	+	+		+	+	+	+	+	+	+	+
Gibbsite	−	−	−	−	−	−	+		+	+	+	+	+	+	+	−
Chlorite	+	−	+	+	+	+	+		−	−	−	−	+	−	−	+

Horizon C	Bulk rock	50-211 μm	30-50 μm	20-30 μm	10-20 μm	2-10 μm	<2 μm	Sub-horizon D7	Bulk rock	50-211 μm	30-50 μm	20-30 μm	10-20 μm	2-10 μm	<2 μm
Quartz	+	+	+	+	+	+	+		+	+	−	−	−	−	−
Microcline	+	+	+	+	+	+	+		+	+	+	+	−	−	−
Oligoclase	+	+	+	+	+	+	+		+	+	+	+	+	−	−
Biotite	−	+	−	−	−	−	−		+	+	+	+	+	M	M
Muscovite	+	+	+	+	+	+	+		+	+	+	+	+	M	M
Kaolinite	+	+	+	+	+	+	+		+	+	+	+	+	+	+
Gibbsite	−	+	+	+	+	+	+		+	+	+	+	+	+	+
Chlorite	+	+	+	+	+	+	+		−	−	−	−	−	−	−

Diffractograms of fresh rock samples 12, 13, and 15 are comparable with 11.

$+$ = present, $-$ = absent, M = undifferentiated 10 Å phase.

Although gibbsite occurs in all horizons the X-ray peak intensities indicate that it is best developed in the D horizon (Table III).

The presence of chlorite and absence of biotite in size fractions < 50 μm in horizons $A+B$ and C, which are more weathered than the D horizons, suggests that much of the chlorite is derived from biotite by weathering.

Kaolinite occurs in all fractions throughout the profile as well as the fresh rock. Significantly, X-ray peak intensities in Table III suggest that greater amounts of kaolinite (like gibbsite) occur in the fine fractions of the D horizons than in the $A+B$ and C horizons.

Both kaolinite and gibbsite were detected throughout the whole range of size fractions studied up to a particle size of 211 μm. It is unlikely that they would form crystals or strong aggregates of this size and the more plausible alternative is that they are pseudomorphing or partially replacing the feldspars. The occurrence of these minerals in the coarser fractions effectively rules out downwashing from the $A+B$ and B horizons as a possible origin.

TABLE III. *Peak intensities (c/s) for kaolinite (7 Å), gibbsite (4·84 Å), and chlorite (14 Å) in the bulk rock and fine fractions from horizons $A+B$, C, and D and sub-horizon $D7$*

	Bulk rock	50–211 μm	30–50 μm	20–30 μm	10–20 μm	2–10 μm	< 2 μm
			Horizon $A+B$				
Kaolinite	n.d.	8·0	8·0	9·5	13·0	6·5	3·2
Gibbsite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8·0
Chlorite	3·2	n.d.	8·0	22·0	43·0	40·0	27·0
			Horizon C				
Kaolinite	14·5	21·0	30·0	43·0	53·0	37·0	38·0
Gibbsite	n.d.	5·0	8·0	19·0	21·0	19·0	24·0
Chlorite	10·0	26·0	72·0	71·0	88·0	84·0	57·0
			Horizon D				
Kaolinite	8·0	57·0	72·0	85·0	76·0	64·0	27·0
Gibbsite	11·0	57·0	54·0	84·0	61·0	195·0	245·0
Chlorite	n.d.	n.d.	n.d.	n.d.	32·0	n.d.	n.d.
			Sub-horizon $D7$				
Kaolinite	24·0	11·0	64·0	80·0	64·0	40·0	24·0
Gibbsite	11·0	11·0	57·0	77·0	112·0	96·0	198·0
Chlorite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detected.

In fig. 5 two distinct quartz distribution patterns can be distinguished characterizing horizons $A+B$ and C on the one hand and D (including sub-horizon $D7$) on the other. The feldspars show similar patterns but with generally higher levels at any given grain size in the upper horizons than in the lower horizons. In horizons $A+B$ and C there are pronounced quartz maxima, which are absent in the D horizons. The maximum in horizon $A+B$ is broader and less well defined than that in the C horizon; the latter has a peak at about 45 μm. One explanation for these maxima is that they are due to Pleistocene wind-blown loess, which has accumulated in the upper parts of the profile. This has been reported by Coombe and Frost (1956) to be an important constituent of the soils of the Lizard. According to Swineford (1955) Western European loess mostly occurs between 30 and 60 μm, which is in reasonable agreement with the present range.

Chemistry of the fine fractions. The coarse fines almost always show trends intermediate between those of the bulk rock and those of the < 10 μm fraction, hence in

fig. 6 they have been largely ignored. It is obvious that greater changes occur between individual horizons in the fine fractions than in the bulk rock.

Silicon is strongly depleted with depth whereas Al shows the reverse trend. Total iron is depleted with depth in the finest fractions but enriched in the coarser ones. The data for iron should be treated with caution since the sesquioxides have been removed
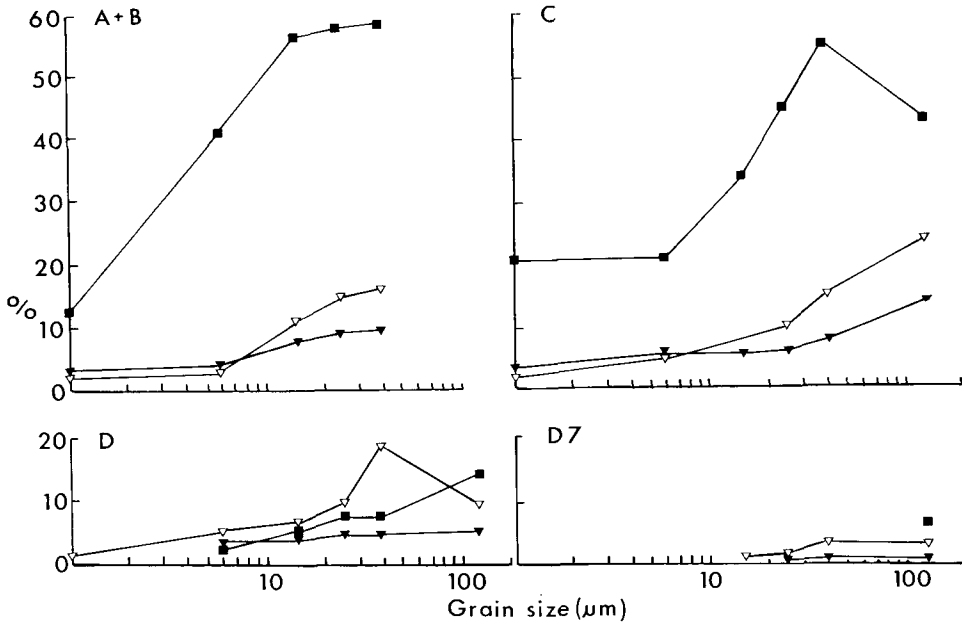

FIG. 5. Variation of quartz and feldspar with grain size in horizons $A+B$, C, and D and sub-horizon $D7$. ■ = quartz, ▼ = microcline, ▽ = oligoclase.

by the dithionite leach and the remaining iron should therefore be located in mineral lattices. On this basis the trend in the coarser fractions agrees with the behaviour of biotite, whereas that in the finer fractions is sympathetic with the chlorite distribution pattern. The high Al and H_2O^+ content of the D horizon fines strongly indicates that gibbsite is present in substantial quantities. Since the Si:Al ratio increases markedly from the D to the $A+B$ and C horizons gibbsite must become quantitatively less important and diffraction data in Table III confirm that chlorite and kaolinite are dominant phases in the $A+B$ and C horizons.

In the < 2 μm fraction of horizon $D7$ only gibbsite and kaolinite were identified, although the presence of small quantities of Mg and K suggest degraded muscovite and biotite or chlorite or both may also occur. Assuming that amorphous alumina and silica and residual mica are negligible and that gibbsite and kaolinite are stoichiometric, normative gibbsite constitutes about 55 % and kaolinite about 30 % of this fraction.

After subtracting the proportion of K resident in microcline from total K in the < 2 μm fraction of horizons $A+B$ and C significant amounts of K remain, which suggests that K-mica is another important constituent together with chlorite and kaolinite.

Magnesium is enriched in the $A+B$ and C horizons, particularly the latter. Chlorite, as the only ferromagnesian mineral in these horizons, presumably contains the bulk of it and the highest concentrations of this mineral therefore occur in the C horizon, a conclusion supported by diffraction data.
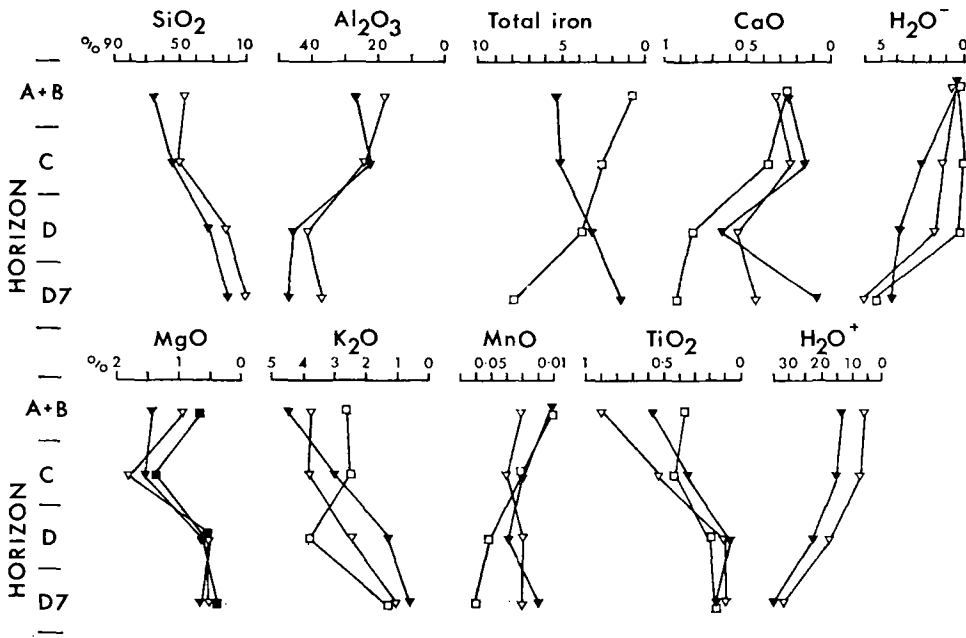
FIG. 6. Variation of fine fraction major and minor element chemistry with depth. For clarity only those fractions necessary to indicate the trends are included and the abscissae simplified. ▼ $- < 2$ μm, ▽ $- 2$-10 μm, ■ $== 10$-20 μm, ⌐ $- 30$-50 μm.

Calcium is depleted in the $A+B$ and C horizons relative to the D horizons except in the < 2 μm fraction of horizon $D7$, where no Ca was detected. This behaviour is opposite to that of oligoclase, yet in the bulk rock samples Ca and oligoclase vary sympathetically. One possible explanation is that kaolinite and gibbsite pseudomorphs after oligoclase in the D horizons still retain a portion of the original Ca.

Manganese maintains a fairly constant level throughout the profile, except in the coarser fractions, where there is a tendency for it to increase with depth. In this respect its behaviour suggests an association with iron, which in the coarse fractions of the D horizon is largely in biotite. This association is not surprising since biotite contains about two-thirds of the Mn in the fresh rock (Rice, 1970). Titanium is enriched in the upper horizons and thus displays the same trend as in the bulk rock.

With few exceptions all the elements in each horizon show significant changes with grain size (fig. 7). Some show linear relationships, others exponential or more complex curves with maxima and minima. This is only to be anticipated, since most elements occur in several primary phases of varying stability and on release become associated with one or more secondary minerals. On the basis of their chemistry the horizons again fall into two groups, i.e. horizons $A+B$ and C, and horizon D including sub-horizon $D7$.
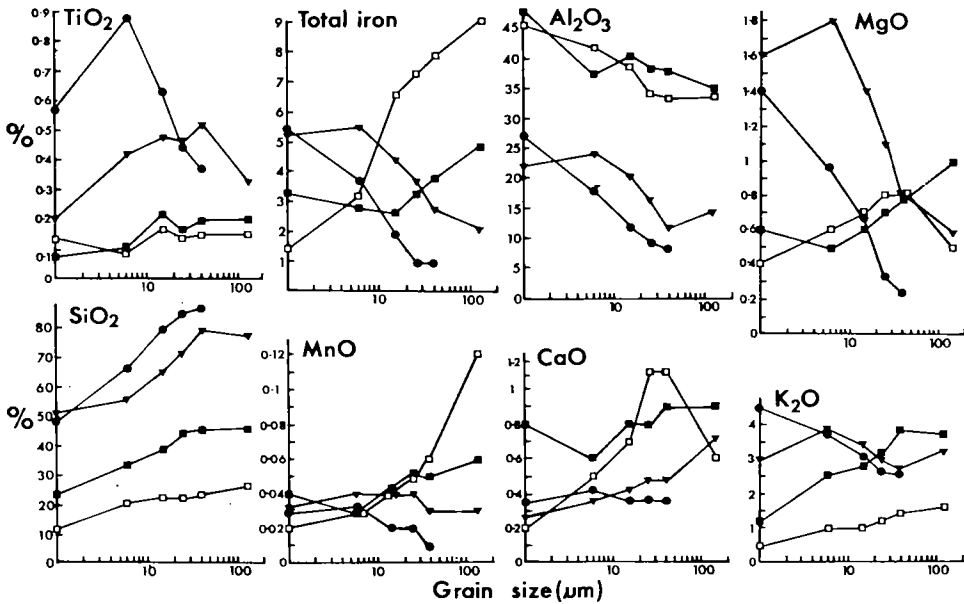

FIG. 7. Variation of eight major and minor elements with grain size in horizons $A+B$, C, and D, and sub-horizon $D7$. ● $- A+B$, ▼ $= C$, ■ $= D$, ☐ $= D7$.

In horizons $A+B$ and C, Al, total Fe, and Mg are enriched in the finest fractions whereas Si is depleted. Data for P are available from horizon $A+B$ only and show that limited enrichment of this element occurs in the finest fractions of this horizon, perhaps due to an association with residual sesquioxides. The behaviour of Al and Si may be attributed to the high Al:Si ratio of the secondary mineral assemblage. The Fe and Mg detected in the finest fractions are presumably present in chlorite.

Potassium is slightly enriched as the grain size decreases in horizon $A+B$ but it maintains a constant level in horizon C. This element is partitioned between microcline and K-mica and the latter phase is enriched in the finest fractions. Manganese exhibits roughly the same distribution pattern as K and is probably mainly located in the K-mica. In the fresh rock muscovite contains about one third of the Mn and so this association is probably primary.

The Ca content of horizon $A+B$ does not vary with grain size whereas in horizon C

it is depleted slightly as this parameter decreases. The bulk of the Ca is located in feldspar.

Titanium exhibits a sharp maximum at about 5 μm and a broad one between 10 and 40 μm in horizons $A+B$ and C respectively. These are probably due to the accumulation of rutile needles; the smaller size and more restricted size distribution in horizon $A+B$ is perhaps indicative of more intensive comminution in this horizon.

In horizon D including sub-horizon D7 the general depletion of Mg, K, Ca, and Si together with the enrichment of Al with decreasing grain size supports the diffraction data that gibbsite and kaolinite are the major phases in the fine fractions of these horizons. The maxima shown by Ca and Mg in sub-horizon $D7$ may be due to apatite and biotite respectively. The sharp decrease of total Fe and Mn in the finest fractions is probably due to the removal of sesquioxides of iron and manganese by the dithionite leach.

Trace element chemistry of the fine fractions. With the exception of Zr no significant interhorizon variation occurs in the bulk samples. However, in the fine fractions considerable variation occurs with depth in the profile and with grain size (fig. 8). The most obvious trend is the enrichment of some elements in the $<$ 10 μm fraction of each horizon with most elements being enriched in the $A+B$ and the least in the D horizons.

A major portion of the Cr, V, Co, Ni, and Zn in the parent rock is contained in biotite (Table IV and Rice, 1970) and it is likely that the feldspars contain the bulk of the Pb, Ba, and Sr. Bradshaw (1967) found 200 ppm Pb and 300 ppm Sr in feldspars from the Carnmenellis granite. Thus a considerable proportion of many of the trace elements examined here are present in three phases, two of which (biotite and oligoclase) are the least resistant to weathering of the major primary minerals. This partly explains why the weathered rock, although affected by a low degree of chemical weathering, contains considerable concentrations of trace elements in the weathering products.

Chromium, V, Ga, Ni, Pb, Zn, and Cu are enriched in the $<$ 10 μm fraction of the $A+B$ and C horizons and Ba and Sn in the same fraction of the $A+B$ horizon only; copper, Pb, and Zn are most enriched, by a factor of at least ten. Fewer elements (Cr, Cu, Pb, and Zn) are enriched in the $<$ 10 μm fraction of the D horizons and of these Cu, Pb, and Zn are again the most enriched. Lead is probably mainly located in K-feldspar in the parent rock and Zn in biotite. However, the copper maximum at about 20 μm in the D horizon suggests that Cu is associated with a fine grained primary mineral and pyrite would seem the most likely host among the identified accessory minerals. Chromium, V, and Co show maxima between 10 and 40 μm in the $D7$ horizon, which suggests an association (like Cu) with a fine grained primary mineral; the most likely possibility is ilmenite, which commonly occurs as inclusions within biotite. The data for Ni suggest it occurs in the biotite lattice and on release behaves like Cr and V. The very high Sn concentrations in muscovite (Table IV) suggest microscopic inclusions of cassiterite. Accumulation of these in the $A+B$ horizon would account for the Sn enrichment observed. In the $<$ 10 μm fraction of the $A+B$ and C horizons
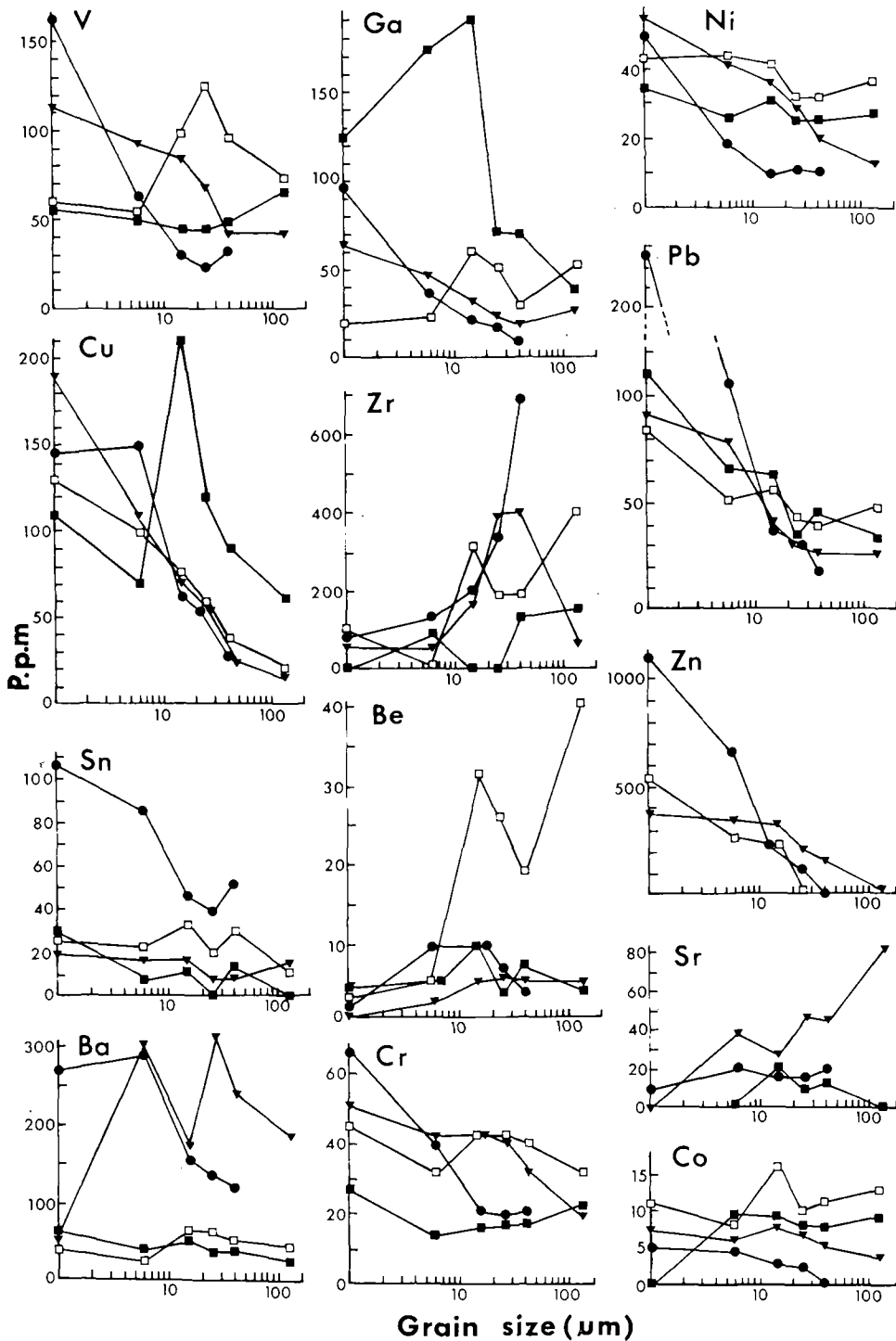
FIG. 8. Variation of thirteen trace elements with grain size in horizons $A + B$, C, D, and sub-horizon D_7. ● = $A + B$, ▼ = C, ■ = D, □ = D_7.

Ga may be substituting for Al in the weathering products. The Ga maximum at about 10–20 μm in the D horizons may be due to accumulation of an aluminium-rich primary mineral such as andalusite. The distribution of Ba in the $>$ 10 μm fraction of the $A+B$ and C horizons suggests the presence of a primary barium-rich mineral—possibly a feldspar. The behaviour of Zr is mainly a function of the stability of zircon. The size of the crystals as indicated by the maximum in the C horizon is consistent with that observed in thin section, i.e. 15 to 70 μm. Strontium and Co are not enriched in the weathering products of any horizon. Beryllium only shows significant change with grain size in the $D7$ horizon, where it is enriched in the coarser fractions. The most likely reason for this is the presence of a primary mineral such as beryl.

TABLE IV. *Trace elements (ppm) in fresh and weathered muscovite and biotite*

Sample	Muscovite fresh 15	Muscovite fresh 13	Muscovite weathered 3 > 211	Biotite fresh 15	Biotite fresh 13	Biotite weathered 3 > 211
Ba	105±25	84±20	160±35	430±100	500±115	250±60
Sr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Co	n.d.	3·2±0·5	4·8±1	16±2	17·5±3	16·5±2
Ni	5·6±1	3·4±1	14±3	48±5	48±5	45±5
Be	8·8±1	7·2±1	7·1±1	2·2±0·3	1·9±0·2	2·7±0·3
Zr	n.d.	n.d.	35±5	n.d.	n.d.	n.d.
Cr	15±2	13±1	28±3	170±20	140±15	110±12
V	40±6	44±6	84±12	250±30	190±25	200±25
Cu	10±1	7·0±1	37±3	5±1	5±1	36±3
Ga	250±30	250±30	380±45	350±40	360±45	390±45
Zn	n.d.	n.d.	n.d.	880±160	830±150	710±130
Pb	5·5±1	2·5±0·5	37±5	n.d.	n.d.	n.d.
Sn	4300±390	1800±160	120±10	84±8	70±7	70±7

Note: 3 > 211 refers to the > 211 μm mica fraction in sample 3.
n.d. = not detected.

Location of trace elements in the < 10 μm fraction. Degraded muscovite (a major component of the < 10 μm fraction in the $A+B$ and C horizons) is capable of concentrating Ba, Ni, Cr, V, Cu, Ga, and Pb, whereas weathered biotite concentrates Cu and is depleted in Ba and Cr (Table IV). The enrichment factors between fresh and weathered muscovite are of the same order as those observed between the < 10 μm and coarser fractions of the regolith and greater enrichments may prevail in the very fine grained mica. Low tin values in the weathered muscovite may indicate that cassiterite has become separated. Only Zn, among the elements enriched in the < 10 μm fraction of the $A+B$ and C horizons, is not associated with the K-mica and this may be due to retention within the biotite at this stage of weathering. The mechanism of the association between these trace elements and degraded muscovite (or Cu and weathered biotite) is unknown but it is possible that they are replacing K in the interlayer position in some way. Potassium is the only major element that is depleted during weathering of muscovite. Degraded muscovite is absent from the < 10 μm fraction

of the D horizons, which suggests that here kaolinite or gibbsite or both may be responsible for concentrating the Cr, Cu, Pb, and Zn. The above data show that at least one of the silicate phases among the weathering products is an important site for trace element enrichment but its importance relative to other silicates, limonite, and organic matter is unknown.

The origin of the profile. In the weathering profile the minerals chlorite, K-mica, and kaolinite predominate in the finest fractions of horizons $A+B$ and C whereas in the D horizons the dominant phases are gibbsite and kaolinite. The available evidence suggests that all the gibbsite and most of the kaolinite and chlorite originated by weathering. K-mica is largely a partial degradation product of muscovite. Broadly speaking minerals such as chlorite and K-mica are typical of brown earths, kaolinite of podzols and laterites, and gibbsite of laterites.

There is evidence that gibbsite, kaolinite, and limonite are now the stable phases throughout the profile, which indicates a regime characterized by a higher degree of leaching than the one where chlorite and K-mica were formed; indeed the presence of gibbsite suggests it is one having lateritic affinities. Pickering (1962) has suggested that a progressive change from brown earth to podzol to laterite could be caused by an increase in the degree of leaching.

An unusual feature of the distribution of kaolinite and gibbsite with depth is that the highest levels occur in the D horizons. In an ideal well-drained profile where the soil solutions move dominantly downwards these should become less reactive with depth, i.e. their pH and base content rises and Eh drops. Accordingly secondary minerals should become increasingly base-rich with depth and this occurs for example in some laterites where gibbsite in the upper part of the profile is replaced by kaolinite lower down. The present profile departs from ideality in that the zone of base-rich minerals is inverted with respect to the base deficient ones. This may be explained by either the D horizon representing the truncated remnant of an earlier profile formed when chemical weathering was more pronounced than at present or the entire profile forming under essentially the same weathering regime but the soil solutions moving through the D horizon were more reactive than those moving through the $A+B$ and C horizons. This would imply that movement was dominantly lateral.

The first theory implies that gibbsite has survived the change of weathering regime from a lateritic to an acid brown earth situation. The age of the truncated profile is problematical but a Tertiary or Interglacial origin seem the only possibilities. However, if Balchin (1967) is correct in his assertion that there was an early Pleistocene 675 ft transgression over the S.W. peninsula then an Interglacial origin would be preferred since weathered rock of Tertiary age in such an exposed position would surely have been removed. Truncation and the deposition of head occurred next probably under periglacial conditions.

The area became afforested in post-glacial times beginning with a pine/birch cover (*c.* 9000 B.C.), which was later replaced (*c.* 5000 B.C.) by oak forest. During this time soil formation would have been initiated and afforested uplands in a temperate climate would probably generate acid brown earths. It seems reasonable therefore to attribute

the formation of the juvenile acid brown earth and in particular chlorite and K-mica to this period. At the beginning of the Bronze Age, c. 2000 B.C., the area probably was deforested. It is suggested that the high rainfall, absence of tree cover, and natural good drainage have subsequently caused the impoverishment of the soil by increasing the degree of leaching until first kaolinite and now gibbsite have become the weathering products. According to this theory there have been two generations of gibbsite.

The second theory suggests that the D horizon was formed when chemical weathering was at a minimum. A likely time and mechanism would be respectively a glacial period and freeze–thaw action. The subsequent history would be essentially the same as the first theory beginning with truncation under peri-glacial conditions. However, the important difference is the postulate that because of the greater permeability of the growan compared with the overlying head and its position on a slope it has acted as an important pathway for the down-slope flowage of run-off water. While the area has been deforested (post c. 2000 B.C.) such flowage would be at a maximum and the soil solutions would also be more reactive than during periods of afforestation. It is suggested that during this period the bulk of the kaolinite and gibbsite was formed in the D horizon, and that because the process has only recently begun the fine fractions only have been affected. Both theories provide an explanation for the origin of the D7 horizon since the flowage of sub-surface run-off water and consequently weathering would be expected to reach a maximum in the D horizon just above bed-rock.

Some aspects of the profile history are uncertain but it seems reasonable to put its age as post-Tertiary, the formation of the acid brown earth as occurring between about 9000 and 2000 B.C., and the present weathering regime as having lateritic tendencies. Although total change is still small the soil is showing signs of developing into a temperate laterite.

Conclusions. Observations in the field together with chemical and mineralogical studies indicate the soil to be a juvenile acid brown earth. It is developed in head, which overlies in situ growan that forms a D horizon. There is a trend towards soil impoverishment, which may have reached incipient laterization. This can be attributed to the high rainfall, absence of tree cover, and free drainage, and is probably a common tendency on the Carnmenellis and other south-west England granites.

On chemical and mineralogical grounds the A+B horizon is the most weathered followed by the C, D7, and D horizons. The D7 horizon probably marks a zone where run-off water, after percolating downwards through the profile, meets bed-rock and continues in a lateral direction down-slope. The following relative stability series of major primary minerals during weathering has been established: biotite < oligoclase < microcline ≈ muscovite ≈ quartz (in order of increasing stability). This only applies to the present profile. The chloritization of biotite and the kaolinization of feldspar, which occur in the parent rock, continue during weathering. Also formed during weathering are gibbsite (probably from feldspar), limonite, and degraded muscovite.

Significant bulk chemical changes occur for Al, Si, Fe^{2+}, Fe^{3+}, total iron, Ca, Mg, Na, K, P, Ti, H, and F, but only Zr of the trace elements. Magnesium, Ca, Na, K, P, and F are depleted in the weathered rock whereas H, Zr, and Ti are enriched.

Zirconium and Ti are enriched because of the resistant nature of zircon and rutile respectively. Manganese shows no significant change. The behaviour of Si, Al, and Fe varies depending on the horizon.

Much greater chemical (and mineralogical) changes occur among the fine fractions, which are both confirmatory and complementary to those occurring in the bulk material. They provide valuable information on the history of the profile, particularly recent trends, since being fine grained they are the first to be affected by a change in the weathering regime.

There has been a redistribution of trace elements within the individual soil horizons between parent rock minerals and weathering products. In the $A+B$, C, and D horizons the following groups of elements are respectively concentrated in the $< 10\ \mu$m fraction: Ni, Cr, V, Ga, Cu, Zn, Pb, Sn, and Ba; Ni, Cr, V, Ga, Cu, Zn, and Pb; Cr, Cu, Zn, and Pb. In the $A+B$ and C horizons there is good evidence that a proportion of all of these elements, with the exception of Sn, are concentrated in degraded muscovite, possibly in the interlayer position. The importance of this phase relative to other silicates, limonite, and organic matter as a site for trace element enrichment is unknown. Tin is enriched as cassiterite and Sr, Be, and Co are lost from the profile.

The evidence suggests the profile was initiated during the Pleistocene but there is some doubt as to when the gibbsite and kaolinite were formed in the D horizon. The D horizon may represent a truncated profile formed either by chemical weathering or by freeze–thaw action during an interglacial period or glacial period respectively. In the latter case it is suggested that the kaolinite and gibbsite were formed by laterally moving solutions after deforestation c. 2000 B.C. The major features of the soil probably developed under oak forest in post-glacial times and reached the stage of a juvenile acid brown earth. Present trends are towards the development of a temperate laterite although it is emphasized that all changes relative to the fresh rock are small.

Juvenile soils of this type will contribute to the local river system silt and sand whose mineral components are essentially the same as the parent granite, but the proportions will differ. This applies especially to the silt where quartz will comprise about 50 to 60 %, the two feldspars about 10 % each, and degraded muscovite (K-mica) most of the remainder. Locally, where the D horizon is being eroded, kaolinite and gibbsite may be important constituents of the finer silt. The amount of clay contributed to the streams will be small (about 2 % of the total removable material) and will be composed of a small proportion of quartz and feldspar together with kaolinite, gibbsite, chlorite, K-mica, limonite, and organic matter. The clay at the beginning of transportation will be substantially enriched in most of the trace elements examined here relative to the coarser fractions and the parent granite.

Finally, the author would like to emphasize the value of including the fine fractions in any detailed geochemical study of weathering and if possible an estimate of the chemical and mineralogical variation within the parent material.

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