The 'toadstone-clays' of Derbyshire.

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AT many places in 'The Peak District' of Derbyshire, the igneous rocks, locally called 'toadstones', have, to varying extents, suffered an alteration with, as a result, the production of clays—locally called 'toadstone-clay'. These clays attracted the attention of the present author some years ago, and since that time, whilst conducting extensive 'field' investigations in the course of a survey of the minerals of Derbyshire, observations on them have been almost continuously made and the deductions drawn therefrom carefully considered.

The igneous rocks of Derbyshire (this vol., p. 60) vary but little in composition and are (with the obvious exception of the pyroclastic rocks) mainly olivine-dolerites and olivine-basalts. They consist of olivine, mostly in the form of phenocrysts and groups or nests of crystals; augite, as large ophitic plates, large and small phenocrysts, irregular grains, and prisms; in a few minor cases an orthorhombic pyroxene; and felspar, giving lath-like and tabular sections, and as microlites. The main felspar may be referred to as near labradorite. H. H. Bemrose considered it to be labradorite-anorthite, and H. C. Sargent described facies containing andesine-labradorite; Sargent also found, in some rocks, a considerable proportion of a felspar which is apparently orthoclase. Ilmenite is usually present in quite small amount; and apatite, as fine needles, may occasionally be seen.

Weathering.—The most conspicuous result of the action of weathering on these rocks is the oxidation of iron, with the production of limonitic and ochreous deposits. Accordingly as there may or may not have been an earlier alteration when the ordinary process of weathering began, and depending on the extent of the former, the product may be an ochreous clay, a very dark-coloured ferruginous earth, or a brown, 'sandy' deposit containing, in addition to limonite, much augite in a fresh condition. The ilmenite also remains fresh, and magnetite is not formed. At Knott Low, near Miller's Dale railway station, where the weathering has proceeded distinctly spheroidally, such a sandy deposit occurs.

'*Toadstone-Clay.*'—In contrast to the phenomena inherent in weather-
ing, there is a widespread form of alteration, by the process of which
the ferrous iron contained in the original rock is not oxidized.   Numerous
exposures of rock which has, to varying extents, undergone this alteration
are to be seen in the Matlock district.   The 'Upper' Lava of the
district—a contemporaneous olivine-dolerite—was cut through in sinking
the shafts of the Mill Close mine near Darley Dale and the following
section was there observed :

Limestone Shale	...	about 230 feet.
Limestone	...	,, 145 ,.
Toadstone-Clay	...	,, 4 ,,
Soft, crumbly, greenish toadstone merging to the solid rock	...	,, 60 .,
Limestone	...	—

Among the material then raised, rock which has undergone varying
degrees of alteration may now be found in the tip-heaps.

Dolerite-Greenstone.—An intermediate stage in the alteration is
represented by a mottled, green-coloured rock which may, perhaps, be
called dolerite-greenstone.

Beautiful specimens of diabantite may be occasionally found in this
rock.   The identity of the mineral was established by a complete
qualitative and partial quantitative analysis of carefully picked fragments ;
in amount, the radicles quantitatively determined are in close agreement
with the theoretical values.   This mineral occurs as radiated spherical
aggregates up to 2 cm. diam.; dark-green in colour; distinctly pleochroic—
in colours from sap-green to bluish-green.   It polarizes in low, first-order
colours ; has a sp. gr. of 2·79 ; and hardness about 2·3.   This chlorite
occurs in association with calcite in a rock consisting mainly of less
definite forms of chlorite.

The rock also contains cavities with a lining of calcite, the free ends
of the acute scalenohedra projecting towards the centre of the cavity.
Such cavities frequently contain an inner deposit of quartz crystals,
which may or may not form a complete filling.   The quartz is sometimes
amethystine.   Ferrocalcite is of not infrequent occurrence infilling
cavities, either alone or with calcite, from which, however, it is sharply
distinct.   In the ferrocalcite no cleavage is visible ; fresh surfaces are of
a pale-grey tint, and possess a waxy lustre, but on exposure a brown,
ochreous film forms over the surface.   It has a specific gravity of 2·83.

Microscopical examination of sections of the main portions of the rock
reveals the fact that the original minerals and structure are both almost

completely lost. The most abundant constituent is a chlorite of pale-green colour—as seen in thin section, but dark-green when in the mass; it exhibits pleochroism (although the absorption is not strong) in colours from yellow-green to deeper green, and anisotropism in greys and pale-yellows of the first order. Quantitative analysis of a sample of fragments of the chlorite aggregates carefully picked from the rock gave the following results :

SiO_2.	Al_2O_3.	FeO.	MgO.	CaO..	CO_2.	H_2O.	Total.
36·24	13·10	21·06	17·18	trace	trace	11·68	99·26

Although the iron present exists mainly in the ferrous state, a little may be present in the ferric condition, but owing to insufficient quantity of sample for separate determination in the above analysis it was all calculated as ferrous oxide. This analysis approximates to those of diabantite and delessite, but not near enough to either to establish identity. The chlorite is probably, as usually is the case, not a definite species. This chlorite exists as finely crystalline, radiated, spherical, and encrusting aggregates, which usually have well-defined boundaries marked by concentrically banded layers of minute particles of a mineral which, under the usual powers of the microscope, appears white and opaque. In a less definite form, chlorite constitutes the bulk of the groundmass of the rock. Here it is not of constant colour, but varies somewhat widely in degree of yellowness; it is irregularly mixed with the other constituents, and also often occurs as a partial replacement of the remaining felspars— when it is usually free from yellowness of tint.

Calcite is plentiful ; it sometimes occurs as a partial filling of vesicle-like masses, but also irregularly in the rock-mass, and as partial replacements. Quartz is of very variable occurrence ; some sections contain little or none, whilst in others it is plentiful. It occurs irregularly in the rock-mass and also in association with the vesicle-like aggregates. Magnetite as minute cubes of secondary formation occurs with, and extruded from, pseudomorphs—principally after augite. Most of the felspar originally present has disappeared, but numerous porphyritic crystals have offered greater, but not complete, resistance to attack, and remain showing varying amounts of corrosion and replacement by chlorite. These remaining felspar crystals are frequently fractured, and the fragments usually show slight relative displacement; thus indicating contraction of the residual deposit as the altering solutions removed soluble constituents.

Examination under a $\frac{1}{12}$-inch oil-immersion objective clearly shows

that the mineral which appears white (by reflected light) and opaque under the usual powers, is a transparent, yellow mineral of very high refractive index and possessing a high (adamantine) lustre. The minuteness of the grains of a very high refractive index packed closely together is the cause of the apparent opacity and whiteness. The mineral can be identified with little doubt as anatase resulting from the alteration of titaniferous minerals such as ilmenite.

It will thus be seen that the rock at this stage consists mainly of an apparently indefinite chlorite; the felspar is not yet all gone; calcite and anatase are the only other substances which are constantly present. The titanium-content of the rock has increased as a result of its concentration in the residue, whilst soluble compounds are removed. Such rock can only be seen when a suitably-altered bed is artificially cut through.

'*Green-Earth.*'—A more advanced stage of the same type of alteration is represented by 'green-earth', and exposures of rock in this stage of the alteration are quite numerous. This material is of quite indefinite composition; it consists essentially of chloritic substances in varying degrees of opacity due to their incomplete further alteration to a white clay. In colour it varies between distinct green and pale greyish-green. Calcite is usually present, and also pyrites, in variable amounts, as disseminated small crystals and groups of crystals.

At about this stage, the material sometimes begins to show traces of a somewhat shale-like type of 'bedding'—due to its being of the character of a residue remaining after the removal, in solution, of quantities of components of the original rock.

The End-Product.—The process when continued further may result in the production of a very fine, smooth, almost white clay, and this is, undoubtedly, only a residue remaining from the original rock, the greater part of which has been removed in solution. The following analyses are of these clays, on samples dried at 100° C. :

		1.		2.		3.		4.
SiO_2	...	45·4	...	49·3	...	51·0	...	52·8
Al_2O_3	...	22·9	...	26·92	...	23·56	...	31·4
H_2O	...	7·6	...	9·5	...	10·1	...	9·75
CaO	...	9·2	...	0·8	...	0·51	...	nil
CO_2	...	7·3	...	nil	...	nil	...	,,
MgO	..	1·6	...	2·3	...	3·37	...	,,
Fe_2O_3	...	nil	...	3·28	...	5·8 ⎫	...	6·0
TiO_2	...	4·4	...	4·3	...	2·94 ⎭		
SO_3	...	—	...	—	...	0·83	...	nil
		98·4		96·4		98·11		99·95

1. Greyish-white clay from sample of 'green-earth', from Milltown, Ashover.
2. Almost white clay, from Ball Eye, Bonsall.
3. Clay, tinted yellow by ochre, from Ible.
4. Specimen of almost pure, washed clay particles from the Ible sample. The amount of material on which this analysis was made was 0·0820 gm. The TiO_2 in this sample was precipitated along with a very small quantity of Fe_2O_3 by means of ammonium nitrosophenyl-hydroxylamine; it was a tolerably pure specimen with little impurity other than inclusions of anatase.

Deducting, from these analyses, the lime as carbonate (1), or gypsum (2 and 3); the magnesia as hydrous silicate; and the ferric oxide as limonite, and then calculating each analysis to 100 % gives the following figures :

		1.	2.	3.	4.	Average of 1, 2, and 3.	5. Theoretical.
SiO_2	...	58·2	56·0	58·1	56·2	57·4	57·46
Al_2O_3	...	31·6	33·7	31·0	33·4	32·1	32·38
H_2O	...	10·1	10·3	10·9	10·3	10·4	10·16

These analyses indicate a compound having the formula :

$$2\,Al_2O_3 \cdot 6\,SiO_2 \cdot 3\,H_2O,$$
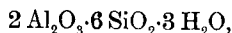
and the exact theoretical composition of such a compound is shown under number 5 above for purposes of comparison. Thus, the analysis of the small quantity of washed particles confirms the suggestive indications of the analyses of the bulk samples from three different beds, that the clays apparently consist essentially of a definite compound of tolerably constant composition. The stability of the compound may not be great, however, under conditions other than those which prevail in situ.

The clay, in the best specimens, is almost white and, when dry, it has a soapy or greasy feel. The mineral occurs as flakes and fragments, mainly of very small size; it shows aggregate polarization and occasionally exhibits a strong ghost of a cross—inherited from the spherulitic aggregate masses of the intermediary mineral from which it has been formed by the removal of iron, magnesium, and some silica. Its specific gravity was determined by dilution of heavy liquids and found to be 2·33. It has a refractive index quite near 1·53 (verified in sodium-light), and possesses quite a distinct individuality, but, on account of the smallness of the constituent particles of the aggregates, the determination of the vibration-direction and optical sign is difficult and uncertain. Between crossed nicols, the tiny, thin flakes show greys to yellows of the first order; the low birefringence was also proved by use of the quartz-wedge.

Anatase in the Clay.—A finely-divided mineral found in the greenstone has been herein mentioned as anatase, and its identification resulted from

the examination of the clay from Ible. The clays contain what appears, under usual magnification, to be a white, opaque mineral in a very finely divided state, and, as in the case of the greenstone, by examination under a $\frac{1}{12}$-inch oil-immersion objective these particles are seen to consist of a yellow mineral of very high refractive index and adamantine lustre. In the clay from Ible, the yellow mineral occurs in sizes of much greater range, and, by heavy-liquid separation, a good, pure crop of the mineral is easily obtained. The fragments are uniaxial and negative, and among them many of the bevelled plates, typical of anatase, are to be found.

Occurrence and Genesis.—' Green-earth ' may be seen in situ in the Jughole Cavern near Darley Dale; in the floor of the Cawdor quarries at Matlock Bridge; in the Side mine under High Tor, Matlock Dale; and at the foot of Long Tor, Matlock Bath. A good occurrence of the end-product, the almost white clay, is exposed at the foot of the Ball Eye cliff in Bonsall Hollow.

That the change has been wrought by the leaching action of percolating meteoric waters seems evident from several features presented by occurrences. A section through the altered beds shows that, apart from the very limited ochreous staining at their surface, the uppermost layer, in occurrences of the more advanced stage of the alteration, consists of the almost white clay; this gradually passes into ' green-earth ' which in turn passes into ' greenstone ' rock, and thence to less-altered dolerite. In many cases the whiter clay has not been produced, and the most advanced stage is represented by the pale-green clay.

It is noticeable that ' green-earth ' is not found in open situations where the ordinary process of weathering has been in operation, but that it is closely connected with the occurrence of considerable amounts of overlying strata. It is the form of alteration which is met with in deep mines and under limestone cliffs. The iron being maintained in the lower state of oxidation throughout the process necessitates the exclusion of free oxygen. This seems to be effected by the presence of sufficient overlying limestone, which, containing as it does, in variable quantities, organic matter in an extremely finely-divided state, may well remove free oxygen from the seepage waters. Furthermore, any free acids present, including carbonic acid, will be neutralized and a non-oxidizing, extremely dilute solution, mainly of calcium bicarbonate, without any free acids, will be produced. The organic (bituminous) matter may supply sulphur compounds to the water and thus, by reaction with the ferrous iron already present, give rise to pyrites. The pyrites appears to be somewhat confined to the uppermost portions of the altered beds, and seems to be

most abundant where the overlying limestone is darkest in colour and most bituminous. The formation of quartz appears to be greatly inhibited, and only produced in the earliest stages.

The process of alteration appears to have continued through long geological periods and is probably in operation at the present time. Examination of all the 'toadstone' outcrops shows that the change has been mainly brought about since the Hercynian movements which produced the mountain system of 'The Peak'. The localities cited are all in low-lying positions, about the drainage-levels of water-courses, and the position of the beds in relation to the local drainage is seen to influence the relative proportions of the phases and total extent of the alteration. Where the 'toadstone' is in the vicinity of the ground-water level, the alteration affects the bed in the same degree for a considerable depth and the transition between the stages is extremely gradual. Inversely, under opposite conditions, at higher levels and especially where the beds dip appreciably in the direction of the flow of the seepage waters, the alteration shows sharper transitions and the rock is affected to a much less depth. Where the same dolerite sheet is to be seen at greater altitudes and where the limestone which lay above it has long since been denuded away, it usually only possesses a thin covering of iron-stained clay. This is evidently due to the alteration having commenced, but the necessary overlying limestone having been early removed. When this took place, the ordinary process of weathering set in, oxidizing the iron remaining in the altered rock, stopping furtherance of the change in depth, and producing a sharp line of demarcation between the clay and the underlying dolerite.

A good example of an occurrence in which the conditions became oxidizing after the 'green-earth'-producing alteration had taken place to a considerable extent, may be seen at the Ashford-in-the-Water end of Monsal Dale. The Ible occurrence is one in which the ordinary process of weathering set in after the other process had gone almost to completion. It is for this reason that it is rather a good material for examination, consisting as it does essentially of the pure clay with the small amounts of the remaining iron, &c., converted to well-known substances.