

# The Mineralogical Composition of some Tasmanian Clays

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WITH TWO FIGURES

## ABSTRACT

An account is given of the mineralogical composition as determined by X-ray, differential thermal and chemical analyses, of some industrially important Tasmanian clays used in brick and agricultural pipe manufacture and as paper fillers. The clay deposits examined are mainly of Tertiary age and are both residual and sedimentary in origin. Kaolin is the dominant clay mineral in all samples with illite as a minor constituent in most; quartz is abundant in the brick and pipe clays. One sample from Surges Bay shows the presence of a mixed-layer mineral of montmorillonite and dioctahedral illite in both randomly stacked and ordered structures. An ordered structure of kaolinite and pyrophyllite or talc may occur also.

## INTRODUCTION

In this paper no attempt has been made to examine systematically the clays of Tasmania but many samples, collected in the course of a reconnaissance survey of the clay industry of Australia as a whole by officers of this Division, have in recent months been subjected to examination by modern physical methods. The clays although of different origins are sufficiently alike to suggest that the results of their analysis could form the basis for future more detailed survey work of the island and hence it is considered of value to publish an account of their mineralogy as determined by X-ray, differential thermal analysis (D.T.A.) and chemical methods.

## SAMPLES

Clays have been examined from Dover and Surges Bay in the south, from Dunrobin in the centre and from South Mt. Cameron and St. Helens in the north-east of Tasmania (see locality map, Fig. I). The samples, taken mainly from operating pits of mining companies, represent most of the better known clay deposits of Tasmania. With the exception of three Permian clays from Dover the clays are all of Tertiary age and for the most part have arisen either directly or indirectly from the weathering of acid igneous rocks.

### *Clays from Dover*

Most of the clays from Dover have been taken from the Granton Brick Company's works where a series of Tertiary lake deposits overlies Permian sediments weathering *in situ*. In all, seven samples have been examined; three of these having been collected by officers of the Division originally

for pilot plant examination and four supplied by G. Hale of the University of Tasmania. Sample 2 represents a clay which forms thin almost vertical "veins" through the main Permian clay body (sample 1) and in appearance is not unlike samples 3 and 4, whitening clays also of Permian age; samples 5, 6 and 7 represent the Tertiary clays of the area. The clays are used mainly for bricks by mixing equal proportions of 1 (Permian age) with the more plastic clays 5, 6 and 7 (Tertiary age) and for agricultural pipes by using the Tertiary clays alone.

#### *Clays from Surges Bay*

The clays from Surges Bay are derived from the weathering of a post-Jurassic syenite *in situ* and their distribution is complicated. The samples examined were obtained from the pit of Non-Metallic Minerals Ltd. where a weathered clay is mined for use as a paper filler. This clay shows interesting pseudomorphs after feldspar.

#### *Clays from South Mt. Cameron and St. Helens*

In the Ringarooma valley sedimentary clay deposits are being worked by the Endurance Tin Mines N.L. at South Mt. Cameron. Here the profile exposed shows sandy gravel from 0 to 2 feet, brown and yellow clays with quartzitic boulders from 2 to 15 feet, white clay with patches stained light-brown by organic matter from 15 to 20 feet, with an underlying yellow clay. Sample 12 is representative of the white clay used as a paper filler, sample 13 of the stained white clay and sample 14 of the yellow clay.

In the Fern Tree River Valley west of St. Helens both sedimentary and residual clays are exposed in separate workings of the Goshen Tin Mines N.L. In one pit cut in the sedimentary clay 2 to 3 feet of sandy cover overlies 6 to 7 feet of clay and sample 15 is representative of the latter. Sample 16 was taken from a second pit cut through to the residual clay and is representative of clay formed from the weathering *in situ* of granite which underlies the sedimentary clays of the area.

#### *Clays from Dunrobin Bridge*

At Dunrobin Bridge near Ouse in central south Tasmania a bauxitic deposit is exposed in the valley of the Derwent River. Sample 17 is from the clay underlying the bauxite.

### EXPERIMENTAL

#### *X-ray Examination*

X-ray photographs were always taken of the whole sample, of aggregates formed from a less than  $2\mu$  clay suspension prepared by conventional sedimentation methods, and of the aggregates after heating to between  $500^{\circ}\text{C}.$ — $600^{\circ}\text{C}.$  for several hours. Where necessary aggregates were also X-rayed after treatment with glycerol. In some instances the material remaining in suspension after centrifuging for several hours at 3000 r.p.m. was collected by flocculating with calcium chloride and examined by the X-ray method. In Sample 11 this finely divided material showed an almost pure separation of a mixed layer lattice mineral.

For most samples the X-ray examination was made with  $\text{CuK}\alpha$  radiation in a camera of small radius (3.00 cm.) which had been modified so

that spacings of the order of 20 Å could be recorded. For one sample much larger cameras of radius 5.73 cm. and 11.46 cm. were used in order to establish the presence of a very high spacing.

#### *Differential Thermal Analysis Examination*

For a detailed description of the equipment used for differential thermal analysis examination in this laboratory see Carthew and Cole (1953), but for the purpose of this paper the apparatus may be described briefly as follows. A vertically mounted electrical resistance type furnace was used with a stainless steel sample block, and the whole heated to 1000°C. at a constant rate of 10°C. per minute. The furnace temperature was controlled and recorded with a Kent single-point temperature recording controller used in conjunction with a Kent type-7 gear box and a type 100-R adjustable transformer. The differential temperature was measured with a platinum 10 per cent rhodium-platinum thermocouple the output of which was amplified by a Tinsley galvanometer-type D.C. amplifier and recorded by an Evershed and Vignoles recording ammeter.

In examining the Tasmanian clays the sensitivity employed was such that the full chart width corresponded to an output of the differential thermocouple of 200 microvolts. Calcined alumina was used as a reference material and 0.8 g. of the whole sample was used in each run.

#### *Chemical Analysis*

Although no chemical analyses were made specifically for this investigation, records of the Division showed that analyses for industrial purposes had been made on a number of samples included in the present paper. The earlier work has greatly helped in making quantitative estimations of mineral composition by X-ray and D.T.A. methods.

### RESULTS

The compositions of the clay samples as estimated from combining X-ray, D.T.A. and chemical analyses are given in Tables II to IV. It will be seen that the clay minerals kaolinite, illite and mixed layer minerals together with quartz, feldspar, gibbsite and hematite have been found present in the samples. No pure montmorillonite type clay mineral has been identified in any sample, although it forms a mixed layer mineral with illite in sample 11.

In estimating the mineral compositions set out in Tables II and IV it has been found necessary to appraise critically the accuracy of the various methods used. Thus the chemical analyses set out in Table I have been of value in giving an accurate estimate of the silica and kaolinite content of the samples and in enabling a correlation to be made with other samples by the D.T.A. method. X-ray examination, particularly of aggregates, has proved most effective in estimating the illite or hydrous mica content of clays especially when the quartz content is low. It, however, gives inaccurate results for quartz when this mineral is present in any quantity despite comparison with known quartz-kaolinite mixtures. It is considered that this error probably arises through variability in crystallinity of different kaolinites which affects the intensity of the diffraction pattern as a whole. The D.T.A. method gives, for kaolinites of comparable crystallinity, an accurate method of estimating the percentage of this mineral in the sample. However,

examination of standard illite-kaolinite mixtures has shown that up to 30 per cent illite may go undetected, due to near superposition of illite and kaolinite endothermic and exothermic peaks and the very low intensity of illite reactions compared with those of kaolinite. Although the kaolinite reactions are visibly reduced in such mixtures, in an unknown material this may be accounted for in other ways such as variable crystallinity of kaolinite or presence of quartz. Quartz has its  $\alpha \rightleftharpoons \beta$  transformation at 578°C. completely masked by the kaolinite endothermic reaction at approximately 600°C. and so can be detected only on a cooling curve by the D.T.A. method if the kaolinite content is appreciable.

Estimates of the kaolinite content based on the area of the endothermic peak given in the differential thermal curve at about 600°C., when compared with those from chemical analyses, yield discrepancies which can be resolved only by assuming that kaolinites of different crystallinities and/or particle size distribution have different heats of reaction and thus different peak areas. The theoretical work of Spiel (1944) and Kerr and Kulp (1948) showed that the area under a peak in the differential thermal curve is proportional to the mass of a component present. It is to be expected that the less crystalline a component the lower would be its heat of reaction and the temperature of its peak. On the other hand varying crystal size has been reported by Spiel (1944) to influence the peak area whereas Berkelhamer (1944) could find no effect. Shearer (1949) on theoretical grounds also concluded that in the range of small particle size ( $2 \mu$  and less) there would be no effect. Although we are in agreement with this conclusion the assumptions made by Shearer that the unit cell is completely broken down after the 600°C. endothermic reaction is not valid since it is well known that destruction of the lattice is complete only at about 900°C. Furthermore, material after heating to 600°C. can readily be re-transformed into a kaolinite type of mineral upon autoclaving. In a recent paper Bramao *et al.* (1952) have shown that the slope ratio of the descending to the ascending parts of the main endothermic peak varies inversely as the particle size.

Recent work by one of us (A.R.C.) agrees with that of Bramao *et al.* and has furthermore shown that although different fractions of a well crystallised kaolinite below  $2 \mu$  in size have different slope ratios they have the same peak area. We have thus concluded that discordant results in estimating kaolinite in the Tasmanian samples arise from kaolinites of different crystallinities having different peak areas and that to estimate accurately this clay mineral by D.T.A. a method is necessary for assessing its degree of crystallinity and correlating this factor with the area under the endothermic peak.

#### *Clays from Dover*

The compositions set out in Table II show that the Dover clays are generally very siliceous kaolinitic clays containing very small amounts of illite. Plasticity where present must arise from fineness of particles rather than from mineral composition. This fact is borne out by D.T.A. records which show from the asymmetric character of the endothermic peak at about 580°C. and the shape of the 980°C. exothermic peak, that the kaolinite is poorly crystalline in samples 1, 5, 7, and 6 (order of increasing kaolinite content). In samples 4 and 3 it is of medium, and in sample 2 of good crystallinity. This is illustrated in Fig. II (A, B and C) which shows the D.T.A. curves of samples 7 (poor crystallinity),

4 (medium crystallinity) and 2 (good crystallinity) taken under the same conditions, the kaolinite content being 55, 55 and 80 per cent respectively.

#### *Clays from Surges Bay*

Table III shows that the clays from Surges Bay are mainly kaolins derived from the breakdown of the feldspars of the parent syenitic rock. Furthermore, the D.T.A. curves indicate that the kaolin is well crystallized in all samples. Although the illite and quartz contents are very low, sample 11 has been found to contain appreciable quantities of a mixed layer mineral of illite and montmorillonite. The presence of this mixed layer mineral is indicated in the D.T.A. curve (Fig. II (*d*)), by an endothermic peak at 690° C. following the kaolinite endothermic reaction at 620° C. In the X-ray patterns it is characterised by lines at 11.60, 5.01 and 3.20 Å (in aggregate photographs) the first of which is replaced by two lines at 13.40 and 9.30 Å upon glycerol treatment and the second and third by lines at 5.36 and 3.40 Å, respectively. This behaviour can be explained as due to a random interstratification of 40 per cent montmorillonite and 60 per cent of a dioctahedral illite similar to that first suggested by Bradley (1945) for the clay mineral "bravaisite". The appearance of a line at 13.40 Å rather than 17.7 Å upon glycerol treatment could be explained as due to a random interstratification of trioctahedral clay mica and vermiculite units similar to that found by Walker (1949) for the decomposition of biotite in some Scottish soils. However, the bravaisite described by Bradley also showed incomplete expansion upon ethylene glycol treatment and furthermore the D.T.A. record, the dioctahedral nature of the intergrown structures and the behaviour of other X-ray reflexions upon glycerol treatment indicate that montmorillonite and illite form the intergrowth in sample 11.

Sample 11 is of additional interest in that its X-ray pattern shows a strong reflexion at 25.6 Å, a further one is suggested at 47 Å and both shift upon glycerol treatment to 28.8 and 51.5 Å respectively. Two other prominent basal spacings at 4.58 and 3.056 Å appear after glycerol treatment. These lines can be explained as due to an ordered interstratification of montmorillonite and dioctahedral illite sheets. Bradley (1950) has suggested an ordered structure of alternate units of pyrophyllite and vermiculite or contiguous pairs of pyrophyllite-like units separated by pairs of layers of water molecules for the clay mineral rectorite. However, the diffraction effects observed here differ from those of Bradley and have consequently been interpreted differently. Ordered structures of montmorillonite and illite have been reported from Queensland (Ferguson, 1950) and such complex structures may not be uncommon in Australian clays.

The possible occurrence together of ordered and randomly stacked structures of montmorillonite and illite has already been suggested by MacEwan (1949) but few samples have been reported in the literature. Further work is being done on the examples known to us and a more detailed account is to be given in a later publication.

Some aggregate photographs of sample 11 show a weak spacing at 16.4 Å unaffected by glycerol treatment. This suggests an ordered stacking of kaolin and pyrophyllite or talc structures.

Much of the work on sample 11 has been carried out on fine fractions obtained by centrifuging a 2  $\mu$  and less fraction for several hours at

3000 r.p.m. This removed the kaolin which forms the bulk of the sample and left a finely divided suspension of mixed layer minerals from which aggregates were formed and powders obtained.

#### *Clays from South Mt. Cameron and St. Helens*

The compositions set out in Table IV shows that the clays from South Mt. Cameron and St. Helens are also mainly kaolins with the illite content low in all and the quartz content low in all but one. The colour of sample 13 is due to organic matter (detected by D.T.A.) and that of sample 14 to hematite. The kaolins of all samples are well crystallised.

#### *Clay from Dunrobin Bridge*

The composition set out in Table IV shows that the clay from Dunrobin Bridge is mainly a mixture of kaolin and gibbsite with a small amount of hematite. The characteristic exothermic peak in the D.T.A. curve at 350°C. (Fig. 2, E) is due to gibbsite and the slight one a little before 300°C. has been attributed by Pask and Davies (1943) to cliachite, a colloidal form of  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . The kaolin of the sample is not well crystallised.

### DISCUSSION

As yet too few samples have been examined to draw definite conclusions regarding the genesis of the clay formations but there are indications that the parent rocks have not exerted any marked influence on the products of their weathering. Little also can be said of the mode of formation of the mixed illite-montmorillonite mineral from Surges Bay, although the intimate stacking required would suggest a transformation from illite to montmorillonite or *vice versa*. The possible occurrence of an ordered kaolin and pyrophyllite or talc structure is also of interest and suggests that detailed sampling at Surges Bay might throw much light on the problem of the role of mixed layer structures on weathering.

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TABLE I

## Chemical Analyses of Some Tasmanian Clays

	Dover			Surges Bay		
	4 HG <sub>1</sub>	5 HG <sub>1</sub>	6 HG <sub>2</sub>	8	9	11
SiO <sub>2</sub>	66.32	76.02	63.70	50.9	45.4	45.82
TiO <sub>2</sub>	1.32	0.61	1.10	0.5	0.7	0.55
Al <sub>2</sub> O <sub>3</sub>	23.18	18.69	21.12	32.5	37.7	39.38
Fe <sub>2</sub> O <sub>3</sub>	1.89	0.24	5.02	1.7	1.8	0.16
CaO	...	...	...	...	...	0.22
MgO	0.82	0.33	0.33	...	...	0.06
K <sub>2</sub> O	1.13	...	0.08	3.5	0.4	0.49
Na <sub>2</sub> O	0.11	0.62	0.71	2.0	2.1	0.23
Loss on Ignition	8.96	6.06	8.72	8.8	11.9	12.67
	103.73	102.57	100.78	99.9	100.0	99.58

- Sample 4. Brick sand clay. Analyst M. Neilson.  
 5. Highly siliceous plastic pipe and brick clay. Analyst M. Neilson.  
 6. Siliceous plastic pipe and brick clay. Analyst M. Neilson.  
 8. Gritty partly weathered clay. Analyst R. D. Hill.  
 9. Non-gritty paper clay. Analyst R. D. Hill.  
 11. Surges Bay clay of higher water content. Analyst M. Neilson.

NOTE.—These analyses have been prepared for industrial purposes and are not of high accuracy.

TABLE II

Estimates of Mineral Composition (in per cent) of Clays from Dover, Tasmania, as determined by X-ray, D.T.A. and Chemical Methods

Designation	Brick sand clays		Whiting clays		Plastic pipe & brick clays		
	1 DT <sub>1</sub>	2	3 DT <sub>3</sub>	4 HG <sub>1</sub>	5 HG <sub>1</sub>	6 HG <sub>2</sub>	7* DT <sub>2</sub>
Kaolin .....	30	80	65	55	40	60	55
Illite .....	15	<5	<5	10	<5	<5**	<10**
Quartz .....	60†	15	35	35	60	40	40
Felspar .....	Trace	....	N.D.	N.D.	N.D.	N.D.	Trace
Colour .....	Pinkish White	White	White	White	Cream	Cream	Brownish- White
Clay mineral of finest fraction .....	....	....	....	....	....	....	Kaolinite and hy- drous mica
Origin of clays .....	Breakdown <i>in situ</i> of Permian sediments				Tertiary lake deposit?		

\*\* Central scattering indicates uneven water layers suggesting a hydrous mica mineral rather than illite.

† Little to no quartz in the 2  $\mu$  and less fraction.

\* This sample has a trace of organic matter.

TABLE III

Estimates of Mineral Composition (in per cent) of Clays from Surges Bay, Tasmania, as determined by X-ray, D.T.A. and Chemical Methods

Designation	Gritty, partly weathered clay	Non-gritty paper clays		
	8	9	10	11
Kaolin .....	65	85	85	65
Illite .....	<5	<5	<5	....
Mixed layer mineral .....	....	....	....	30
Quartz .....	....	....	<5	<5
Felspar* .....	35	15	....	....
Sodium chloride .....	Trace?	Trace?	....	....
Gibbsite .....	....	Trace?	....	....
Colour .....	White	White	Greyish White	White
Clay mineral of finest fraction .....	N.D.	N.D.	Kaolinite and illite	Mixed layer mineral
Origin of clays .....	Weathering of syenite <i>in situ</i>			

\* The felspar in sample 8 contains both K and Na types, but that of sample 9 mainly Na.

TABLE IV

Estimates of Mineral Compositions (in per cent) of Clays from South Mt. Cameron, St. Helens and Dunrobin Bridge, Tasmania, as determined by X-ray and D.T.A. methods.

Designation	South Mt. Cameron			St. Helens		Dunrobin Bridge
	12	13*	14	15	16	17
Kaolin .....	75	85	80	75	55	50
Illite .....	10	10	10	10	10	<5
Quartz .....	<5	.....	1 or 2	<5	35	.....
Felspar .....	Trace	Trace	5	Trace	Trace	5
Hematite .....	.....	.....	10	.....	.....	10
Gibbsite .....	.....	.....	.....	.....	.....	30
Colour .....	White	Cream	Yellow	White	Grey	Brown
Clay mineral of finest fraction .....	Kaolin					.....
Origin of clay .....	Tertiary sediment derived from weathering of adjacent granite			Weathering of granite <i>in situ</i>	Clay underlying bauxite	

\* Contains organic matter.

Sample 16 contains much coarse gravel.

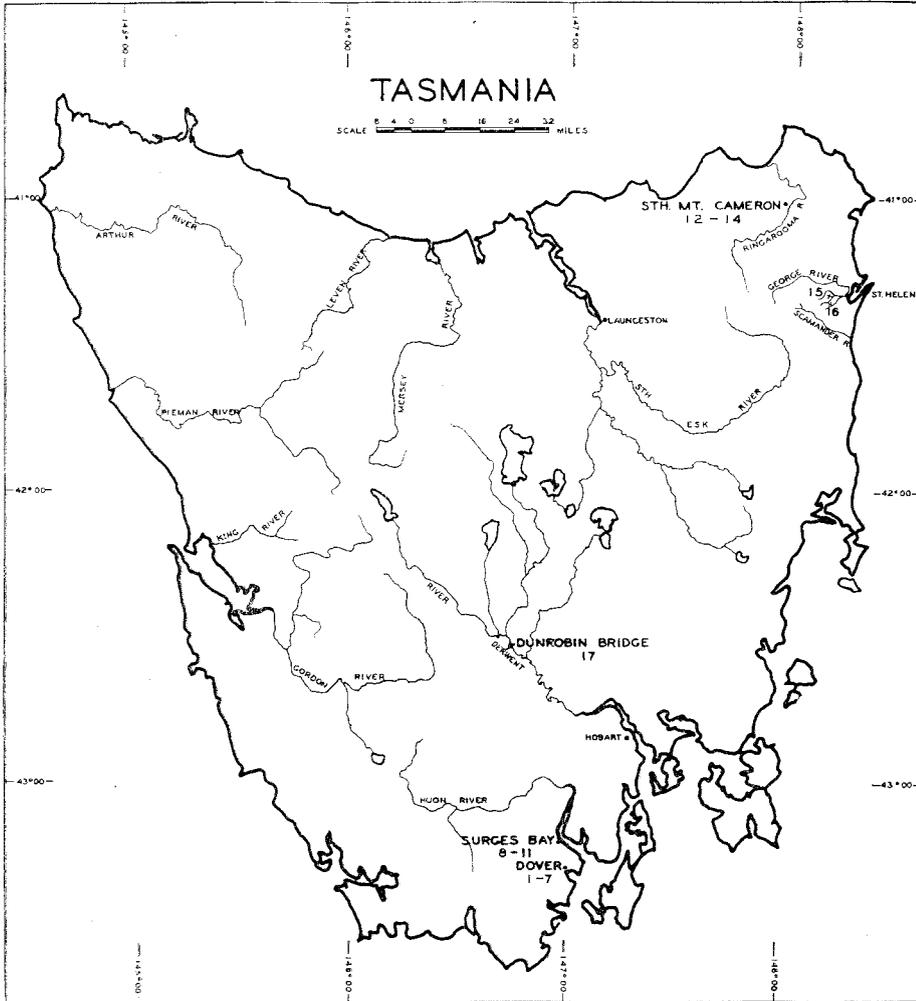


FIG. 1. Locality plan showing source of clay samples

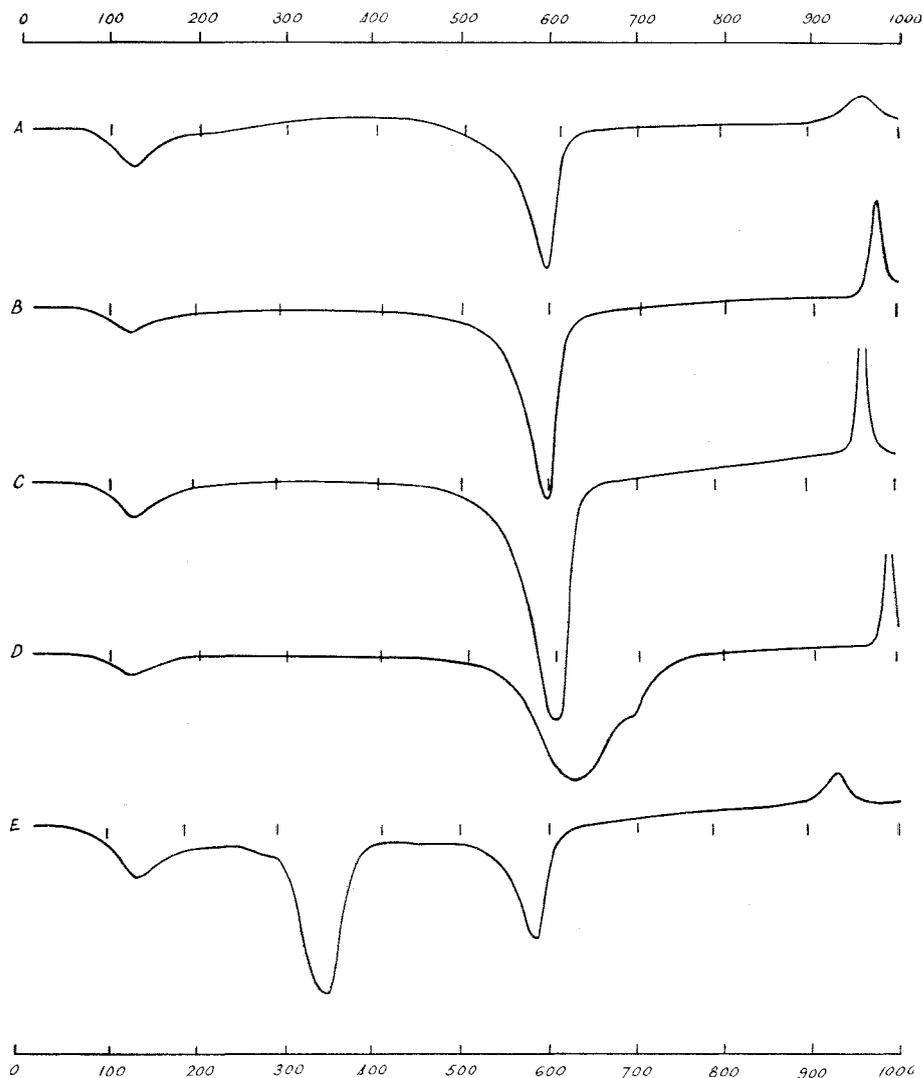


FIG. 2. D.T.A. curves of some Tasmanian clays

- A. Sample 7 a plastic pipe and brick clay from Dover. Kaolin is of poor crystallinity; organic matter is present.
- B. Sample 4 a whiting clay from Dover. Kaolin is of medium crystallinity.
- C. Sample 2 a vein of white plastic clay in brick sand clays from Dover. Kaolin is of good crystallinity.
- D. Sample 11 a paper clay from Surges Bay. Kaolin is of good crystallinity. The endothermic peak at 690°C. is due to a mixed layer mineral.
- E. Sample 17 a bauxitic clay from Dunrobin Bridge. Kaolin is of poor crystallinity. The endothermic peak at 300°C. is due to cliaichite and that at 350°C. to gibbsite.