Residual clays formed by the extensive leaching of Tertiary dykes in the Sydney district are predominantly kaolinitic, though illite is frequently present to the extent of 30%. The clays contain a relatively high percentage of titania, much of which occurs as distinctive leucoxene octahedra, believed to be pseudomorphous after "titaniferous magnetite". There is an association of illite with these octahedral forms of leucoxene.

INTRODUCTION.

The mineralogy of the Tertiary dyke clays occurring in the Sydney district is of interest for two reasons. Firstly, mineralogical data may enable the more effective commercial utilization of these materials; and secondly, such data may contribute to the elucidation of wider problems concerned with clay, soil and laterite genesis.

The present study arose from independent observations by both authors. One of us (F.C.L.), during a broader investigation of N.S.W. commercial clays, previously had determined the clay minerals of the Sydney deposits, whilst the other first detected and checked by X-ray diffraction methods the presence of microscopically visible leucoxene of unusual characters in some of the same dyke clays.

MINERALOGY AND ORIGIN OF THE DYKE CLAYS.

The commercial dyke clays of the Sydney district are located principally in the French's Forest area where they extend in a westerly trending belt from Narrabeen Lagoon to Asquith, a distance of approximately twelve miles. The dykes vary in width from a foot or two up to sixteen feet and have been worked to a depth of 40 feet or more. Some of the individual dykes comprising the system extend for several miles. Occasional short N-S trending dykes intersect the main belt.

The country rock is generally sandstone of the Hawkesbury Formation but shale lenses of the same formation occasionally form the enclosing medium.

The parent material of the clays was not observed at any point on the present survey; however, the frequent occurrence throughout the Sydney area of fine grained dolerite dykes and other intrusions of Tertiary age leaves little doubt that the parent materials of the clays were of similar composition and that the environmental conditions in the French's Forest area were favourable for the conversion to clay. The favourable conditions alluded to are the altitude of the region, the permeability of the Hawkesbury sandstone, and,
contingent on these, the considerable depth to the water table. Morrison (1904) noted that the dykes intruding the Hawkesbury Formation were almost invariably weathered to considerable depth whilst those intruding the Wianamatta Group were fresh. He attributed this to differential weathering.

The clays are usually white but lack homogeneity and considerable areas are iron stained. Impregnation of the sandstone walls by iron oxides and hydroxides is common but metamorphic effects from the original dykes appear to be slight.

![Differential Thermal curves of Dyke Clays from the Sydney Area.](image)

Examination of samples of the dyke-clays by X-ray, thermal and chemical techniques has shown that kaolinite is the predominant clay mineral, occasionally to the exclusion of all others, but illite is frequently present and at times comprises as much as 30% of the clay mineral content.

The variability in mineral composition is evident by the differential thermal curves (Fig. 1). The sample from St. Ives is that of a well crystallized kaolinite and contrasts quite markedly with the illite-bearing kaolins from the Narrabeen Lagoon and Belrose areas.

For the formation of kaolinite from a rock of doleritic composition the complete removal from the system of the alkalies, alkaline earths and iron, together with approximately 50% of the silica is necessary. A consideration
Table I.
Chemical Analyses of Dyke Clays and Parent Material.

<table>
<thead>
<tr>
<th></th>
<th>I.</th>
<th>II.</th>
<th>III.</th>
<th>IV.</th>
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<td>SiO₂</td>
<td>43.6</td>
<td>49.9</td>
<td>43.1</td>
<td>42.5</td>
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<td>Al₂O₃</td>
<td>37.8</td>
<td>29.0</td>
<td>34.0</td>
<td>15.7</td>
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<tr>
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<td>2.3</td>
<td>0.7</td>
<td>3.5</td>
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<tr>
<td>TiO₂</td>
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<td>5.9</td>
<td>5.7</td>
<td>1.9</td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>2.7</td>
<td>2.3</td>
<td>0.7</td>
<td>1.8</td>
</tr>
<tr>
<td>Na₂O</td>
<td></td>
<td></td>
<td></td>
<td>3.1</td>
</tr>
<tr>
<td>H₂O⁺</td>
<td>9.6</td>
<td>9.5</td>
<td>12.3</td>
<td>2.2</td>
</tr>
<tr>
<td>H₂O⁻</td>
<td>2.6</td>
<td>0.3</td>
<td>3.0</td>
<td>0.6</td>
</tr>
<tr>
<td>Total</td>
<td>99.6</td>
<td>99.2</td>
<td>99.5</td>
<td>—</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>SiO₂/Al₂O₃</th>
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<th>1.72</th>
<th>1.27</th>
<th>2.70</th>
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<tbody>
<tr>
<td>Al₂O₃/TiO₂</td>
<td>12.60</td>
<td>4.82</td>
<td>6.00</td>
<td>8.0</td>
<td></td>
</tr>
</tbody>
</table>

II. "  "  "  M.L. 40, "  "  "
III. "  "  "  Por. 341, "  "  "  "  Gordon,"  "  "  "
IV. Average of seven dyke rocks from the Sydney area after H. P. White and J. C. Mingaye (1904).

Of the chemical analysis (Table 1) of three dyke clays and the average for seven dolerites of the Sydney district shows this trend. Goldschmidt (1937) has shown

(see Fig. 2) that the stability of the various ions in a leaching environment is a function of the ionic potential \((Z/r)\). After Goldschmidt, 1937.

![Text-fig. 2. — Stability of the various ions as a function of the ionic potential \((Z/r)\). After Goldschmidt, 1937.](image)
aluminium were the most stable and the alkalies and alkaline earths the least stable, silica occupied an intermediate position which depended on the pH of the leaching solutions. A spectrographic analysis (see Table 2) carried out on three dolerites and three dyke clays from the Sydney district supports Goldschmidt's findings. However, potash behaves anomalously in two of the dyke-clays and it is significant that both of these clays contain illite. Apparently the ability of potassium to enter into twelve co-ordination in the formation of the hydrous mica not only prevented its loss from the system but, further,

| Table 2. |
| Spectrographic Analysis. |
| Element. | I. | II. | III. | IV. | V. | VI. |
| Li | T | — | — | T | M | — |
| Na | S | S | S | T | W | W |
| K | M | M | M | — | M | M |
| Mg | V.S. | V.S. | V.S. | W | W | W |
| Ca | S | S | S | W | W | W |
| Cu | M | M | M | W | W | W |
| Fe | S | S | S | M | M | M |
| Mn | S | S | — | — | — | — |
| Pb | W | W | W | M | W | W |
| Sn | — | — | — | — | — | — |
| Ti | M | M | M | S | S | S |
| Zn | T | T | — | — | — | — |

V.S., very strong; S, strong; M, medium; W, weak; T, trace.
I. Dolerite Dyke, Bondi.
II. ,, ,, Narrabeen.
III. ,, ,, Sill, de Burgh's Bridge.
IV. Dyke clay, St. Ives.
V. ,, ,, Belrose.
VI. ,, ,, Oxford Falls.

enabled the stabilization of some of the silica by the formation of the illite—2:1 (silica to alumina)—lattice as opposed to the 1:1—lattice of kaolinite, which the leaching conditions favoured. Jackson *et alii* found illite common in the highly leached kaoline of Hawaii, some of which contained titania in excess of 30%.

**Mineralogical Form of the Titania.**

Previous references to the mineralogical form of the titania present in various clays are somewhat speculative; thus the titania has been referred wholly or partly to the following mineral groups:

1. Doubtful titanium compounds not visible macroscopically (Goldschmidt, 1954; McLaughlin, 1954).
2. Anatase detected by X-ray analysis but not represented by microscopically visible particles (Brindley and Robinson, 1947; Nagelschmidt *et alii*, 1949; McLaughlin, 1955).
3. Microscopically detectable discrete crystals of various titanium minerals (Simpson, 1928; Carroll, 1934; Brindley and Robinson, 1947; Frederickson, 1948).
4. Microscopically visible leucoxene as rounded or angular grains or earthy or crust-like material associated with minerals of group 3 (Edwards, 1942; Frederickson, 1948; Goldman, 1955). Leucoxene varies in crystallinity and purity but usually it gives the X-ray powder pattern of rutile, anatase, brookite or sphene (Tyler and Marsden, 1938; Frederickson, 1948; Allen, 1949 and 1956; Golding, 1955.)

In the Sydney dyke-clays examined, much of the titanium occurs as microscopically visible leucoxene grains many of which exhibit well faceted but skeletal octahedral forms. The grains are dull and cream coloured in reflected light, and opaque to transmitted light but some show a pale cloudy aggregate polarization indicative of their polycrystalline (leucoxenic) constitution. The grains have similarities to the mat-surfaced grains present in some dune-sands (Golding, 1955) but differ from them in being more friable and in displaying faceted forms. The powdered leucoxene gives the X-ray pattern for anatase.

Leucoxene-rich concentrates were prepared by sieving suspensions of clay to recover the plus 50 micron material, which was then fractioned in bromoform.

The light bromoform fractions of most samples consisted of clay flakes and pellets usually peppered with small faceted leucoxenes or with blebs or plates of leucoxene. A few grains of wind-blown quartz, derived from the surrounding sandstone, also occur.

The heavy bromoform fractions of most samples consisted largely of leucoxene octahedra 0.1 to 0.2 mm. wide showing hopper or hollow faces (Figs. 1-5 and Figs. 7 and 8) or parallel growths (Fig. 6). A little attached clay, predominantly illite, was present and thin sections of the octahedra revealed triangular illite-filled centres surrounded by leucoxene, itself containing clay-filled pores. In one sample from St. Ives faceted forms were absent, the grains being ovoid, with tubular structures and pitted surfaces. It is significant that illite was not detected in this sample.

It is estimated that at least one half of the titanium shown in analyses II and III (Table 1) is present as visible leucoxene, and of this amount, about one third is present as the coarser faceted forms recovered in the heavy fraction.

**Origin of the Leucoxene.**

While some of the leucoxene particles may have been derived from ilmenite, most grains evidently are pseudomorphs after a titaniferous mineral of octahedral habit. Such requirements for the parent crystals might be fulfilled by anatase, perovskite or "titaniferous magnetite".

Leucoxene is known to develop during the weathering of those titaniferous minerals which also contain readily leachable ions such as iron and calcium. By growth of larger crystallites at the expense of the smaller, the leucoxene tends to build up single crystals of TiO₂ (Tyler and Marsden, 1938; Golding, 1956). The reverse process, and in particular the breakdown of single crystals of anatase to leucoxenic anatase seems unlikely.

Octahedral pseudomorphs of leucoxene believed to be after perovskite occur in certain titaniferous iron ore deposits of specialized paragenesis (Broughton and others, 1950). The presence of perovskite in the Sydney rocks, or its formation during their weathering, also appears unlikely.

The common occurrence of skeletal and titaniferous accessory iron ores in basic rock favours the third possibility. Thin sections and fragments of fresh dyke rocks from several localities in the Sydney district revealed abundant iron ore particles of a shape and size comparable to that of the smaller leucoxenes. Particles corresponding to the larger (and well faceted) leucoxenes, however,
were not observed. A single black magnetic octahedron, 0.07 mm. wide, from the Peates Ridge rock showed one face with a triangular central depression, the crystal being either a hollow skeletal form or a zoned crystal in which, presumably, a corroded magnetite core is surrounded by a more titaniferous shell. Such forms, if larger, could account for some of the faceted leucoxenes observed.

In slides of coarser rocks (from Prospect) larger iron ore particles occur, and these, occasionally, show triangular reflection patterns suggesting exsolved ilmenite lamellae lying in the octahedral planes of magnetite (Edwards, 1952). Such intergrowths however would not give rise to discrete octahedral pseudomorphs.

It is inferred that the leucoxene in the clays is derived mainly from “titaniferous magnetite” the precise characters of which are in doubt. Also it seems likely that the parent rocks of several of the clays sampled were somewhat coarser in grain size than is the case for most of the fresh rocks examined.

The weathering environment favoured the dissolution of the parent “titaniferous magnetite” with removal of the iron in the ferrous state and the hydration of the titanium to form titanic acid. Due to the presence of other ions, particularly the alkalies, in the leaching solutions, the titanic acid had limited mobility and tended to be precipitated in the gel form possibly entrapping some of the alkalies. As crystallization of the gel proceeded to form anatase, the released potash reacted with silica and alumina with the formation of illite, thus accounting for the intimate association of the two minerals.

ACKNOWLEDGMENTS.

The authors are indebted to Dr. H. Hofer and Graeme T. See for spectrographic and chemical analyses respectively.

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— 1952. “The Ore Minerals and their Textures.” This Journal, 85, 35-36, Pl. II, Fig. 6.


MINERALOGY OF COMMERCIAL DYKE CLAYS IN SYDNEY DISTRICT.


**EXPLANATION OF PLATE I.**

Figures 1 and 2. Octahedral leucoxene pseudomorphs from clay at Belrose. X 80.

Figures 3 and 4. Octahedral leucoxene pseudomorphs showing hollow and stepped-in faces from clay at Belrose. X 160.


Figure 6. Parallel growth pseudomorphs in leucoxene from clay at St. Ives. X 160.

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