CHAPTER 3

SAMPLING AND MINERALOGY OF BRINGELLY SHALE

§3.1 INTRODUCTION

The objectives of this chapter are to present details of the Bringelly shale from the four sites used in this study. This includes the location of the sites, their lithology and the techniques of sampling from these sites. An examination of the mineralogy and micro-structure of Bringelly shale is also included. These were investigated using a variety of techniques including x-ray diffraction, optical microscopy, and scanning electron microscopy. Laboratory characterisation studies of this shale have been limited to the claystone-siltstone materials which are the predominant lithology in Bringelly shale. Outcomes of the study in this chapter will be linked to the engineering and physical properties of Bringelly shale in the following chapters.

§3.2 LOCATION AND ACCESSIBILITY

Within the south west of the Sydney Metropolitan area, four separate sites were selected for sampling and field study. A location map including the general geology of the area is shown in Fig.3.1. The sites are active clay shale quarries and major current sources of brick clay and fill material in the Sydney region. A network of
Figure 3.1 Geological map showing the location of the study area

well-paved roads traverses all localities as shown by the topographic map of the Sydney area shown in Figure 3A.1 in Appendix 3A. Access to the sites is further facilitated by numerous property tracks. All sites required entry permission from the owners, and compliance with site safety precautions. The location of each site can be determined from its grid reference on the Penrith 1:100,000 sheet. Details of locations including grid references and lithology are summarized in Appendix 3A.

§3.3 AN OVERVIEW ON THE GEOLOGY OF THE SITES

The geology of the Bringelly shale within the Wianamatta group, and the engineering geology of the Sydney basin were discussed by Herbert (1979). Rocks of sedimentary origin are the dominant rocks in the Sydney region. They have been deposited within

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a broad zone of depression known as the Sydney basin. In the Sydney basin the
Hawkesbury sandstone is overlain by a series of fine grained rocks known as the
Wianamatta group. This group occupies the central portion of the Sydney basin
(Fig.3.2) extending about 50 km to the west of Sydney, from Port Jackson to Penrith,
and about 80 km north-south from Windsor to the Picton area. The Wianamatta group
has a maximum recorded thickness of 304 m (Herbert, 1980). The Wianamatta group
consists of three members Ashfield shale, Minchinbury sandstone, and Bringelly
shale. A thickness of 257 m is the maximum recorded for Bringelly shale near
Cobbity in the Sydney metropolitan area (Lovering, 1954; Herbert, 1979).

Bringelly shale is interpreted as a coastal alluvial plain sequence which grades up
from a lagoonal-coastal marsh sequence at the base to increasingly more terrestrial,
alluvial plain sediments towards the top of the formation. It is also classified as a
formation of a Mid-Triassic age with lithologies that comprise claystone, siltstone,
laminitite, sandstone, and tuff (Helby, 1973).

The main engineering geological features of the Sydney basin have been discussed by
Herbert (1979). In this section, an overview of the geology, stratigraphy, structural
geology, and engineering geology of the Sydney basin are reproduced and salient
details are reported. Details of the lithologies at the four sampling locations are
presented in Appendix 3A.

§3.4 SITE AND SAMPLE SELECTION

In order to select appropriate sites for this study, a comprehensive survey within the
Sydney basin was undertaken in an effort to locate sites that covered an extensive area
of the Bringelly shale. The Penrith 1:100,000 geological map and 1:25000
topographic maps were used to locate sites that comprised layers of shale that best
represented the Bringelly formation and that were easily accessible. Site
investigations and sampling were based on the geology and stratigraphy of the
Bringelly shale that has been described and reported by Herbert (1979).

Although the lithological types such as laminitite (interbedded sandstone and siltstone),
sandstone, and carbonaceous claystone are apparently randomly distributed
throughout the stratigraphic section of Bringelly shale, in any one place however, there is a degree of order both in succession, thickness, and volumetric significance. This had to be considered prior to sampling. For instance, it was important to consider the general distribution pattern of the main components of the lithology where claystone and siltstone represent 70%, sandstone and laminate 25%, coal and highly carbonaceous claystone 3%, and tuff 2% (Herbert, 1979). In this study, the intention was to collect specimens limited to the claystone-siltstone materials that comprise the majority of the Wianamatta group shales. For more consistency, the study has only considered the intact rock properties.

Due to the lack of natural outcrops, it was advantageous to carry out all sampling from active quarries where visual investigation and sampling were cost effective. Four major working quarries in the greater west of Sydney were selected for the purpose of this study. The four sites are located within an area of about 22 km in diameter in the western and south-western parts of Sydney. They are located within the Bringelly formation (Fig. 3.2) in an area of gently to moderately undulating countryside within the interbedded claystone and siltstone of the Bringelly shales. As explained in chapter 2 the Bringelly shale is underlain by the Minchinbury sandstone, a relatively thin layer typically 6m thick, and this is underlain by the Ashfield shale (Herbert, 1980). Prior to sampling, frequent visits to the sites allowed review of existing data relevant to each site. These available data were studied with emphasis being given to geological and geotechnical features of the Bringelly shale. Field investigation based on visual examination was carried out on vertical profiles composed of units of the Bringelly formation at each site. In most sites, the exposure of these units was developed after the rocks were ripped with an excavator PC1800 (Fig. 3.3a).

The typical exposed profile of all sites composed of grey siltstone at the bottom, overlain by fresh claystone which is about 0.4 to 0.5m below the soil and weathered rock interface. Thin laminate horizons occur occasionally throughout (Fig.3.3b). An attempt was made to collect samples as fresh as possible while the mining operation was in progress. The collected samples were required to be sufficiently large in size and quantity to enable a range of different laboratory tests to be performed.
Figure 3.2  Detailed distribution of sampling sites within claystone and siltstone of the upper Bringelly shale.

M: Mulgoa
B: Badgerys creek
H: Horsley park
K: Kemps creek

Chapter 3 – Sampling and Mineralogy of Bringelly Shale
Figure 3.3a Removal of weathered shale to obtain fresh samples using Komatsu PC 1800 at Badgerys Creek site

Figure 3.3b Typical exposure of Bringelly shale units at Kemps Creek site
Sampling was carried out in accordance with the field guide on the engineering grade classification scheme for weathered rock (Brown, 1981). Blocky samples of shale ranging from fresh to extremely weathered were obtained from the four sites. At the Kemps creek site additional samples were obtained by drilling one borehole. This was carried out using a conventional 51mm core diameter diamond drill with water flush. The borehole was drilled at 90 degree to the horizontal i.e. vertically and was carried out by a large truck mounted drilling rig hired from Jeffery & Katauskas Pty Ltd. as illustrated in Figures 3.4a,b.

![Preparation prior to coring and large truck mounted rig](image)

Figure 3.4a,b preparation prior to coring (a) and a large truck mounted rig (b) after set up at Kemps Creek site
Block samples from each site were placed in special thick plastic bags, labelled, and firmly, tied while the 51mm diameter core samples were coated with a moisture sealant called “valvoline tectyle” before being wrapped with polythene film “glad wrap” and placed in plastic bags. All samples were stored at room temperature to maintain their natural moisture content prior to laboratory testing.

Only a few samples were obtained from the borehole coring at Kemps Creek. During coring, significant amounts of core were lost, and very few lengths of core greater than 100mm were recovered. This appears to be typical of coring operations in Bringelly shale where low values of RQD are commonly reported (Corkery et al., 1980; MacRae et al., 1990). However, visual examination and logging of the core run indicated that the material was fresh and dominated by an alternating sequence of clayey and silty bands. Some of these bands were slightly carbonaceous with occasional spotted siderite nodules. Coloured photographs of core samples from different sites showing the recovery condition of Bringelly shale are shown in Figures 3.5a,b.

(a)

![Recovered core samples from boreholes at Badgerys Creek](image)

Depth (m) 13.00 to 17.00

(b)

![Recovered core samples from boreholes at Kemps Creek](image)

Depth (m) 9.00 to 13.00

Figure 3.5a,b  Recovered core samples from borehole at Badgerys Creek (a) and Kemps Creek site (b)
§3.5 MINERALOGY AND STRUCTURE

Clay is a term that is used to refer to a type of sediment (based on particle size) and to a type of mineral. Clay minerals are a weathering product of the disintegration and chemical decomposition of igneous rocks and of some types of metamorphic rocks. A study of the mineralogy of claystone-siltstone of the Wianamatta group by Herbert (1979) indicated that clay minerals comprise from 45 to 65% of the material in the upper Bringelly shale and that quartz represents 25 to 52% while the lower 30m of Bringelly shale is composed of 40 to 60% of clay minerals and 20 to 45% quartz. Herbert also indicated that minerals other than clay and quartz were detected and represented approximately 10 to 16%.

The most important factors that characterise clay mineralogy are particle size and shape. In their natural settings, they have a phyllosilicate or sheet like structure and range in size downward from approximately 4 micron. Clay minerals have a common sheet-like structure that is comprised dominantly of hydrous alumino-silicates, with iron or magnesium replacing the aluminium, with aluminium occasionally replacing the silicon and with other elements, such as potassium, sodium, and calcium involved in the lattice in some way. When the replacement occurs between elements of different valency, the clay particles carry an electric charge on their surface. Thus clay minerals can attract other charged ions such as dissolved cations in ground water.

Because of their large surface area and other physical properties, clays behave plastically when wet, but become hard and brittle when dry. These properties among others have a significant influence on the engineering behaviour of shale.

It is generally considered that the clay / quartz ratio, the clay mineralogy, and cementation are the most significant factors influencing the engineering behaviour of shales. In order to study the distribution of minerals within the rock formation, a variety of techniques including optical microscopy, x-ray diffraction, transmission electron microscopy, and scanning electron microscopy have been used to investigate the micromorphology and mineralogy of Bringelly shale. Qualitative analysis of the observations has been used to provide insight into the geological history.

Chapter 3 – Sampling and Mineralogy of Bringelly Shale
This section will discuss basic characterization of the clay mineralogy of the Bringelly shale. The study has been limited to the claystone-siltstone materials which are the predominant lithology in Bringelly shale. Data will be provided on preparations, methodology, and equipment used in the study of mineralogy and microstructures of the material. The qualitative and quantitative analyses results of x-ray diffraction, optical microscopy, scanning electron microscopy, and carbonate and organic contents will also be presented.

§3.5.1 Preparation of clays for X-ray diffraction spectra

§3.5.1.1 Investigations and methods of preparation

X-ray diffraction is an extremely useful, and usually the main tool for qualitative analysis of clay minerals in soil, rock, or sediment samples. In some cases it can also be used to give an approximate quantitative estimate of the relative amount of particular minerals present (Carver, 1971; Calvert, 1989; Moore, 1997). Two methods of mounting the fine-grained mineral to be x-rayed were used in this study:

1. oriented mounts formed by settling the clay slurry on a glass slide or ceramic tile, and
2. unoriented mounts of dry powdered shale in aluminium holders.

To prepare samples for x-ray diffraction, representative samples of Bringelly shale from the four sites with different degrees of weathering were selected. The procedures for x-ray diffraction analysis and interpretation followed Carroll (1970), Brown (1961) and Calvert (1989).

Non-orientated preparations are necessary to determine diffraction maxima other than the \{001\} basal spacing series. Since the clays have a natural tendency to be orientated, they most often give poor non-basal reflections. To make powder samples for x-ray diffraction, both the oriented and non-orientated samples were finely ground by a ball mill. Representative samples of < 425 \(\mu m\) particle size were placed with randomly oriented particles in the sample holder prior to subjecting then to x-ray analysis. It is

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important however, to make sure that the sample is lightly packed into the shallow cavity holder. Care was taken to avoid pressure orientation during the placement of the powder, and thus reducing the possibility that peaks of some mineral could be enhanced at the expense of others.

The concept of preparing the oriented aggregate samples is based on separating out the clay-size fraction of the sample, usually the < 2 μm fraction, and preparing a sample with all the flaky particles oriented parallel to their basal or [001] crystallographic plane. To prepare the oriented samples, some of the powder was diluted in distilled water in a 100 cc measuring cylinder after treatment with ethylene glycol that prevent coagulation of the particles during preparation. The solution was then stirred, and allowed to settle for about 8 hours. The top 10 to 20 cc of solution in the measuring cylinder was taken by a pipette and centrifuged for 15 minutes at 3000 rpm. After decanting the water, the concentrated suspension (slurry) containing the fine fraction is dropped on to a small glass slide, and held there as a globule by surface tension. The clay particles settle on their [001] planes, and evaporation of the water leaves an oriented film that can be placed in the x-ray beam. To achieve more reliable analysis, the clay fraction of oriented samples were treated in various ways, and a symbol is used for each treatment throughout the text and figures:

i) air drying (a), the initially prepared oriented aggregate was placed in an incubator under a controlled level of humidity,

ii) glycol saturation (g), placing the air-dried samples in an atmosphere of ethylene glycol vapour to introduce the vapour into interlayer area of any expandable clay, and

iii) heating to 450°C (h), to drive off the hydroxyl or crystal lattice water. This allows the structure to collapse to the lowest base unit.

The qualitative and quantitative analyses of the clay minerals were based on the interpretation of the x-ray diffraction pattern. These patterns were produced by using a Philips model 11300 x-ray diffractometer and also a Siemens D5000 powder diffractometer. The x-ray diffractometer is run by Siemens software, Diffract V3.0, installed on a PC 486-Dx33. This gives users access to a powder diffraction data base
with more than 60,000 standard data files to enable qualitative analysis. For quantitative analysis, *SIROQUANT V7* program running under Windows was also used. The $d\{001\}$ spacing of the material, after each treatment was used to provide further data to identify the clay mineral present. All results were checked against results manually calculated from the diffraction patterns.

In this study, the oriented clay was x-rayed from $2^{\circ}$ to $50^{\circ}$ along the $2\theta$ axis, using $CuK\alpha$ radiation and a scanning speed of $1^{\circ} 2\theta$/minute. The intensity of each mineral is detected from diffracted rays showing on the diffractogram and measured by the count per unit (CPU). Interpretation and presentation of data was carried out on a range that is based on the crystalline structure of the clay minerals which suggests that the most important diffractions from an x-ray beam occur within the $2 – 37^{\circ} 2\theta$ scanning distance (Klug et al., 1962). This allows for detecting the first five $\{001\}$ basal spacings of well crystallised chlorite and / or mica minerals, and also for the basal spacings of other clay minerals with phyllosilicate structure.

X-ray traces of treated and untreated samples from fresh and weathered shale were interpreted and abbreviation was used to label the peaks on the diffraction patterns.

§3.5.1.2 *XRD results*

Sixteen samples of Bringelly shale were analysed as part of this study to identify clay and non-clay minerals present. Qualitative analysis of the of x-ray diffraction patterns of the less than 2 microns fraction from each site did not show any significant differences in mineralogy (Fig. 3.6). The analysis has shown that mixed layer clay and kaolinite are the dominant clay minerals in the Bringelly shale, and that on average, mixed layer clay is more abundant. The specimens of the oriented mounts from the four sites are dominated by the mixed-layer clay mineral (*MLC*) as evidenced by the altered illite peak at $10\AA$ which becomes symmetric after treatment and gives rise to a broad diffused peak between 10 and $14\AA^o$. This peak profile is mainly due to irregularly mixed layers of illite and smectite. Powder patterns run on the representative samples of Bringelly shale have shown that the commonest non-clay mineral present is quartz. However, other minerals such as feldspar, albite, anatase,
and siderite were also detected. Illite has a strong 10Å peak and a rather weak 5Å peak on the x-ray diffraction pattern which may be associated somehow with the illite possibly having a detrital origin. This will be further discussed in the following sections.

The current results indicate that mixed-layer clay in the four sites is more abundant than kaolinite and individual illite as it can be noticed from the areas under the peaks of these clay minerals. Qualitative analyses of the orientated clay specimens from all sites have indicated the lack of a separate montmorillonite fraction (M), except in the extremely weathered material. The analyses also indicated that a strong 7.1Å kaolinite peak (K) with about 6000 count per second (CPU) was measured on the diffractogram of the fresh material. A similar intensity of kaolinite from diffracted rays (CPU) was also measured on the diffractogram of the weathered one. The strong 11Å peak of expandable mixed layer clay, as observed from the glycolated pattern has indicated that illite-smectite (I+S) forms an important constituent of the less than 2 micron fraction of the shale samples. The collapse of the 11Å peak to 10Å on heating and the non-existence of a 22Å super lattice structure are evidence for the presence of irregularly interstratified illite-smectite mixed-layer minerals. In general, mixed-layer clay minerals may represent an intermediate stage between the component phases in the weathering or diagenesis process.

The relative proportions of illite (I) and smectite (S) within the interstratified material can be roughly estimated from the d-spacing on glycol treatment (Fig.3.6g). This should be 10Å for illite and 17Å for smectite. The fact that the material only swells to about 11Å with glycol suggests that the mixed-layer clay material is itself also mainly made up of illite.

In order to differentiate between the first order kaolinite 7.1Å and second order 7Å chlorite, representative fresh and weathered samples were x-rayed after heating to 450° C. The subsequent x-ray diffraction patterns after heat treatment (Fig. 3.6h) showed only a presence of peaks in the 7Å area and no peaks in the 7.1Å were detected. This indicates that the (001) kaolinite had collapsed, and confirms the
Figure 3.6  Typical x-ray diffractogram, <2 µ fraction of fresh Bringelly shale untreated and treated samples (Badgreys Creek)
presence of (002) chlorite in the samples of Bringelly shale. For the extremely weathered shale, the analysis has shown montmorillinite in the glycol treated pattern and no sign of chlorite (Ch) in the treated and / or untreated pattern (a). This confirms the transformation of chlorite to montmorillonite at an extreme degree of weathering (Fig. 3.7).

In this study, interpretation of mineral abundance was carried out using the quantitative analysis method adopted by Carver (1971). The results, shown in Table 3.1a, were in agreement with those obtained after running the Siroquant software program. The process of weathering causes a breakdown of what is believed to be cemented clay particles, with the clay mineral content remaining constant. In this study, clay mineral analysis of four different degrees of weathering at the four sites has indicated that montmorillonite has formed due to the increasing degree of weathering. It also suggests that the absence of chlorite in the weathered material is a result of chemical and physical breakdown.

Several different classifications of the clay minerals have been proposed over the years (Brown, 1961; Grim, 1986; Gillott, 1968; Carroll, 1970; Velde, 1985; Chamley, 1989). For practical purposes, however, clay minerals may be classified according to their swelling property. From the engineering viewpoint, the amount of swelling is important in understanding the geotechnical behaviour of clay bearing soils and rocks (e.g. shale). The outcomes of this study on the upper Bringelly shale indicated that the swelling clay minerals (mixed-layer clays) of fresh Bringelly shale constitute about 40 percent of the clay minerals while the non-swelling clay minerals (mica group, kaolin group, and chlorite) represent 60%. The mixed-layer clay minerals have properties intermediate between illite and smectite such that illite dominated mixed-layer clays have limited expansiveness while smectite dominated mixed-layer clays are most expansive. These clay minerals are known as swelling clay minerals with interlayer water in their structure. Their structure and properties are responsible for the swelling of Bringelly shale. From the engineering viewpoint, the amount of swelling in these minerals is important in understanding the geotechnical behaviour of clay bearing soils and rocks (e.g. shale).
Figure 3.7 Typical x-ray diffractogram, <2 µ fraction of extremely weathered Bringelly shale untreated and treated samples (Badgreys Creek)
Table 3.1a Average mineral composition of the clay fraction at different degrees of weathering in the Bringelly shale

<table>
<thead>
<tr>
<th>mineral</th>
<th>% clay mineral in each state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fresh</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>33</td>
</tr>
<tr>
<td>Illite-Smectite</td>
<td>40</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>-</td>
</tr>
<tr>
<td>Illite</td>
<td>21</td>
</tr>
<tr>
<td>Chlorite</td>
<td>6</td>
</tr>
</tbody>
</table>

The clay properties are susceptible to variations in the thickness of their interlayer horizons that can be caused by different cations and different water contents and this gives the smectite its distinctive swelling property. The interlayer water molecules in swelling clay are part of the overall layer-lattice structure of this group of minerals (Reynold, 1980; Velde, 1992). However, the clay minerals without interlayer water molecules, such as illite and kaolinite do not expand significantly when wet (Brindley & Brown, 1980) due to bonding between constituent layers and the charge deficit on the crystal lattice. In kaolinite, oxygen atoms in the tips of the two-thirds of the tetrahedra layer are also shared by the octahedra layer. The remainder is made up of hydroxyl. This gives a strong covalent bond between the two layers. For the illite, the $K^+$ ion between the 2:1 layers is less tightly held, and it may be replaced by other ions such as $Ca^{2+}$, $Na^+$, and $Mg^{2+}$.

The x-ray powder diffractometry study indicated that the other significant non-clay minerals are siderite and feldspars, anatas, and albite. The quantitative methods used in this study indicated that the mean clay mineral content is about 51% while the non-clay minerals from the four sites represent 49% (Table 3.1b). The results of the analyses were in agreement with previous studies of the Wianamatta group (Table 3.2) that were undertaken by Loughnan, 1960; Herbert, 1979; and Ghafoori, 1995.
Table 3.1b  Average clay and non-clay minerals composition
(whole rock) in the Bringelly shale

<table>
<thead>
<tr>
<th>Bringelly shale site</th>
<th>Kaolinite %</th>
<th>Illite %</th>
<th>Illite-Smectite %</th>
<th>Chlorite %</th>
<th>Non-Clay %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kemps Creek</td>
<td>16</td>
<td>11</td>
<td>22</td>
<td>4</td>
<td>47</td>
</tr>
<tr>
<td>Horsley Park</td>
<td>16</td>
<td>9</td>
<td>22</td>
<td>3</td>
<td>50</td>
</tr>
<tr>
<td>Badgerys Creek</td>
<td>17</td>
<td>12</td>
<td>23</td>
<td>3</td>
<td>45</td>
</tr>
<tr>
<td>Mulgoa</td>
<td>17</td>
<td>12</td>
<td>17</td>
<td>2</td>
<td>52</td>
</tr>
</tbody>
</table>

Table 3.2  Average mineral composition of the clay fraction in the Wianamatta group shales

<table>
<thead>
<tr>
<th>Rock type</th>
<th>Kaolinite %</th>
<th>Illite %</th>
<th>Illite-Smectite %</th>
<th>Chlorite %</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bringelly shale</td>
<td>45</td>
<td>35</td>
<td>20</td>
<td>-</td>
<td>Loughnan (1960)</td>
</tr>
<tr>
<td>Ashfield shale</td>
<td>55</td>
<td>45</td>
<td>-</td>
<td>-</td>
<td>Loughnan (1960)</td>
</tr>
<tr>
<td>Ashfield shale</td>
<td>60</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>Herbert (1979)</td>
</tr>
<tr>
<td>Ashfield shale</td>
<td>56</td>
<td>44</td>
<td>-</td>
<td>-</td>
<td>Ghafoori (1995)</td>
</tr>
<tr>
<td>Bringelly shale</td>
<td>33</td>
<td>21</td>
<td>40</td>
<td>6</td>
<td>William (current)</td>
</tr>
</tbody>
</table>

These studies indicate that there are very significant differences in the clay mineralogy of the two shales (Ashfield & Bringelly) from the Wianamatta group. The main difference is the large amount of mixed-layer, illite-smectite, in the Bringelly shale. Loughnan (1960) reported mixed-layer clay minerals within Bringelly shale, but these only comprised 20% of the clay fraction. The greater amount of mixed-layer clay detected in this study could be the result of improvements in the analytical techniques, or may reflect variability in the shale.

In this study, tests on extremely weathered material have revealed that weathering of Bringelly shale is associated with changes in mineralogy. It was found that chlorite and some illite had been broken down and / or transformed to mixed-layer clay minerals as indicated from the corresponding increase in the latter. This was also
associated with formation of small montmorillonite fraction. These changes will tend to increase the reactivity of the residual soil compared to the parent shale. This trend is evident in the liquid limit of the crushed shale which increases from 30 for fresh shale to over 50 for extremely weathered shale (Section 4.2.4)

The results of the qualitative and semi-quantitative analysis indicate that 38% of the non-clay minerals is quartz. Other non-clay minerals such as feldspars and carbonate compounds were also detected by the x-ray analysis however, it was decided to confirm the presence of clay and non-clay minerals by conducting further examination and testing such as scanning microscopy, petrographic examination, and chemical analysis. Details of these tests are in the following sections.

§3.5.2 Scanning electron microscope

The scanning electron microscope (SEM) with energy dispersive x-ray spectroscopy analysis (EDS) has been used in this study. It is a useful tool that can offer an insight to the micro-morphology and mineralogy of a rock. It also provides x-ray maps showing the distribution of elements across the field of view. The scanning electron microscope has been less successful in the study of argillaceous rocks, than for other rock types because of their small voids and low porosity. However, recent improvements in back-scattered detectors have allowed more accurate information about micromineralogy and petrography. This has been achieved by a technique that produces a high resolution surface image via backscatter and secondary scatter electron detector (Krinsley and Manley, 1989). Several researchers have employed this recently improved technique to examine the micro-structure of shale rocks, some of which have been reviewed in Chapter 2.

§3.5.2.1 Preparation of the polished sections

Samples for the microscopic studies were carefully cut from the intact specimens with dimensions approximately 15 mm in diameter and 10 mm thick. They were first air dried and then oven dried at 60° C for approximately 24 hours. They were then vacuum impregnated with an epoxy resin for approximately 2 hours to allow the resin to fill all the voids between the grains and were heated at approximately 60° C
overnight to cure the impregnated resin. Resin impregnation was employed to enhance image resolution.

The resin impregnated sections were then polished with abrasive paper for more than 2 hours to obtain a suitable surface. It was necessary to grind and polish the specimens perpendicularly to the bedding plane to give a suitable surface for observation in the desired direction. Great care was necessary at this stage to prevent the shale particles from being removed during the polishing. For this reason, progressively finer grades of abrasive paper were used, with the final abrasive paper having a 1 \( \mu m \) particle size. The samples were then coated with a very thin film of carbon in a vacuum evaporator to eliminate charging and also to minimise a possible additional peak of carbon. A thin film of gold provides better image due to high electrical and thermal conductive properties, but it would lead to an additional peak that could be ambiguous. Carbon coatings are preferable when carbon element is not the focus of the analysis and also when specimens are to be subjected to x-ray microanalysis (Goldstein et al. 1981).

The finished polished sections were examined in a Phillips 505 scanning electron microscope (SEM). Selected areas of the polished sections were photomicrographed, and the micro-mineralogy of Bringelly shale was evaluated using x-ray analysis.

Thin sections of Bringelly shale were also examined under an optical microscope. The main objective was to investigate the size and shape of grains and nature of cement within the shale. Such information could provide additional evidence on the history and nature of the materials.

§3.5.2.2 Microscopic examination and results

The prepared samples of Bringelly shale were examined in both the secondary electron (SE) and backscattered electron (BE) modes with the SEM operating at 20 kV and with the electron beam normal to the specimen surface. In order to get a high quality image, it is a common practice during the adjustment to saturate the white and
or black areas. Once the contrast range has been achieved, the specimen is then scanned slowly to produce the digital image.

The magnification chosen was varied between 200 and 5000 times, as this proved most useful in observing the detailed structure. It was found in early trials that the secondary mode appeared to give a better image contrast than the backscattered mode particularly with samples having low void ratios. This was also reported by (Stanley, 1993) who suggested that the region generating backscattered electrons is larger than that of secondary electrons, namely several tens of nm. He also reported that at magnification of 400x and higher, backscattered electrons give poorer spatial resolution (Fig. 3.8a). In the secondary mode, good resolution can be achieved at much higher magnification (Fig. 3.8b).

Selected areas of the polished sections were photomicrographed, and the predominant elements present were identified and confirmed by subjecting the samples to energy dispersive x-ray spectroscopy analysis (EDS). This was used for quantitative chemical analysis of Bringelly shale samples. Once the secondary image has been stored, the SEM was operated in the x-ray mode and a trace obtained to determine the elements present in selected regions of the sample. This enables windows to be drawn about each elemental peak for use in the produced x-ray mapping. The clay minerals and other mineral components were differentiated on the basis of their chemical composition as indicated by qualitative x-ray microanalysis.

Samples examined under the scanning electron microscope are presented as micrographs. Figure 3.8a shows plates of clay minerals oriented parallel to the stratification. A high resolution surface image at magnification of 5000x was produced at the central region of the image via EDS. The examination of the image in SE mode (Fig. 3.8b) shows the embedded smectite minerals surrounded by oriented flakes of illite. The ultra-thin window EDS x-ray detector attached to the SEM was used to record the responses from certain elements to enable chemical analysis from areas as small as 2 μm². In this analysis, responses from elements are greatly affected by their atomic mass. Low atomic mass of elements such carbon and oxygen reflect
Figure 3.8 Photomicrographs of polished sections showing the maximum possible magnification for acceptable resolution (a) back-scattered mode and (b) secondary mode.
low intensity colour compared to high intensity colour reflected from the constituent elements of mica and siderite for example.

Photomicrographs showing the structure and mineral constituents of the shale are given in Figures 3.9 to 3.12. Mineral compositions typical of clay minerals are indicated from the presence of (K, Mg, Al, Si and O) in Figure 3.9b. Similar minerals distributions were indicated from other areas of the micrographs identified as clay particles. The presence of Fe, C, and O in the x-ray spectroscopy from the same specimen suggests the presence of siderite (FeCO₃). Further analysis shows that the black particles in the SE mode photograph at (800x) magnification are siderite. Micro-cracking was also detected by the presence of the pronounced wavy cracks vertically oriented (Fig. 3.10a). It is believed to be a result of dissolution of carbon content as indicated by the presence of C and O elements of the spectral analysis (Fig.3.10b).

At higher magnification (1600x) a white globular cluster with wavy curved features is evident in Figure 3.11a. This morphology is distinctive of smectite (Smart and Tovey, 1981; Coulthard et al., 1993). The EDS response for this particle cluster is shown in Figure 3.11b. The elemental response is also consistent with smectite. The wavy shape is believed to be caused by compaction (water loss) to low porosity (Coulthard et al., 1993). Fig. 3.12a shows a quartz grain mineral, this is confirmed from the presence of Si and O in the EDS responses (Fig.3.12b). The quartz from Mulgoa site can be seen as a big grain surrounded by minor smectite as indicted by the white small globular cluster in the photo.

Aluminium and silicon are good indicators of clay minerals, and large amounts were detected in the samples of Bringelly shale. However, it should be noted that the relative magnitude of the peaks in the spectral analyses could not be used to infer the amount or the size of different mineral species.

Thin sections of Bringelly shale were examined for the petrographic analysis with ordinary and polarized light. The visual analysis of samples from the four sites was made using a BHSP Olympus Polarising Microscope. The examination at magnification of 20x revealed the main components of Bringelly shale samples to be clay and non-clay minerals as expected and also indicated the presence of organic
Figure 3.9(a,b) a typical mineral composition of Bringelly shale. Siderite (red arrow), mica (blue arrow).
Magnification = 200

Figure 3.10a  Orientation characteristics showing micro-cracks
(red arrow)

Figure 3.10b  Spectral analysis of the white region in
the top left hand side of the photomicrograph
(blue arrow).

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Figure 3.11a,b  Scanning electron micrographs showing spectral analysis of a globular cluster of smectite mineral (red arrow)
Figure 3.12a,b Scanning electron micrographs and spectral analysis of a large quartz particle
matter. Studies using polarized light have detected an alteration of some minerals, for example, biotite has changed to chlorite and mica (muscovite) has been altered to illite. Chlorite is indicated by the green colour in the centre of the photo (Fig.3.13a) while illite is shown by its characteristic platy crystals with irregular edges and white to silver colour (Fig.3.13b). In this photo, presence of grains with a mix of white and yellow colour indicates a middle stage of alteration from mica to illite.

Non-clay minerals such as siderite, feldspar, quartz, and organic matter are disseminated within Bringelly shale (Fig.3.14a,b). The thin sections have revealed that siderite comprises about 2 to 4% compared to other components, while feldspars represent 4% to 7%. These results are very close to the results obtained from x-ray powder diffractometry analysis. The current results show no significant difference in mineralogy between the sites. As specimens have been obtained from different locations and at different depth within the shale sediment column the similarity suggests the continuity of the deposition cycle without interruption and consistency in post depositional processes such as weathering, sediment diagenesis, and hydrothermal alterations. The agreement between mineralogy and structure at the different sites also appears to rule out the possibility that structural events (fault, folds, thrust, unconformity, etc.) might have had an influence on the mineralogy within the selected site area.

The vaguely scattered black fibres across the micrograph suggest the presence of organic matter. Further investigation to affirm the presence of these organic fibres will be discussed in the next section. The microscopic examinations suggest that clay minerals and siderite are the prime cementing material in the shale. The average amount of siderite in the specimens is only 3% so bonding from this material must be limited. Recrystallisation of mica at particles contact has dominated a large part of the specimens. Based on this observation, it is believed that recrystallisation is the main cause for the bonding between particles. The textural changes such as irregular edges, curly surfaces, and fragmental shapes of the crystals could be a result of recrystallisation processes during diagenesis. It is also possible that recrystallisation of mica was a response to high temperature and pressure during sediment burial. However, the irregularity in the borders of the illite crystals also suggests that some
(a)
Chlorite grain (red arrow)

(b)
Mica (purple arrow), Biotite (red arrow), and Mica to Illite (blue arrow).

Figure 3.13a,b  Photomicrographs under polarised light.
Magnification = 25
Figure 3.14a,b Chlorite (blue arrows) and Siderite (red arrows) cement, disseminated between Quartz in a siderite dominated sample. Polarized light (a) and ordinary light (b). Magnification = 25
illite is detrital in origin, indicating that recrystallisation is limited and that bonding may not be that strong.

§3.5.3 Carbonate and organic contents

Based on the visual examinations, x-ray diffraction, and scanning electron microscopy, there is evidence supporting the presence of carbon and organic matter. This was observed from the analysis of the dark and light particles shown in the photomicrograph (e.g. Fig. 3.15a). Elements such as Fe and C were also detected by the spectral analysis (Fig. 3.15b). In order to verify the percentage of total carbon including organic and inorganic material, further tests were performed. The tests were performed on samples from three sites namely, Kemps Creek, Badgerys Creek, and Horsley Park. Specimens from each sample were taken and three different test methods were used. Only two samples were tested on LECO analyser.

Details of the three methods used in this analysis are described below:

(i) The acid soluble weight loss

This method was adapted from Twenhofel and Tyler (1941) who measured the carbonate content in calcareous sediments. In summary, the procedure is as follow:

1. Add dilute HCl to a known dry weight shale sample, until visible chemical reactions are complete. (over night in this study);
2. Wash the sample with distilled water; and
3. Dry and then weigh the sample.

The carbonate content is calculated from the formula:

\[ C_T = \frac{(W_o - W_f)}{W_o} \]  

(3.1)
Figure 3.15 Organic matter of Bringelly shale (a) as affirmed by SEM (red arrows) and (b) EDS analysis as indicated by the high peak of Carbon
Where $W_0$ and $W_f$ are the initial and final dry weight of the sample respectively, and $C_T$ is the assumed total carbonate content. It should be noted that the treatment of samples by using dilute $HCl$ may decompose other constituents.

(ii) Carbon analysis

In this method a special device was used to measure the total carbon and organic contents. The method is very accurate and can be performed in a very short time (Golchin et al., 1994). Prior to the test, samples were first checked with $HCl$ for the presence of carbonate. As carbonate was detected in the specimens, the total carbon content $C_T$ and organic carbon $C_o$ of the fine-ground shale passing 250 micron sieve were determined by dry-combustion with a LECO CNS-2000 analyser (LECO Corporation, MI, USA). Inorganic carbon $C_I$ can be determined from the difference between $C_T$ and $C_o$.

(iii) The Australian standard

This method, A1289.D1.1 – 1977 was used to measure the organic matter content. It should be mentioned here that carbon is only one component in any organic matter which is comprised of other components such as hydrogen, oxygen, nitrogen and smaller quantities of sulphur and other elements.

The results of the analyses are presented in Table 3.3. The table shows different percentages of total carbon ($C_T$), inorganic carbon compounds ($C_I$), and organic carbon ($C_o$). The results suggest an average of 2% total carbon by weight and also suggest values of 1.7% and 0.3% for organic and inorganic carbon respectively. Since the carbon in the siderite ($FeCO_3$) is about 3% by mass. In this study, siderite content of 0.3% would be expected as inorganic carbon content in Bringelly shale. This figure is about 10% of the amount of siderite determined earlier in the current study (Section 3.2).

The relatively high amount of ~1.5% of organic matter from the laboratory tests is consistent with the difference between the approximate total amount of carbon content (2%) and the amount of inorganic carbon (~0.3%) in the specimens. However,
it must be noted that the low value of inorganic value was also detected from the random scatter and dissemination of siderite during the scanning and microscopic examination of the specimens (Section 3.4.2.2). The laboratory tests and microscopic examinations are evidence that the organic content could contribute to cementation. Nevertheless, the relatively high amount of organic carbon and organic matter may support a proposition by Herbert (1979) who described the depositional environment of Bringelly sediments as a fluvial flood basin.

### SUMMARY

Block and core samples from a depth of 8 to 10 metre below the natural topographic surface were collected from four sites representing a large area of western Sydney. Based on visual assessment, the Bringelly shale examined in this study consists basically of claystone and siltstone.

The mineralogy of the collected samples was examined by x-ray diffraction, electronic scanning microscopy, and optical microscopy. X-ray diffraction analysis of the Bringelly shale shows montmorillonite only in the extremely weathered shale. The x-ray diffractogram of the less than 2 micron fraction shows that mixed layer illite-
smectite is the dominant clay mineral in Bringelly shale, while kaolinite is the major non-swelling clay mineral. Quartz was found to be the major non-clay component of Bringelly shale.

Quantitative chemical analysis of samples from Bringelly shale showed that Aluminium, silicon, and oxygen, and potassium were the main constituents. Iron, magnesium, and carbon were also detected in most of the samples. The presence of iron and carbon within Bringelly shale indicated the presence of siderite, while presence of carbon and oxygen confirm the minor components of organic matter.

Petrographic studies, comprising optical microscopy and scanning electron microscopy, have been used to investigate the microstructure and nature of cementation in the Bringelly shale. Examination of thin sections from all sites confirmed the presence of non-clay minerals such as feldspars, siderite, and also some disseminated organic matter within the clay minerals. All techniques that were used in determining the mineral constituents of Bringelly shale agreed that the major constituent of 51% is clay minerals while the remainder is for non-clay minerals. The major non-clay minerals are Quartz with 38%, feldspars 6%, siderite 3%, and 1.5% of organic matter.

The microscopic examination has suggested that minerals such as siderite, feldspar, organic matter, and some recrystallisation of mica could contribute to cementation. It is believed however, that recrystallisation processes are the prime cause of bonding in Bringelly shale as it shows from the characteristic boundaries and irregular edges of mica minerals in the microscopic image. The process may have occurred during diagenesis and was responsible for inducing a reorientation in the crystal lattice of clay mineral grains. However, none of these mechanisms is well developed and cementation is expected to be weak.