THE COMPOSITION
OF
MODERN CARBONATE SEDIMENTS
IN THE
SOUTH EAST OF SOUTH AUSTRALIA.

A thesis presented
by
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TABLE OF CONTENTS.

Page.

ABSTRACT

TABLE OF CONTENTS (continued)

APPENDIX. Inserted in folder inside back cover.

Compilation of Data on all Samples Discussed.

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

In the South East of South Australia an extremely fine-grained white carbonate sediment is found. This carbonate sediment, known locally as pipe-clay, has been observed in active precipitation from the waters of the Coorong and the shallow lagoons south of the Coorong. Similar surficial 'pipe-clay' has been found on Kangaroo Island and at Streaky Bay. Eleven feet below the present surface of Lake Eyre a pipe-clay layer a foot and a half thick was encountered. At shallow depths (up to 4 feet), in the interdunal areas of the South East Province pipe-clay has been found covered by sand and soil. Thus, it is a relatively wide-spread phenomenon.

The dominant minerals of pipe-clay are calcite and dolomite. Calcite is always present, dolomite is usually present, but often in small amounts (about 20%). Calcite always contains some $MgCO_3$ in solid solution. The composition range of calcites in pipe-clays is ($Ca_{77}Mg_{23}$) to ($Ca_{98}Mg_2$). Dolomite usually has composition of $Ca_{56}Mg_{44}$ with a range from $Ca_{50}Mg_{50}$ to $Ca_{56}Mg_{44}$ in the pipe-clay samples studied.

The ratio of calcite to dolomite is variable. It changes with locality and distance below the surface in any one locality. In one of the shallow lagoons south of the Coorong, Lagoon M, dolomite decreased relative to calcite with depth, but two small dolomite increases were noted in the 29 inches of pipe-clay. In Kingston Lake, another shallow lagoon 7 miles south of Lagoon M, the reverse was true: dolomite increased relative

to calcite in depth. It was noted that the composition of the magnesian calcite became more magnesian when the amount of dolomite increased. The pipe-clays collected in active precipitation showed an increase in dolomite the further south the specimen was collected in the Coorong, and a maximum amount of dolomite relative to calcite was found in the precipitating pipe-clays of Kingston Lake. Approximately equal amounts of dolomite and calcite were precipitating here.

From this evidence it is obvious that,

A), dolomite is not forming as a secondary alteration product from the breakdown of unstable magnesian calcite, or both lagoons would have shown dolomite increasing with depth. The fluctuations of the amount of dolomite relative to calcite can be explained by changes in the environment of precipitation,

B), the conditions most favourable for the precipitation of dolomite are found in the lagoons and there appears to be a gradual increase in the amount of dolomite as we procede south in the Coorong, probably indicating gradually changing conditions. Thus the optimum conditions for the precipitation of dolomite should be able to be established from a close scrutiny of the South East occurrences.

The cause of the precipitation envisaged by the writer is the elevation of the pH of the Coorong and lagoonal waters to a value such that dolomite precipitates as well as calcite. Plant photosynthesis is suggested to be the major factor in changing the pH.

Quartz, halite and clays (kaolin, illite and montmorillonite) are found in all pipe-clays in small amounts, along with the major carbonate minerals. Quartz is wind blown sand from the dune ranges nearby. The halite forms from the evaporation of the waters from which the pipe-clay precipitates and the clays are judged to be wind-blown from nearby soil. Gypsum, also formed by evaporation and celestite are minor constituents of most pipe-clays. Plant and calcareous shell material are ubiquitous.

Celestite appears to precipitate from the waters at the same time as the carbonates. Sr analyses of all the samples collected shows that the South East province is Sr rich compared to the average figure for limestones over the world (0.06%). The recent precipitating pipe-clays are the highest in Sr as a group and the pipe-clays in general are higher than the sands. The pipe-clays contained between 0.3% and 1.12% Sr and the sands from 0.001 to 0.3% Sr. Lagoon M is strikingly rich in Sr throughout the 29 inches of pipe-clay. No explanation for this marked local enrichment could be found.

INTRODUCTION

In 1929 Sir Douglas Mawson described a pale-grey, fine-grained carbonate sediment found on the surface of a lagoon in the South East of South Australia. It was locally known as "pipe-clay" and analysis showed that Mg was present in high proportions. The dominant mineral constituent was presumed to be dolomite.

The South East of South Australia was known to be a limestone province and, as Mawson's (1929) paper indicated, possibly a good area for the study of modern carbonate formation. It was not until 1955 however, when Dr. B.G. Forbes briefly examined the sediments in two lakes south of the Coorong as part of his Ph.D. thesis, that the pipe-clay received further notice.

In November 1955 Professor A.R. Alderman in a trip through the South East came upon a singular phenomenon. One of the lagoons south of the Coorong was milky with a fine-grained white precipitate which was still in suspension in the shallow waters. A specimen of this milky water was brought back to the University of Adelaide for identification.

It was at this juncture that the writer entered into the study of the carbonates from the South East of South Australia. The material in suspension proved on X-ray analysis to be largely a mixture of calcite and dolomite.

In the same lagoon where the water sample was collected a bore hole showed several feet of similar carbonate sediment.

In a comparable lagoon but some 50 miles south several feet of this same fine-grained white sediment was found. It appeared as though the fine-grained white carbonate sediment was common in the lagoons of the South East. Here was a unique opportunity. The chance to observe, describe and analyse a modern sediment in the process of formation.

As the investigation of the carbonate sediment progressed it became obvious that a detailed mineralogical approach would be necessary in describing and identifying the white sediment and as a consequence several mineralogical and crystallochemical problems came to light. However, in order that the processes of formation of the carbonate sediment could be fully understood other aspects would have to be thoroughly investigated as well. The relation of plant activity to the precipitation was unknown in detail and suspected to be essential. A floral and faunal study of the life in the Coorong and the lagoons would be necessary. The water which precipitated the carbonate sediment approximates sea water in salt composition and some knowledge of the solution chemistry would be invaluable.

Before the processes of formation of the sediment could be ascribed an accurate description of the constituents in the sediment and their relation to one another must first be made. It is hoped that the following pages will provide the description of the white, fine-grained sediment which will enable those more qualified to evaluate further the possible methods of formation using other lines of approach.

A brief geographic and geologic description of the South East province is given followed by a discussion of the term "pipe-clay". Some pertinent crystallochemical data from recent laboratory studies on carbonates precedes the main body of the thesis. These data were included in the hopes that they would be helpful in understanding the problems encountered in defining the carbonates. There is a section devoted to the Sr content of the samples, as the South East was discovered to be not only rich in carbonates but rich in Sr as well. In summary, some of the general chemical theory involved in the precipitation of carbonates is given.

I am deeply indebted to the University of Adelaide for the project grant which enabled me to pursue this investigation. However, were it not for Professor A.R. Alderman, I should not have even known about the carbonate problem in the South East and his interest and guidance throughout the work has been stimulating. I also want to thank friends overseas with whom I corresponded on items of mutual interest, Dr. E-an Zen and Mr. Robert Schmalz of Harvard University, Mr. and Mrs. Brian Smith of Meningie have helped most materially in all stages of this work not only with their general knowledge of the area and for allowing the writer to stay on their property but for their keen interest in all aspects of the problem. Dr. K. Norrish and the staff of the C.S.I.R.O., Division of Soils, have been more than generous in allowing me to use their X-ray Diffractometer and X-ray Spectrograph as well as identifying several clay minerals and offering useful suggestions.

Mr. John Hutton, C.S.I.R.O., has analysed a number of specimens and advised the writer on the chemical problems which arose. Miss A.M. Swan expertly drafted many of the figures. Last but certainly not least I want to thank my husband, Dr. B.J. Skinner without whose criticism and assistance this work would never have been contemplated.

GENERAL GEOLOGY

The South East province of South Australia extends from Meningie in the north to Mt. Gambier in the south, from Naracoorte in the east to Robe in the west, an area of about 7500 square miles. It is an area of low relief. The dominant topographic feature is a number of sub-parallel dune ranges which trend northwest-southeast, paralleling the coastline. The dune ranges in the southern half of the province are widely separated by flats which contain marshes, intermittent and permanent lakes and swamps. The relief between the ranges and the interdunal flats is about 100 feet. In the northern portion of the province the dunes converge and the interdunal flats are usually poorly defined or non-existent. The northern sector has not been mapped in detail and roads are only now in the process of being built to allow access to this area.

The general geologic picture of the South East province as given by Hossfeld (1950) and Sprigg (1952) is that the ranges are remnants of coastal dunes of Quaternary age left stranded by the fluctuations of sea level and the gentle warping of the coastal plain on which the dunes were developing. There are eight well defined dune ranges and many branches or subdunes described in detail by these authors.

A map of the South East province is presented in Fig.1. The map includes all the localities referred to in this discussion. It is a compilation from the maps of both Hossfeld and Sprigg as well as the Military Topographic Sheets of Naracoorte, Penola, Pinnaroo and Baker. The names of the dune ranges used in this discussion are those given by Sprigg (1952).

Most of the drainage in the area is subsurface in the Mid-Tertiary bryozoal limestones which underlie a large part of the South East province. There is no major stream cutting the dunes at right angles to allow drainage to be carried the shortest distance to the sea. Due to a slight tilt of the area all the surface drainage has in the past proceeded very slowly toward the northwest, eventually emptying into the lakes at the mouth of the Murray River and thence to the sea. During recent years one main and many subsidiary drains have been constructed cross-cutting the dune ranges in the southern portion of the South East. The construction of these drains has allowed the swampy portions of the interdunal flats to be turned into pasture. As yet no major drain comparable to Drain L in the south of the province has been constructed north of the Naracoorte-Kingston train line. The interdunal flats inland in the northern sector are still swampy and undeveloped.

Some of the wider flats separating the dune ranges in the southern South East contain permanent lakes such as Bool Lagoon in the Naracoorte-Cave interdunal area. Lake Hawdon in the Dairy-Woakwine interdunal area also contains some permanent water in the southern portion even though Drain L passes through the northern portion of the lake. Just landward of the Robe Dune are large permanent lakes: Lake Eliza, Lake St. Clair, Lake George and Lake Bonney.

In the northern half of the South East province, where the dunes converge, there are a few isolated permanent lagoons, but the region is mostly an area of swampy flats and low dune ranges of no simple pattern.

The dunes consist of quartz sand and shell fragments and are often cemented on the crests by kunkar limestone. The dunes support some of the indigenous vegetation, in particular tea tree. Interdunal flats usually contain much marsh and tussock grass as well as tea tree and she-oak. Algae, water plants, small molluscs and crustacea thrive in the pools and large shallow lagoons which are found in many interdunal areas. The species thriving here are able to cope with seasonal droughts and rejuvenate with the winter rain.

The average annual rainfall in the north of the province is 15 inches, in the south 34 inches. Kingston, for example, has an average of 24 inches. The mean maximum temperatures are highest, 80°F., in February and lowest in July, 40°F. The rain, concentrated in the winter months, is channelled into the interdunal areas. These flats are impervious due to the formation of a kunkar layer in depth. As the summer progresses, the water may evaporate in the more shallow areas of an interdunal flat and leave a white powdery residue. Most of the interdunal flats, however, remain completely saturated during the entire year, provided the year has not been exceptionally dry.

The Coorong

The most striking feature in the whole of the South East province is the Coorong. This extremely narrow, attenuated body of sea water extends ninety miles south east in an arc from Meningie toward Kingston. It is separated from the open sea over its length by a narrow strip of sand dunes known as Younghusband Peninsula. The Coorong is only about 3 to 5 miles wide in the upper, northern end and narrows to a half-mile wide at its southern extent.

The southern extent of the water in the Coorong is variable with the season. During the winter rains the water may extend to about 25 miles north of Kingston, whereas at the end of the summer the water may have retreated to Salt Creek, exposing the floor of the southern end of the Coorong.

Between the southernmost extent of water in the Coorong during winter, and Kingston, are a series of swamps and attenuated intermittent lagoons. Two large examples of intermittent lagoons in this area have been labelled Kingston Lake and Lagoon M on the accompanying map. These two lagoons may completely fill with water during a very wet winter, but usually do not contain any water by the end of the summer in March.

The surfaces of the exposed southern end of the Coorong and the two lagoons further south are covered at the end of the summer with a white, extremely fine-grained, sediment known locally as 'pipe-clay'. The pipe-clay has been observed precipitating from the waters of these lagoons and the southern end of the Coorong during the late spring and summer months. The surface presented is so smooth and even that the road, which usually runs along the eastern edge of the Coorong, has, at the appropriate time of the year, a 'summer pipe-clay track'. This track, actually marked on the maps, is on the dried floor of the southern end of the Coorong.

The Coorong, in times past, obviously extended all the way south, including the present intermittent lagoons and swamps, almost to Kingston. Residents of the Coorong area have noted that land, originally under water part of the year, is now used for grazing year round. The sea is gradually retreating from the southern end of the Coorong.

The Coorong indicates the origin of the other interdunal areas further inland. The present Coorong is at a stage in the formation of an interdunal area where the attachment to the sea can be seen and studied. It is probable that the sea will eventually retreat leaving only a narrow interdunal flat to separate Younghusband Peninsula from the mainland. The vegetation and sand blown inland from the dunes will cover over the white powdery pipe-clay and the Coorong will have the same aspect as the inland interdunal flats.

During this investigation bore holes were put down in many of the inland interdunal areas. Usually the upper inches in the bore showed soil formed from the decaying plant material and sand. Below the soil was a layer of sand containing a great deal of plant and shell fragments and white powdery material. Gradually, in depth, the white powdery material increased in proportion to the other constituents. Occasionally, some distance below the surface, a layer is encountered which consists of at least 80% white powdery material. This layer is identical in physical and chemical composition to the pipe-clay exposed on the surface of the Coorong and the lagoons south of it. The inland interdunal areas were once at the same stage as the Coorong is today.

The pipe-clay found in depth in the interdunal areas is the same as that in the process of formation in the Coorong and the lagoons south of the Coorong today. The conditions prevailing in times past must have been similar to those prevailing now.

The composition of the waters from the Coorong, Kingston Lake and the ground water, as exemplified by Drain L is compared in Table 1 to sea water (Alderman and Skinner, 1957). The average sea water, of Sverdrup (1942), and sea water near Adelaide are both given. From Table 1 it is obvious that the water in the Coorong and Kingston Lake have approximately the same relative chemical composition as sea water, though the

TABLE 1

Saline content of water samples

	Coorong			Kingston Lake			Sea		Drain L		
	3½m. S.E. Salt Ck.						Near Adelaide	Sverdrup	Near Robe		
Month	June	Nov.	Jan.	June	Nov.	Jan.			June	Nov.	Jan.
No.	1	2	3	4	5	6	7	8	9	10	11
Cl.	55.9	55.8	55.8	56.0	55.9	55.3	55.5	55.04	48.5	49.9	50.1
SO_4	7.5	7.6	7.6	6.3	6.2	7.5	7.9	7.68	9.5	8.7	9.6
CO_3	0.1	0.2	0.1	0.3	0.5	0.1	0.2	0.41	6.1	5.2	4.8
Na	31.8	31.9	31.7	34.3	34.1	34.2	32.2	30.62	27.3	29.0	28.3
Ca	1.0	0.9	1.0	0.8	0.6	0.4	1.1	1.15	4.0	2.8	1.3
Mg	3.7	3.6	3.7	2.3	2.5	2.6	3.8	3.69	4.6	4.4	5.8
%Salinity	7.05	4.7	5.4	3.33	2.44	22.6	3.8	3.5	0.27	0.25	0.28

salinity may differ. The ground water of Drain L is quite distinctive when compared to the others, especially in the relative amounts of calcium and carbonate. It should be noted then, that there are two different types of water in the area. The lagoons and the Coorong are similar to sea water while the ground water is brackish but essentially lacustrine in character.

THE COMPOSITION OF 'PIPE-CLAY'

The term 'pipe-clay' is used in the South East of South Australia to mean the fine-grained white sediment found in the Coorong, the lagoons to the south of the Coorong and in many isolated shallow depressions in the region. The pipe-clay may be exposed on the surface or covered by later sediments and soil.

Isolated shallow depressions, locally called 'clay pans', are found scattered throughout the region, particularly in the northern half of the southeast province. Some clay pans may now be covered by a soil layer, but remain depressions in the topography usually surrounded by tea tree. A bore put down in these clay pans may encounter a typical white pipe-clay. An X-ray examination of pipe-clay from clay pans to the east of Meningie (Samples A.245-4, 6, 8) showed gypsum the dominant mineral with minor halite, quartz and clay minerals. The extent of the gypsum deposits is not known in detail, but is is apparent from the present study, and from work by the Waite Institute soils surveyors, that all the small isolated water soakages where salinity is high, are rich in fine-grained gypsum. Although this gypsiferous precipitate is called pipe-clay, it will not be further discussed in this work.

South of the Coorong, but in the same general topographic declivity, are a number of lagoons. Some of these lagoons are 'salt pans'. As the name suggests, the white surface layer of salt pans is predominantly halite.

By far the most abundant type of powdery white material in the area is found on the surface of the dried southern end of the Coorong and most of the lagoons south of the Coorong. This is the classic pipe-clay of the South East and is quite different in both origin and composition from the fine-grained white sediments described above. The Coorong pipe-clay is composed of exceedingly fine-grained carbonate minerals, calcite and dolomite, with minor amounts of quartz, clay minerals, halite, celestite, hydrocarbon organic material and calcareous shell fragments. It is this fine-grained carbonate pipe-clay that concerns us in the present study.

The term 'pipe-clay' is, of course, a misnomer, but has become so entrenched that it was thought best retained in discussing the complex carbonate sediments of the South East of South Australia. An exact definition of the term 'pipe-clay' as it is used in this thesis can now be given. Pipe-clay is a white or light grey, extremely fine-grained sediment which consists largely of magnesian calcite and calcian dolomite and may contain varying amounts (i.e. less than 20% total impurities) of any or all of the following: gypsum, halite, quartz, celestite, kaolinite, montmorillonite, illite, hydrocarbon organic matter and calcareous shell fragments. The amount of calcian dolomite relative to magnesian calcite is variable. Pure magnesian calcite pipe-clay samples are not uncommon. More often dolomite is present in small amounts (5-15%) and frequently the calcite/dolomite ratio appears to be close to 50/50. Occasionally dolomite is the dominant phase present. However, no sample has been examined where dolomite was the only fine-grained carbonate present. Dolomite does not occur without calcite.

The Minerals in Pipe-clay

Of the minerals included in the pipe-clay, the carbonates are the most important. An entire chapter has been devoted to discussing the variations in their compositions. At this point it is sufficient to say that the calcite and dolomite are rarely pure compounds. Both calcite and dolomite usually contain some magnesium or calcium respectively, in solid solution. A great deal of experimental work has been carried out in the system Ca-Mg-CO_3 and the deviation of this natural occurrence from the experimental work is most interesting.

The gypsum occurring in the pipe-clay is always less than 5% of the sample. Although crystals can sometimes be seen under the binocular microscope, the identification has been made by means of X-ray diffraction. Halite is always a major contaminant reaching perhaps 7% of the total. The halite can easily be dissolved in distilled water and does not upset any of the determinative techniques. Both halite and gypsum, often found as macroscopic crystals, are almost certainly formed by evaporation of the waters (in the Coorong and lagoons).

Quartz is found in all the pipe-clay samples in small amounts. It always occurs as colourless anhedral grains, generally rounded and abraded. The source of the quartz is probably the local beach sand dunes from which it is transported by the wind. Some samples collected in this study were quartz sands which contained some fine-grained white carbonate. It is probable that the carbonates have been deposited in the sand directly. The carbonate-rich sand is not a pipe-clay as defined although the source and method of deposition of the carbonate is probably the same as for a true pipe-clay. In fact, often a carbonate-rich sand is found below or above the true pipe-clay as a transition zone from a quartz sand to a pure pipe-clay. A more complete picture of the transition will be presented later in this discussion.

Celestite, never more than 3% of the total sample, has been discussed fully in Chapter V, as the occurrence of this mineral with the carbonates has a special importance. The celestite precipitates with the carbonates from saline solution.

Clay minerals are found in all the pipe-clay samples in varying amounts and in varying proportions, though montmorillanite is always predominant. Kaolinite and illite have also been identified. A true pipe-clay must contain less than 20% of these clay minerals, and most of them do in fact contain a good deal less than this. An interesting fact came to light when three deep bores were put down in Kingston Lake. The bore put down into the present bank of the Lake contained considerable clay material, particularly montmorillanite (about 10-15% of the total). A second bore - put down at the edge of the actual water in the Lake contained much less clay material. The third bore in the Lake centre contained no more than 2-3% clay minerals all together. The origin of the clay is uncertain, but considering the distribution in Kingston Lake, it seems likely that it is windblown from the surrounding soil areas.

Flora and Fauna in Pipe-clay

Fragments of the shells of molluscs, pelecypods, ostracods and foraminifera have been identified in many of the samples, though no systematic effort has been made to study the animal remains. Forbes (1955) gave a tentative identification for some pelecypods in his thesis. Spore cases, often coated by carbonate material, as well as much plant detritus, are found in the pipe-clays. These organic remains are either indigenous, wind or water transported.

It is probable that most of the calcareous remains are indigenous and that the plant material is about equally divided between indigenous and foreign material.

Physical Properties of Pipe-clay

Pipe-clay acts, in many respects, like a true clay mineral. When wet it is very plastic and sticky. It apparently swells slightly with water since cracks are often found in the surface layers during the summer dry period. The grain size of the carbonate particles in the pipe-clay is important in explaining the physical properties. Electron micrographs of the pipe-clay sediment still in suspension in the water of Kingston Lake have been made by Mr. J. Farrant of the Chemical Physics Section, C.S.I.R.O., Division of Industrial Chemistry. Rhombohedra up to 20 microns in diameter were found, but the usual grain size was less than 1 micron, though it was apparent that the grains were still single crystals. The small grain size is characteristic of the precipitated carbonate minerals in all the pipe-clays studied.

TABLE 2

Pipe-clay Localities in South Australia

Locality	Sample No.	Thickness Inches	Depth Inches	Carbonate Minerals	Composition of carbonate minerals
Naracoorte-Harper Interdunal Area					
Naracoorte Creek 2-4 m.W. of Naracoorte	W1(4) W1(5)	24	36-60	Cal.	Cal.$(Ca_{91}Mg_9)$
Bool Lagoon	W6 (2)	24	6-30	Cal. and minor Dol.	Cal.$(Ca_{94}Mg_6)$ $(Ca_{98}Mg_2)$ Dol. $(Ca_{50}Mg_{59})$
East Avenue-West Avenue Interdunal Area					
Bull Island near W. Avenue Range (Drain)	D17 D18 D19	36	8-44	Cal and minor Dol.	Cal $(Ca_{88}Mg_{12})$
Reedy Creek-Dairy Interdunal Area					
Conmurra H.S. Drain L.	W10(3)	3	48-51	Cal.	Cal.$(Ca_{88}Mg_{12})$
Dairy-Woakwine Interdunal Area	A78-15 1 23	42	0-42	Cal and Dol.	Cal.$(Ca_{84}Mg_{16})$ Dol.$(Ca_{56}Mg_{44})$

TABLE 2 (cont.)

Lake Hawdon North				Cal.dominant in depth	Cal.$(Ca_{98}Mg_{2})$
W.Edge Davy Denning swamp - 15 miles inland from Coorong	U7 (4)	3	4-7	Cal. and Dol.	Too broad to be measured accurately
Coorong					
10 m. S.E. Salt Creek Causeway	A78-1	0	0-½	Cal.and minor dol.	Cal.$(Ca_{84}Mg_{16})$ Dol.$(Ca_{55}Mg_{45})$
	D59	2	0-2	Cal.and minor dol.	Cal.$(Ca_{88}Mg_{12})$
5 m.S. of Causeway	A78-35 36	1½	2½-4	Cal.and minor dol.	Cal.$(Ca_{88}Mg_{12})$
12 m.S. of Causeway	D57	35	2-37	major dol. and minor cal.	Dol.$(Ca_{50}Mg_{50})$ Cal.$(Ca_{84}Mg_{16})$
Lagoon					
W. Edge	D46,D47	3	0-3	Cal.and dol.	Cal.$(Ca_{81}Mg_{19})$
S.end, Centre	D49-D51	12	0-12	major dol. minor cal.	Dol.$(Ca_{54}Mg_{46})$ Cal.$(Ca_{81}Mg_{19})$
Centre	S4-1 S4-29	29	0-29	Cal.and dol.	Cal.$(Ca_{81}Mg_{19})$
W.Edge, S.end	D53	8	0-8	Cal.and dol.	Cal.$(Ca_{88}Mg_{12})$ Dol.$(Ca_{55}Mg_{45})$

TABLE 2 (cont.)

Kingston Lake					
Centre	A78-6,7	4	0-4	Cal.and dol.	Cal. ($Ca_{91}Mg_9$) Dol. ($Ca_{56}Mg_{44}$)
W. Edge	D34-D41	6	0-6	Cal.and dol.	Cal. ($Ca_{91}Mg_9$) Dol. ($Ca_{56}Mg_{44}$)
Centre	S1-1 - S1-3	$1\frac{1}{2}$	$0-1\frac{1}{2}$	Cal.and dol.	Cal. ($Ca_{84}Mg_{16}$) Dol. ($Ca_{56}Mg_{44}$)
W. Edge	S2-1 - S2-10	5	0-5	Cal. and dol.	Cal. ($Ca_{77}Mg_{23}$) Dol. ($Ca_{56}Mg_{44}$)
W. Bank	S3-3 - S3-13	11	2-13	Cal.and dol.	Cal. ($Ca_{88}Mg_{12}$) Dol. ($Ca_{56}Mg_{44}$)
Kangaroo Island	-	0	0	Cal.	
Streaky Bay	-	2	0-2	Cal.	
Lake Eyre	-	20	132-152 or 11'-12'8"	Dol.	

DISTRIBUTION OF PIPE-CLAY

Carbonate pipe-clay has been found in many interdunal areas in the South East as well as on Kangaroo Island, in Lake Eyre and at Streaky Bay on Eyre Peninsula, South Australia. In order to give some idea of the distribution and carbonate composition of all the pipe-clay samples examined Table 2 accompanied by Fig.2 is presented. This is only a summary of the pipe-clay samples studied and more detailed descriptions of the individual samples will be found under the appropriate headings in the body of the text. In the text, samples other than pipe-clay have been discussed as well. For clarity, the discussion of samples is on the basis of geographic position rather than the mineralogy or chemistry of a sample. Each sample collected has been discussed in detail under the appropriate interdunal position. A compilation of all the data on each sample is presented as an Appendix.

From Table 2 it is apparent that few pipe-clay samples have been found in the interdunal areas, compared to the present Coorong and the lagoonal extensions south of it. Many samples were collected in the inland interdunal areas, but the pipe-clay often occurs below the surface soil cover and is not easily found. Therefore, studies of the pipe-clay have naturally centered on the Coorong and its lagoons. Not only are the deposits obvious but pipe-clay can be observed in active precipitation from the waters in this locality and hence the method of formation should be able to be assessed.

It is interesting that, with the exception of Lake Hawdon North, the interdunal pipe-clays contain mostly calcite with only very minor dolomite. Kingston Lake contains calcite and dolomite in about equal proportions and Lagoon M contains dolomite as the dominant phase. In the Coorong calcite is the dominant phase. The variation of the calcite/dolomite ratio and the possible reasons for it are discussed later.

The composition of the calcite is variable. There does not seem to be any distinct relation between locality and composition. Calcites from the interdunal areas show compositions from $Ca_{84}Mg_{16}$ to $Ca_{98}Mg_{2}$. Calcites from the Coorong and lagoons show compositions from $Ca_{77}Mg_{23}$ to $Ca_{91}Mg_{9}$. As a generality the calcites in the Coorong and lagoons are more magnesian-rich and the calcites in the process of forming today are the most magnesian-rich in the area.

It is also obvious that the pipe-clay in a particular interdunal area does not occur at a uniform depth below the surface, nor does there seem to be a uniform thickness. The first point may well be explained as due to later irregularities in the development of the soil and vegetation cover. The lack of uniformity of thickness is also apparent in the modern lagoons and Coorong, and is probably controlled by the rate of infilling of the lagoons by detritus and by the length of time that the precipitation process has been in operation in a given area.

The pipe-clay from Kangaroo Island came from an interdunal flat near the beach at Kingscote, and may have formed under similar conditions to the interdunal pipe-clays in the South East. The Kangaroo Island material was not collected by the author and its location and occurrence are known only by second hand verbal report. The material is white and plastic and in all respects similar to the South East pipe-clay. It is composed of magnesian calcite, clay minerals and halite. There is no dolomite present.

The pipe-clay from Streaky Bay, South Australia, was collected by Dr. A.W. Kleeman. Although not strictly an interdunal area, the locality is very low lying and may fill with shallow water during the winter months. It is in very close proximity to the sea. Again, the material has the same appearance and properties as the South East pipe-clay. It is also composed of magnesian calcite, clay minerals and halite, but no dolomite is present.

In Lake Eyre, Bonython (1956) found a pipe-clay layer consisting of dolomite with impurities from 11 feet to 12 feet 8 inches below the surface of the lake. X-ray examination of the pipe-clay showed that besides the dolomite, quartz, illite, kaolin, palygorskite and gypsum were present.

It is probable that modern carbonate pipe-clays will be found to be widespread. Neither the occurrence studied nor those mentioned from Kangaroo Island, Streaky Bay or Lake Eyre will form large limestone or dolomite deposits when indurated. The particular environment studied: shallow water, possibly intermittently filled bays and lagoons, certainly is not conducive to the formation of massive and extensive carbonate deposits. Therefore, although the pipe-clay is of interest as a modern sediment it is unlikely that it can be directly related to any very extensive deposits of a similar composition in the past. The main interest in studying the pipe-clays is to define the precipitates and the conditions of precipitation accurately. In the present study an attempt has been made to accurately define the precipitates.

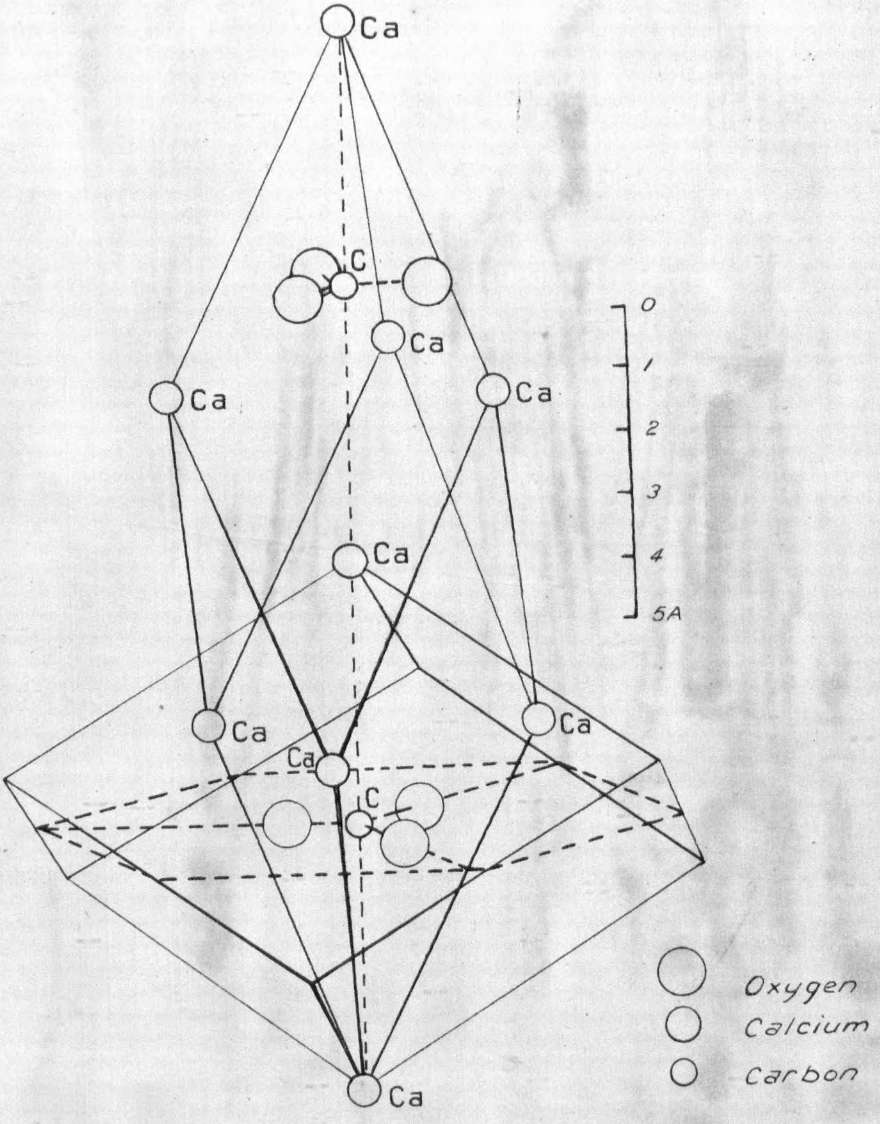


Fig. 3 *Unit cell of Calcite*

THE ELONGATE CELL IS THE TRUE UNIT CELL. THE SQUAT CELL IS THE CLEAVAGE RHOMB.

CRYSTAL CHEMISTRY

Before entering on a more specific discussion of the pipe-clay sediments from the South East of South Australia it was thought necessary that pertinent background be given. Therefore, the following section contains a summary of the crystal chemistry of the carbonate minerals, calcite and dolomite, and the methods and results of previous investigations in the study of fine-grained carbonate sediments. Utilizing this data the South East pipe-clay deposits can be brought into perspective with the recent experimental work on the Ca-Mg-CO_3 system. Following the summary of the crystal chemistry, the methods of investigation used in this study are briefly described.

Structures of Calcite and Dolomite

Calcite and dolomite are calcium and calcium-magnesium carbonates respectively with rhombohedral symmetry. The symmetries of the rhombohedral carbonates are usually referred to the cleavage rhombs even though Schiebold (1919) showed that the simplest (unit) cell of calcite is an elongated rhomb. Fig.3 gives the relation between the true or unit rhomb cell and the cleavage rhomb cell. Miller indicies used in this paper refer to the true rhomb cell as given by Bradley, Burst and Graf (1953).

The cleavage rhomb of calcite may be thought of as a distorted cube with a three fold axis vertical. Using this property, the calcite structure can be demonstrated by analogy. Starting with the cubic NaCl structure and replacing the Na atoms by Ca atoms and the Cl atoms with CO_3 groups, the planar CO_3 groups cause a compression of the cube along the three fold axis resulting in a rhombohedron. The (111) planes are populated alternately by CO_3 groups and cubic closest packed Ca atoms. Each CO_3 group lies half way between upper and lower groups of three Ca atoms. O atoms lie on the two fold symmetry axes which intersect in the C atom. A three fold screw axis passes through the Ca atom in the (111) direction. A (101) glide plane with a translation of c/2 completes the symmetry picture of calcite placing it in the space group $R\bar{3}c$.

Bragg (1937) suggested that dolomite had a structure very similar to calcite except that every other (111) plane of Ca atoms was replaced by a plane of Mg atoms. Bragg's suggestion is correct and causes a symmetry reduction. The ordered substitution of Ca planes by Mg planes and not random substitution of Mg in Ca positions is responsible for the unique dolomite structure. The succession along the (111) direction in dolomite is Ca, CO_3, Mg, CO_3 . . . compared to Ca, CO_3, Ca, CO_3 . . . for calcite. The non-equivalence of the Ca and Mg atoms in the structure removes the two-fold symmetry axes and the glide plane causing the space group of dolomite to degenerate to $R\bar{3}$.

X-ray powder diffraction patterns of calcite and dolomite are very similar. However, the ordered substitution of Mg for Ca in the dolomite structure and the consequent symmetry reduction causes additional reflections not found in the powder pattern of calcite, namely: (100), (221), and $(1\bar{1}1)$. True structural dolomite $(R\bar{3})$ with ordered Ca and Mg can be differentiated from calcite containing 50% $MgCO_3$ in solid solution, where Ca and Mg are disordered, by the presence of the dolomite ordering reflections in X-ray diffraction patterns.

Polymorphs of $CaCO_3$

$CaCO_3$ is trimorphous. Aragonite is an orthorhombic polymorph and vaterite, so far found naturally only in certain gastropod shells, is probably a hexagonal polymorph (Olshausen 1924-25). The calcium ion has a radius of 1.06Å in the $CaCO_3$ polymorphs. The ionic size of Ca is such that calcium carbonate readily forms either of the polymorphs calcite or aragonite. Cations with a larger ionic radius than 1.06Å form orthorhombic carbonates of the aragonite type. The carbonates of Sr, Pb and Ba are of this type. Cations with an ionic radius less than 1.06Å form carbonates of the calcite type, and have rhombohedral symmetry. The carbonates of Mg, Fe, Zn, Mn, Cd are of the calcite type. Very little is known of the crystallography or of the occurrences of vaterite, and it has not been possible to satisfactorily account for its formation. From crystallochemical data there does not seem to be any reason for vaterite to form as a stable phase.

Solid Solution in Calcite

The calcite structure often takes other ions into solid solution. These foreign ions cause the unit cell to either expand or contract depending on their ionic radius. The ions of large ionic radius, Sr, Ba and Pb, enter the calcite structure in very limited amounts. The small amounts of these large ions that do enter the calcite structure cause the unit cell to expand and hence favour the formation of the more open aragonite structure. For this reason Sr, Ba and Pb tend to concentrate in aragonite (Graf and Lamar 1955). Small ions such as Mg, Fe, Zn, Mn, and Cd tend to be concentrated in the calcite structure. All of these elements form extensive solid solutions with calcite and all of them cause the unit cell to decrease in size. Zn and Cd are not often associated geochemically with calcite so one does not have to worry about their presence in most calcites. Mg, Fe and Mn, however, are often associated with calcite in nature and one must always look for them in dealing with calcite or dolomite deposits.

The change of unit cell dimensions in the calcite structure can be detected very accurately by measuring shifts in the interplanar spacings (d spacings) as recorded in X-ray powder diffraction patterns. Many investigators have related the magnitude of the change in d spacing to the amount of foreign cation in solid solution. To measure the change in unit cell dimensions the strongest reflection of the rhombohedral carbonates is usually selected. The (112) reflection

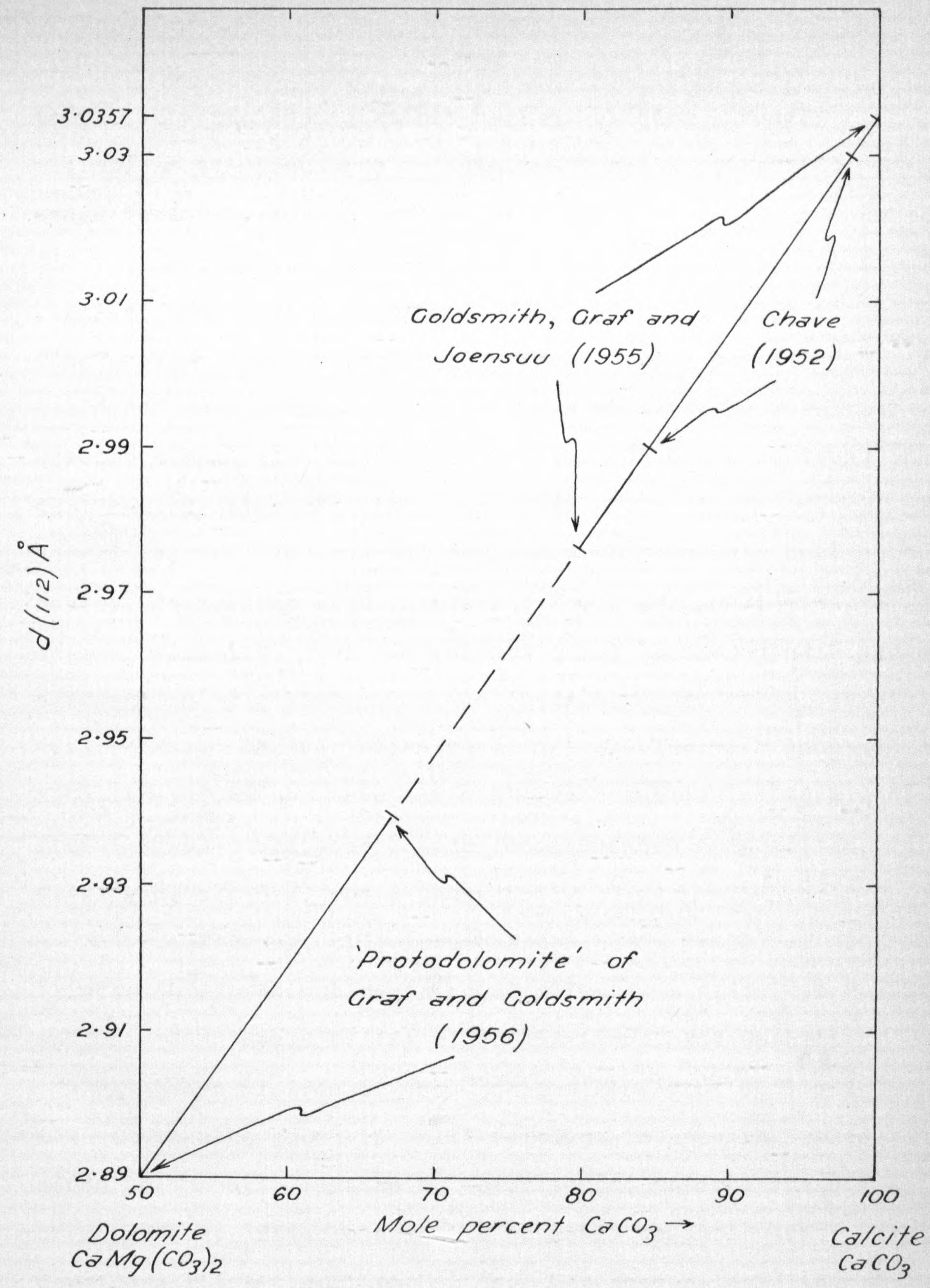


Fig. 4 Relation of d(112) and composition of calcite and dolomite

is not only the strongest reflection but also strongly influenced by variations in both the a and c axis directions and accordingly is most suitable.

Chave (1952) chemically analysed the calcitic hard parts of many living organisms and found up to 29 wt.% (34.2 mol.%) $MgCO_3$ in solid solution. From 2 to 16% by weight of $MgCO_3$, Chave found a linear relation between the calcite composition and d(112). Above 16% $MgCO_3$ he found that the relation deviated from linearity. Spotts (1952) correlated decreasing d(112) spacings of some West Australian coastal carbonates with increasing $MgCO_3$ up to 10.36 wt.%.

Goldsmith, Graf and Joensuu (1955) constructed diagrams relating Mg substitution for Ca in calcite to several crystal reflections. The variation in d(112) spacing with increasing $MgCO_3$ they found to be a straight line function, (Fig.4). Linear relationships were also found between composition and d(521), d(663, 552) and d(444).

Spectographically pure calcite has a d(112) of 3.0357Å (Birge 1941). Stiochiometric dolomite has a d(112) of 2.890Å and magnesite has a d(112) of 2.745Å (Graf and Goldsmith, 1955). Extrapolation of the straight line plot obtained with increasing $MgCO_3$ in solid solution in calcite passes close to the d(112) value of dolomite and through the d(112) of magnesite. This relation is possibly coincidental considering the structural differences between calcite and dolomite.

The a and c axis values of calcite, dolomite and magnesite also fall on straight lines when plotted against composition. Graf and Goldsmith (1955) have shown however that extrapolation of the straight line functions of the a and c axis values of Mg rich calcites deviates considerably from the ideal a and c axis curves at high Mg concentrations. This suggests that in the high Mg content calcites the contraction of the a and c axes is not uniform. Graf and Goldsmith also examined Chave's (1952) work and found that the deviations from linearity of d(112) at high Mg values were unreal and that in fact a linear function did occur. Since calcite is rhombohedral they concluded that the linear relation between d(112) and composition in calcite arose as a consequence of the unequal axial contraction. Further, the "fortuitous" linear relation passing close to the d(112) of dolomite is also a consequence of the inclination of the (112) plane to the a and c axes.

Solid Solution in Dolomite

Substitution of Fe, Mn, Co, Pb, Zn, and Cd may occur in the Mg positions in the dolomite structure and less commonly Fe and Mn may substitute in the Ca position (Palache, Berman and Frondel, 1951).

Wyckoff and Merwin (1924) substituted Fe for 30% of the Mg positions in dolomite wihout detecting a change in cell size greater than the experimental error in their relatively crude equipment. However, Zen (1956) plotted five analysed dolomites on a triangular diagram of $CaCO_3$-$MgCO_3$-$FeCO_3$ and demonstrated a relation between composition, ordinary index of refraction and d(112). One dolomite with only 48 mol.% $CaCO_3$ compared to 51% $CaCO_3$ for the other samples gave the smallest d(112) spacing. Thus, although the change in the d(112) spacing with change in composition is small Zen demonstrated a real shift with composition change.

Mg substitution in calcites in equilibrium with dolomite has been determined experimentally at high temperatures and pressures. Graf and Goldsmith (1955) suggest from their work that a slight but real excess of Ca is present in dolomites in equilibrium with magnesian calcites at high temperatures. The amount of excess Ca which can be tolerated without a loss of the ordering reflections is not known. Approximately 5 mol.% $CaCO_3$ in excess of stoichiometric proportions was found in low-temperature dolomites from some western Pacific Islands (Graf, personal communication 1957). These high Ca dolomites showed a weakening of the ordering reflections relative to the other reflections. Also, c axis reflections and especially the high angle c axis reflections tended to be smeared out toward higher 2θ values (lower d spacings), while the a axis reflections remained relatively sharp. Graf further observed this smearing out of the reflections in single crystal work on small crystals of Ca-rich dolomites, while similar studies on stoichiometric dolomite did not show the effect. The effect therefore is not one of grain size but is related to the structure. The explanation is that a range of periodicities exists along the c axis of the dolomite analogous to mixed layer stacking in clays. As discussed previously, stoichiometric dolomite has a repetition along the c axis of Ca-Mg-Ca-Mg. The non-stoichiometric Ca-rich dolomites may have a number of different stacking arrangements and these arrangements give rise to the asymmetry of the c axis reflections.

Graf and Goldsmith (1956) have produced a low temperature "protodolomite" from Ca-Mg carbonate gels, and the "protodolomite" contained more Ca than stoichiometric dolomite. They called the material "protodolomite" because it had the composition of dolomite and the X-ray diffraction spacings of dolomite but lacked the ordering reflections necessary to define the ordered structure. The composition was not that of pure dolomite but was about $Ca_{60}Mg_{40}$ although material as high as $Ca_{67}Mg_{33}$ was obtained. The composition was found by measuring the d(112) value and assuming linearity with composition.

Summary of the Crystal Chemistry

In the foregoing discussion it has been satisfactorily established that a linear relation exists between composition and d(112) for magnesian calcites where the substitution of Mg for Ca takes place in a random or disordered fashion. It is also well established that dolomite does depart from stoichiometric proportions of Ca and Mg. The effect of Ca substitution for Mg in the dolomite lattice is to reduce the intensity of the dolomite ordering reflections in X-ray photographs, and also to increase the lattice parameters. The true relation between dolomite composition and d(112) is not known. As discussed in detail previously a straight line function obtained by projecting the magnesian calcite function through dolomite is a possible function with a high degree of accuracy. This straight line function has been used in the present study and it is ~~not~~ believed that any deviations from linearity which may exist are insignificant.

For the sake of clarity and expediency in this discussion, a system of formula presentation has been adopted for magnesian calcites and calcian dolomites. The molar percentage of each carbonate fraction is recorded. Thus $(Ca_{80}Mg_{20})$ means magnesian calcite containing 20 mol.% $MgCO_3$ and 80 mol.% $CaCO_3$. The brackets show that the calcium and magnesium ions have structurally equivalent positions in the lattice and hence that Mg is present as a solid solution. On the other hand, the formula $Ca_{50}Mg_{50}$ indicates a dolomite containing 50 mol.% $CaCO_3$ and 50 mol.% $MgCO_3$. The absence of brackets around the formula indicates that the calcium and magnesium ions do not have structurally equivalent positions.

CRYSTAL CHEMISTRY OF CARBONATES IN PIPE-CLAY

Pipe-clay from the South East of South Australia is almost entirely composed of carbonates with a grain size about one micron. The very fine grain size precludes the use of optical methods to study their compositions. Staining techniques have also been tried and found unsuccessful because of grain size and lack of coherence of the samples. X-ray powder diffraction and electron microscope techniques are the only methods useful for handling such fine-grained material and of the two methods, X-ray powder diffraction yields by far the most data.

Bulk chemical analyses of a number of pipe-clay samples reported by Alderman and Skinner (1957) are presented in Table 3. The analyses show that Ca, Mg and CO_2 are the major components. Silica and alumina are contained in the quartz and clay contaminants. The sulphate is accounted for by the presence of gypsum and celestite. The ferric iron is present partly as goethite, although in the Kingston Lake samples no separate iron mineral has been identified. Ferrous and ferric iron were not separately determined in the samples and it is impossible to say what proportion, if any, of the iron present occurs as ferrous iron in the carbonate structure. Since the amount is very small anyway, and since actual iron bearing minerals have been demonstrated in some samples, it is considered safe to assume that the carbonates are iron-free in determining their compositions by X-ray powder diffraction. Manganese has not been detected in these or

TABLE 3

Composition of carbonate sediments

	A78.1	A78.17	D.41	D.45	USE 7-4	W 6-4
SiO_2	8.24	6.86	19.42	29.00	17.24	54.34
Al_2O_3	1.11	1.21	1.21	2.28	1.19	13.92
Fe_2O_3	0.81	0.29	0.25	0.40	0.43	4.44
CaO	28.61	34.77	28.61	31.78	30.70	3.11
TiO_2	-	-	-	-	-	0.56
MgO	10.64	11.22	9.42	1.34	10.83	3.75
CO_2	33.26	39.39	32.50	26.05	35.90	6.43
SO_3	1.46	0.27	0.43	0.63	0.02	0.19
NaCl	7.88	1.01	4.29	5.18	0.07	0.48
Total Water	5.64	2.67	1.84	2.26	2.96	12.06
Acid Insoluble Organic Matter as Carbon	1.28	0.34	0.17	0.57	0.42	0.59
	98.93	98.03	98.14	99.49	99.76	99.87

SAMPLE A78.1	10 miles south of Salt Creek (Coorong). Surface layer.
SAMPLE A78.17	Lake Hawdon North. 12 to 18 inches depth.
SAMPLE D.41	Kingston Lake. 1½ to 6 inches depth.
SAMPLE D.45	Kingston Lake. 33 to 36 inches depth.
SAMPLE USE 7-4	Kercoonda. 4 to 7 inches depth.
SAMPLE W.6-4	Bool Lagoon. 24 to 36 inches depth.

any other samples and hence can be ignored in the discussion of composition.

Most pipe-clay samples contain two carbonate phases. The fine grain size precludes any attempt to physically separate the two carbonates so the only possible method of determining the composition of the carbonates is to measure their lattice parameters and use the data already outlined. The d(112) value is easily determined since the (112) reflection is the most intense reflection for both calcite and dolomite.

Pipe-clays contain magnesian calcite or magnesian calcite and calcian dolomite. A third carbonate phase is always present in the form of shell fragments. This impurity makes it impossible to determine the composition of the carbonates or to make accurate predictions from the bulk analysis of the pipe-clay, for it has proven impossible to obtain a completely shell free sample. The shell fragments can be readily separated by means of X-ray powder diffraction however, since, they have a different composition from the precipitated magnesian calcite, and hence have a different d(112) from the precipitated calcite. The difference is sufficiently large that the two diffractions can be easily resolved. The intensity profiles of pipe-clay samples from Kingston Lake given in Fig.11 show the three distinct carbonate phases to which the writer refers. This figure illustrates more clearly than any verbal description the method of distinguishing the shell calcite from the precipitated calcite and dolomite.

Calcian Dolomite in Pipe-clay

The dolomite present in pipe-clay is true structural dolomite. In samples where dolomite predominates over calcite the ordering reflections of the dolomite can be clearly seen on X-ray powder diffraction patterns. (See Fig.6). Graf and Goldsmith's (1956) experimental work suggested that "protodolomite" might form by low temperature precipitation. In the South East of South Australia this is definitely not the case.

Stoichiometric dolomite, having a Ca:Mg ratio of 1:1 has a d(112) of 2.890Å. The dolomites in the South East pipe-clays all have a d(112) greater than this. The most usual d(112) is 2.91Å. The structure expansion, of which this larger d(112) value is an expression, is almost certainly due to solid solution of $CaCO_3$ in the dolomite. Theory predicts that when a solid solution of this type occurs there should be a reduction of the intensity of the ordering reflections. Unfortunately, the X-ray powder patterns obtained from the pipe-clays are not clear enough to demonstrate this point. A d(112) of 2.91Å corresponds to a 6 mole percent excess $CaCO_3$ in the dolomite structure. This value was determined on Graf and Goldsmith's straight line function for composition versus d(112) and is subject to the reservations previously outlined for calcian dolomites.

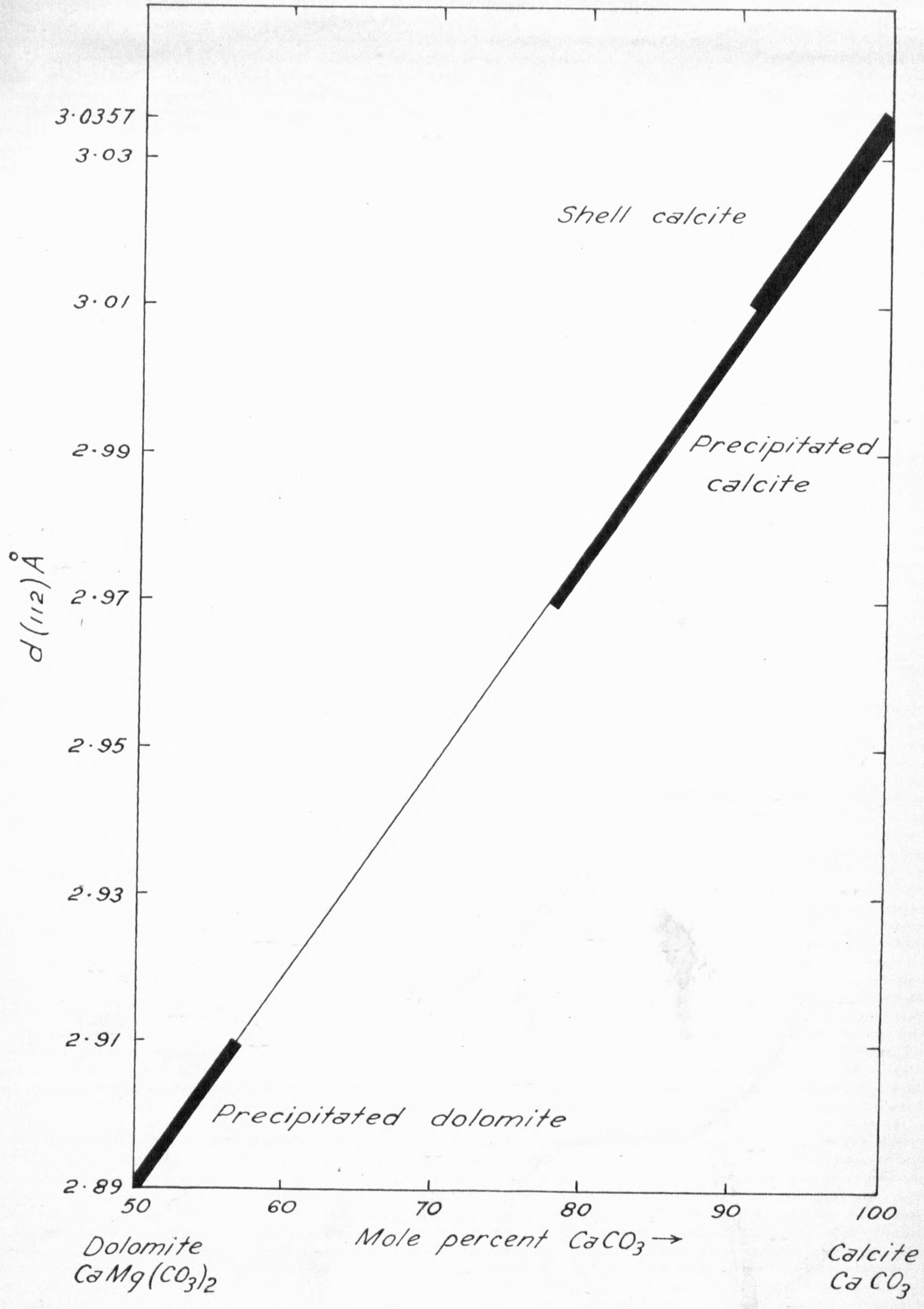


Fig. 5 Composition variation of the carbonates in pipe-clay

Magnesian Calcite in Pipe-clay

Every sample of precipitated calcite examined contains $MgCO_3$ in solid solution and hence should be called magnesian calcite. The d(112) value of pure calcite is 3.0357Å. Any random replacement of Ca by Mg reduces this value, as discussed previously, and provides an accurate measure of the extent of replacement.

In the pipe-clays examined the magnesian calcite had a range of d(112) values from 2.97Å to 3.03Å, corresponding to a composition range of $(Ca_{78}Mg_{22})$ to $(Ca_{98}Mg_2)$.

The calcite in the shell fragments is considerably less magnesian than in the precipitated calcite. Shell calcite has a d(112) range of 3.01Å to 3.04Å corresponding to a composition range of $(Ca_{91}Mg_9)$ to $(Ca_{100}Mg_0)$. By far the largest proportion of the shell calcite has a d(112) of 3.04Å. These figures cannot be considered as highly accurate however, since detailed studies were not carried out on the shell material.

Fig.5 illustrates diagrammatically the composition range of the magnesian calcite, calcian dolomite and shell calcite found in the pipe-clays examined.

Asymmetry of X-ray diffraction profiles

Intensity profiles of the (112) reflections have been made for the carbonates in the pipe-clay samples (see Chapter VII). In many cases the (112) reflections have broad and asymmetric profiles. The broadening of the profiles of both calcite and dolomite is probably a particle size effect (Klug and Alexander, 1954). The broadness and position of the profiles is such that in cases where both magnesian calcite and calcian dolomite are present the profiles overlap and interfere with each other. The profiles are asymmetric toward each other, i.e. the dolomite profile is asymmetric toward lower θ angles and the calcite is asymmetric toward higher θ angles. Graf, Blyth and Stemmler (1957) have found asymmetry in dolomite profiles toward higher θ angles. They demonstrated this to be due to various stacking sequences of the Ca and Mg planes. In the South East pipe-clays the dolomites have not been observed asymmetric toward higher θ angles but this may partly be a limitation in the method of investigation. Magnesian calcite, when found as a pure phase, does not appear to show an asymmetric profile (Fig. 7, No. 21). This suggests that the asymmetry is at least partly due to mutual interference of the two carbonate reflections and lack of resolution in the method.

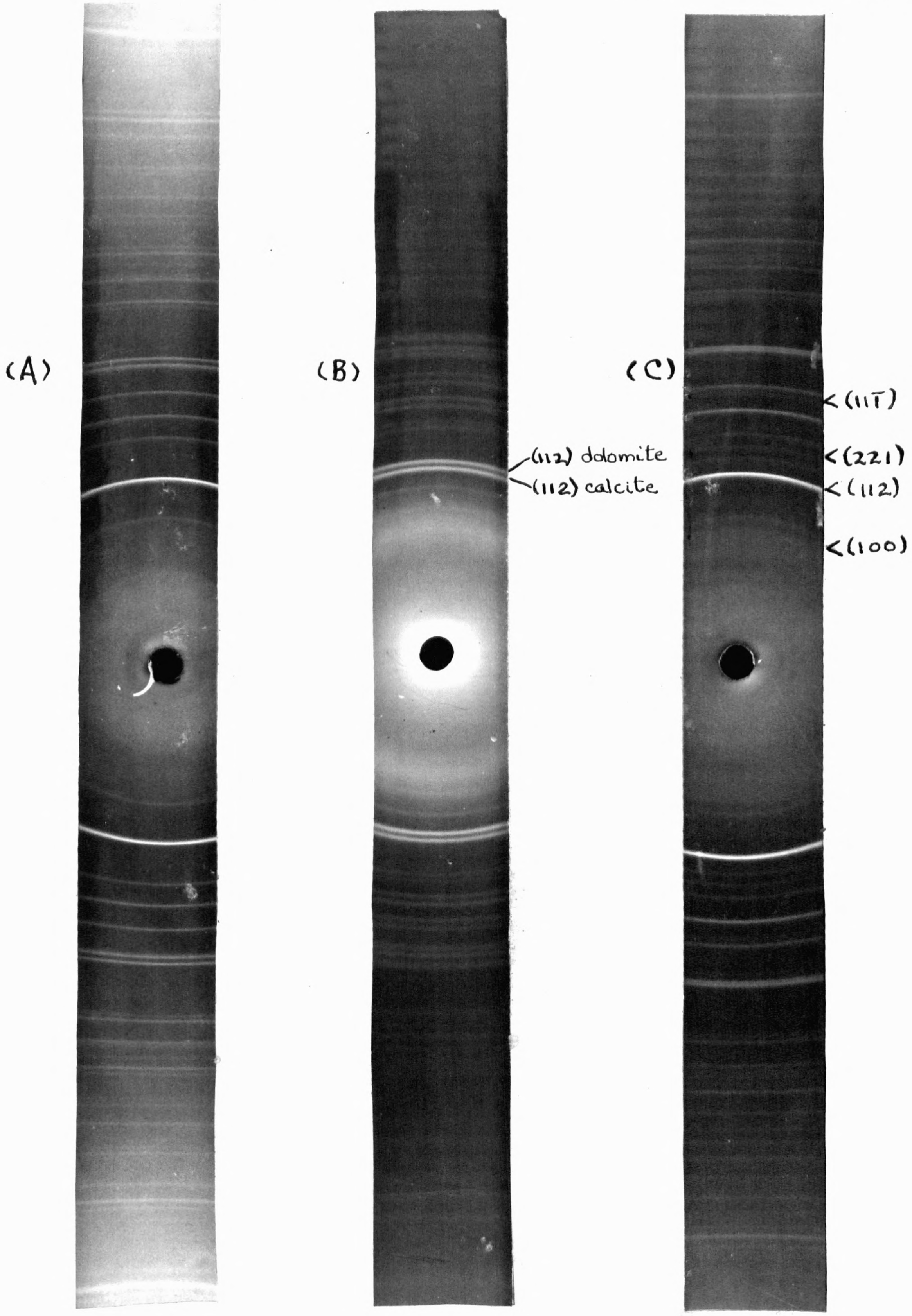
Another possible cause for asymmetric profiles is the presence of a reflection from another mineral which might fall in between the two carbonate reflections. One to three percent celestite has been identified in the pipe-clay samples. Two equally strong reflections from celestite are found at 2.97Å and at 3.295Å. The 3.295Å reflection, which occurs in such a position that it is not interfered with by carbonate reflections, is easily detected. In intensity profiles of the pipe-clay samples which contained the minor celestite, the 3.295Å reflection could not be detected above background. It is doubted, therefore, that the asymmetry of the profiles of most of the carbonate samples can be ascribed to the presence of the strong reflection of celestite at 2.97Å. Montmorillonite, which has been identified in a number of samples can also have a strong reflection lying between the (112) reflections of calcite and dolomite. The strength and position of the montmorillonite reflection depends on many factors, but primarily on the absorbed ions. Any concentration process whereby the carbonate minerals are removed by acid leaching and the montmorillonite separated for study, greatly affects the montmorillonite. The montmorillonite reflection will not be observed in the same place, nor with same intensity in the concentrated sample. It is possible then that the asymmetry of the carbonate profiles is partly due to interference of a reflection from a clay mineral. This suggestion is certainly substantiated for samples collected near the edge of Kingston Lake (Bore Hole S3, see Fig.10) where the montmorillonite content is so high that it is barely possible to separately resolve the individual carbonate reflections.

A further explanation for the observed asymmetry is that the pipe-clays may not contain carbonates of definite composition and that a range of compounds exist that are not evenly distributed about the dominant composition. This does not appear to be the case however, since the effect would be most obvious where one of the carbonates greatly predominated over the other. When one of the carbonates is present in much greater quantities than the other the effect is least marked. The only possible explanation for the asymmetry of the carbonate (112) reflections then is the mutual interference of two adjacent peaks. The presence of other minerals than carbonates is a contributing but minor effect.

The nature of the pipe-clay samples is such that very accurate results are not obtainable. The methods of study and their limitations are discussed below.

Fig. 6

X-RAY POWDER DIFFRACTION PHOTOGRAPHS OF (A) CALCITE, (B) DOUBLE CARBONATE PIPE-CLAY SAMPLE D17 AND (C) DOLOMITE.



X-RAY METHODS

Two methods of recording X-ray powder diffractions patterns were used in this study. For identification of all the phases present and for all general work, X-ray powder diffraction photographs were made. Either 57.3 or 114.57 mm. diameter powder cameras were used throughout. Co K_α and Cu K_α radiations were used for irradiating the samples. Samples were prepared for photography by rolling out a 0.05 mm. diameter spindle of the sample mixed with flexible collodion.

Since film is especially sensitive in recording weak reflections, powder photos were used for picking up the ordering reflections of dolomite. Fig.6 shows X-ray powder photographs of a dolomite-rich pipe-clay, a pure calcite and a pure dolomite. The dolomite ordering reflections are marked with arrows. From these films the broad nature of all the reflections in the pipe-clay film can be seen. It is obvious that accurate measurement on pipe-clay films is almost impossible. The d(112) reflections of calcite and dolomite were measured with a Hilger and Watts Rule no. L.85. The measurements were corrected for film shrinkage by using quartz as an internal standard. The accuracy of the measurement is ± 0.01Å.

The second method used, an X-ray high angle goniometer or Diffractometer, made it easier and more convenient to measure the d(112). This method uses a Geiger counter to record the diffracted X-rays and give a measure of the intensity of the diffracted beam. The instrument used was the Philips High-angle Goniometer owned by the C.S.I.R.O. Soils Division.

Samples were prepared by pressing the material into the aluminium holders supplied with the machine. As a check on the machine alignment and on the accuracy of measurement, a quartz sample was prepared in the same manner as the pipe-clay samples and the $(10\bar{1}1)$ reflection measured. The $d(10\bar{1}1)$ of quartz is known with great accuracy (Keith, H.D., 1956), and since the reflection is very sharp a good estimate of the accuracy of measurement can be obtained. The corrections were never more than 0.01° 2θ. The nature of the reflections given by the pipe-clay samples does not warrant the use of internal standards as the individual reflection positions cannot be reproducably measured to better than $\pm$ 0.01° 2θ. The pipeclay samples were run at a goniometer rotation of $1/8^\circ$ 2θ per minute, a chart speed of 5 mm. per minute, a time constant of 10 and a counting rate of 300 counts per second. When the intensity of a particular reflection was greater than this a 0.002 or 0.004 Al foil was inserted in the path of the X-ray beam to reduce the intensity. A diffractometer record from 33.5° 2θ to 36.5° 2θ was sufficient to bracket the d(112) reflections of calcite and dolomite.

Intensity measurements of the X-ray reflections can be used to determine the amounts of phases present in mixtures. Where only two major phases are present, graphs can usually be drawn relating amount of phase present to intensity of an individual reflection. A great deal of time and effort was expended in trying to develop this method for determining the relative amounts of dolomite and calcite in pipe-clay. The work was unsuccessful for two reasons. The first reason is the interference between the calcite and dolomite d(112) reflections. Since it is necessary to determine the total intensity of each reflection by measurement of the area under the profile, any interference increases the uncertainty. Secondly, a peculiar mechanical effect appears when pure dolomite is finely ground. This effect reduces the intensity as the grain size is reduced. This anomaly has not been explained and is still being investigated. It is not possible to get satisfactory calcite to dolomite ratios in pipe-clay samples because of the reflection interference and accordingly this line of attack was abandoned. However, it is possible to estimate roughly from the peak heights the relative amounts of the two carbonates. From experimental work it appears that the intensity of the dolomite (112) reflection is approximately equal to the (112) reflection intensity of calcite. Therefore, it is possible to estimate in a general way, the relative proportions of calcite and dolomite present in pipe-clays.

The usual method of measuring the angular position of a reflection from the intensity profile is to determine a number of midpoints along the profile and project the line connecting the points to the background intensity. This method was not entirely practical for the broad asymmetric profiles of the pipe-clay carbonates. Where asymmetry is present only the top half of the profile was considered to be free from interference, and hence only the top half of the profile was used for measuring angular positions. The projection of the mid-point line to background was carried out as usual and this point on the background drawn vertically down to the degree markings on the chart. The angular position of the profile could then be read directly.

Sometimes the profiles were so poorly resolved that even the simplifications discussed above were unreasonable. In these cases measurements were not attempted.

DESCRIPTION AND DISCUSSION OF INDIVIDUAL SAMPLES

The following chapter is a detailed discussion of all the samples studied. It has been broken down into sub-headings as follows. Firstly, samples collected prior to the present study by Professor Alderman and Dr. B.G. Forbes. Secondly, samples from interdunal areas in the lower South East. Thirdly, samples from the interdunal areas in the upper South East. Fourthly, samples from the Coorong and associated lagoons. Finally, samples of pipe-clay collected in the process of precipitation.

Samples Collected Prior to the Present Study

The original pipe-clay samples, which essentially initiated the present study, were collected by Professor A. R. Alderman and Dr. B.G. Forbes in 1955. Dr. Forbes (1955) gave general descriptions and rough bulk chemical analyses for these samples in his thesis. The A-78 series (University of Adelaide, Accession Series) samples were studied further in the present investigation using X-ray diffraction techniques. The following section is a summary of these studies.

A78-1 and A78-35 are surface samples from the southern Coorong which contain calcite and dolomite. Other samples such as A78-2 and A78-36 contain only calcite while A78-37, from a roadside lake five miles southeast of the Causeway is pure gypsum. The variable character of materials called "pipe-clay" is demonstrated very well by this series of samples.

Two very interesting bore holes were made at the same time as the surface samples were collected. One of the bores was put down in the lagoon 10 miles north of Kingston, now called Kingston Lake and the other bore was in Lake Hawdon, well to the south of Kingston Lake.

The bore hole in Kingston Lake had a depth of 29", although only a few inches of the profile were pipe-clay. The surface sample (0-2") A78-6 contains dolomite, $Ca_{56}Mg_{44}$ as the dominant mineral, a small amount of magnesian calcite ($Ca_{91}Mg_{9}$), minor shell calcite, celestite and quartz. A fine fraction floated off this material in water gave an excellent diffraction pattern of almost pure dolomite which allowed the ordering reflections to be clearly seen. A78-7 (2-4") also showed dominant dolomite. However, A78-8, 9 and 10 (4-20") which are really shelly quartz sands rather than pipe-clay, showed only a trace of dolomite but considerable magnesian calcite with a composition of ($Ca_{95}Mg_{5}$). At the bottom of the bore hole (27-29") sample A78-13 is a grey sand and dolomite is definitely not present. Calcite ($Ca_{95}Mg_{5}$) is the only carbonate mineral present. It is possible that the calcite ($Ca_{95}Mg_{5}$) is in fact fine shell material. However, detailed work has not been done to elucidate this point.

The bore hole in Lake Hawdon North showed a much thicker section of pipe-clay in the 77 inches of its depth. The surface (0-2") pipe-clay sample, A78-15 contains only a trace of dolomite but contains a dominant magnesian calcite with a composition of ($Ca_{84}Mg_{16}$) and a d(112) of 2.99Å. An intensity profile showed the (112) reflection to be asymmetric towards high 2θ angles, but at least some of the asymmetry is due to the presence of celestite. The next three pipe-clay samples in the hole, A78-16, 17 and 18 (2-18") contained dolomite $Ca_{56}Mg_{44}$ with a d(112) of 2.91Å as the dominant carbonate mineral. These three samples contained a smaller amount of magnesian calcite, minor shell calcite, celestite and quartz. An intensity profile from A78-17 showed the dolomite (112) reflection to be very sharp but the lower portion of the profile was interfered with by the celestite and magnesian calcite reflections. Sample A78-19 (18-24") contained no dolomite but contained abundant calcite with a composition of ($Ca_{95}Mg_{5}$) and a d(112) of 3.02Å. Dolomite however, was found in A78-20 (24-30"). The X-ray diffraction photograph of this sample showed sharp dolomite reflections and broad magnesian calcite reflections. A78-22 (30-39") and 23 (39-42") do not contain any dolomite. Samples A78-24 - 31 contained only calcite and graded from dark grey pipe-clay to a brown clay which gave off a smell of H_2S.

From the study of these preliminary samples further collecting in the Coorong and other interdunal areas in the South East of South Australia was undertaken to establish the extent of the carbonate pipe-clay deposits. By far the bulk of the pure pipe-clay on the surface is in the Coorong and in the lagoons to the south of it. However, pipe-clay has been collected below the present surface in other areas and many places were sampled where presumably precipitated carbonates have been contaminated by wind and water borne impurities.

Fig.1 which is a map of the South East Province should be referred to as all the samples discussed are located on the map. The map will be found in a pocket at the back.

Samples Collected from Interdunal Areas in the Lower South East

Not all carbonate bearing samples collected in the interdunal areas in the South East can be called pipe-clay in the sense that the Coorong deposits are pipe-clay. Many samples contain calcite and/or dolomite in minor amounts. The dominant minerals are frequently quartz and clays. It is believed that the carbonates present in these samples may have formed in the same manner as the pipe-clay carbonates and hence should be included in this discussion. It is probable that carbonate-poor samples represent a later stage in the lagoonal history when wind and water borne clays and sands and organic matter from plants growing in the lagoons were filling the lagoons at the same time as the carbonates were precipitated. An interdunal bore-hole will often reveal a soil containing minor carbonates, perhaps up to 20% of the whole, below which is a dark grey, quartz-rich clay material containing fine-grained carbonates. The grey clay layer generally grades into a lighter grey and more carbonate-rich layer at depth. Eventually this clay material will contain sufficient carbonate (greater than 80%) to be called pipe-clay. Secondary kunkar is often encountered at depth and this increases the difficulty of getting satisfactory samples of the primary carbonates.

The process of contamination of pipe-clay carbonates can be observed at the margin of the modern Coorong and lagoons to the south of the Coorong. Plants which can tolerate continuous inundation grow out from the bank and stabilize the surface. They provide the necessary conditions to start the formation of a true soil. They not only supply organic matter to the soil but also act as collecting blanket for wind blown material. Pipe-clay collected from the margin of Kingston Lake sometimes contained as much as 20% clays and quartz while material from the centre of the lagoon contained only 2 or 3% extraneous material. This marginal region is only intermittently flooded and naturally the intensity of carbonate precipitation is much reduced here compared to the lagoon proper.

In general, the accurate compositions of carbonates occurring in samples consisting largely of quartz and clays were not determined. It was felt that the large amount of ions other than Ca and Mg present, especially Fe, precluded the use of X-ray data based on a two component system of Ca-Mg carbonates to determine the composition of the carbonates. Although Fe may not be present in the carbonate minerals it cannot be proved. The discussion therefore will mention the carbonate phases in the quartz sands and clays but will be more concerned with the true pipe-clay that has been discovered in depth in the interdunal areas.

Sub-section headings in this part of the thesis refer to the interdunal areas delineated by Sprigg (1952). Starting with the most easterly and probably the oldest interdunal area and working west towards the present sea stand I shall first discuss those samples collected at or below the Naracoorte-Kingston train line. South of this train line is considered the lower half of the South East province.

(a) Naracoorte-(Harper, Stewart, Cave) Range Interdunal Area

Bore-hole W1, on the Naracoorte Creek, 2.4 miles west of Naracoorte on the main road, showed two feet of brown and red clay. The clay contained about 30% calcite with a d(112) of 3.04Å indicating that little or no magnesium carbonate is present in solid solution. Over the next three feet the clay becomes more carbonate rich. The sediments become lighter grey in colour with depth until at four feet a very light grey pipe-clay occurs. The pipe-clay is a single carbonate phase; a calcite with a d(112) of 3.01Å indicating a possible composition of $(Ca_{91}Mg_9)$.

Bore W2 was taken in the same interdunal area as W1, at the edge of a swamp. The top 18 inches of W2 was a dark brown highly fossiliferous soil containing large shells and a great deal of plant material. The calcite in the sample appeared to be almost pure calcite. Below the 18 inch soil layer the sample became lighter in colour due to a larger content of quartz. Only clay minerals, quartz and a little calcite from fine shelly material were identified on X-ray diffraction photographs. White nodules were occasionally found in the lighter grey lower levels. The nodules were made up of quartz grains cemented with calcite and are presumably secondary kunkar type nodules.

Bore W6 was taken 13 miles south of W2 in Bool Lagoon. Bool Lagoon fills with water from winter rainfall and about 16 square miles of low lying swamp may become inundated. W6 was taken on the south-western corner on the lagoon which is flooded every year since it is the lowest part of the lagoon. The ground was saturated and moss growing on the surface made it spongy underfoot. Black soil with small white calcite nodules formed the upper 6 inches of the bore sample. From 6 to 24 inches a fine-grained light grey soil was found and this material can properly be called pipe-clay. In the pipe-clay both quartz and clay minerals were present but dolomite and calcite were the dominant phases. The depth of the pipe-clay is unknown as water welled up in the hole to within 2 feet of the surface and adequate samples could not be collected. X-ray powder diffraction photographs of the pipe-clay showed both calcite and dolomite. Both minerals give quite distinct but slightly diffuse diffraction lines. The calcite has a composition of ($Ca_{94}Mg_6$) and the dolomite a composition of $Ca_{54}Mg_{46}$.

(b) Stewart-Woolumbool, Peacock-Baker and East Baker-West Baker Range Interdunal Areas.

Bores W3, W4 and W5 were all collected along the main road west of Naracoorte at low points in the topography. These low points were considered to be the interdunal flats, but between these dune ranges there are no well defined and extensive interdunal basins. None of the samples contained carbonates, but were largely quartz. It is presumed that these samples are wind blown quartz from the sand dunes or are residuals from original water laid sands.

It is sometimes difficult to establish the width and extent of the flats between some dune ranges due to coalescing dunes and to poorly defined dunes. Since the location of the samples also depends partly on the roads and tracks giving access to the area it is not surprising that some samples were free of carbonates. It is possible that pipe-clay exists at depth in these interdunal flats and that the location of the bores in the present study were not satisfactory to establish the position. Present evidence suggests however, that some interdunal flats do not contain pipe-clay deposits.

(c) West Baker-Ardune Range Interdunal Area.

Sample D26 was collected south of Lucindale in the Ardune-West Baker Range interdunal flat. Only a surface sample could be collected as a hard kunkar layer was encountered at 8 inches below the surface. Calcite is a component of the soil, but it is probably secondary. If pipe-clay layers exist, they are below the kunkar.

(d) Ardune-East Avenue Range Interdunal Area

Two bore holes were put down in this interdunal flat. One is 4 miles west of Lucindale on the main road. The other is 5 miles south of the main road on the edge of St. Helena Swamp.

The St. Helena Swamp bore hole, samples D22 to D25, showed 18 inches of black soil containing very little carbonate. The next foot was lighter in colour but did not contain much more carbonate than the surface material. From 30 to 36 inches depth the sample was still lighter in colour and still contained dominant quartz, but considerably more fine-grained carbonate as well as a little shelly material are present. Intensity profiles of the (112) reflections of the carbonates showed a broad profile extending from pure calcite with a d(112) of 3.04Å, which is probably shell material, to a calcite with a d(112) of 3.00Å, a composition range of $(Ca_{100}Mg_0)$ to $(Ca_{88}Mg_{12})$. Dolomite was not identified in the samples.

Samples D27 and D28 were from the more northerly bore on the main road. Kunkar was encountered at 15 inches. The overlying soil showed calcite and a minute amount of dolomite in the X-ray diffraction photographs. The carbonates act as a cement for large anhedral quartz grains and form white sandy lumps in the grey soil. This carbonate material may well be secondary in the soil. The chance that secondary dolomite is forming in the soil is interesting and should be considered as a possible mode of origin for the mineral. This point could well bear further investigation.

(e) <u>East Avenue-West Avenue Range Interdunal Area</u>.

The interdunal area between the East and West Avenue Ranges is broad and well defined. Samples D29 to D32 were collected from a bore near Bull Island. The upper 14 inches showed very minor carbonates in a dark grey soil. From 14 to 19 inches a nodular whitish coloured clay soil contained both dolomite and calcite though quartz and clay minerals were dominant. The carbonates were very fine grained and appeared to act as a cement for the larger quartz grains. At 19 inches an impenetrable layer was reached which also consisted of dolomite and calcite with quartz and clay minerals. The material was very compact and rock like but did not seem to be nodular and it is unlikely that it is a kunkar or secondary carbonate. It has the appearance that one would expect an indurated impure pipe-clay to have.

Also in the East Avenue-West Avenue Range interdunal area, but 11 miles south of Samples D29 to D32, a bore was put down very close to the West Avenue Range. After 8 inches of black soil which graded into a lighter grey soil, a distinct white coloured layer was reached. Sample D16, taken from the white layer showed fine-grained calcite, large quartz grains, plentiful organic remains as well as clay minerals. D17, taken 12 inches below D16 is a true pipe-clay. Both calcite

($Ca_{95}Mg_5$) and dolomite, $Ca_{50}Mg_{50}$, of a very fine grain size typical of pipe-clay were found in D17. Some compaction had occurred in the sample and the fine grained carbonates acted as a loose cement for the minor quartz grains and the plentiful shelly material present. An X-ray powder diffraction photograph of the fine-grained pipe-clay carbonates in this sample showed all the reflections of calcite and dolomite very distinctly, including the dolomite ordering reflections. A diffractometer study of a representative sample of this material showed that the (112) reflection of the dolomite is only half as intense as the (112) reflection of the calcite. This indicates that magnesian calcite is the dominant phase in this pipe-clay. D18, collected 12 inches below D17 showed large white gastropod shells and much plant remains in a great deal of fine-grained light-coloured carbonate. A small amount of dolomite can be detected, but calcite ($Ca_{88}Mg_{12}$) made up the largest portion of the sample. D19, the sample at the bottom of the hole was taken 1 foot below D18 and 4 feet below the surface, and was almost at water level. Both calcite and dolomite were present in this sample but calcite ($Ca_{91}Mg_9$) was by far the dominant phase. Both quartz and shelly material were more abundant in this sample than in D18.

This last bore hole appeared to be in a particularly low part of the interdunal flat. In fact, the sample was taken in one of the drains that remove water which collects in these interdunal areas, and channel it out to major cross-dune drains through which it flows to the sea. The construction of these drains has dried the swampy interdunal areas allowing the former swamps to be used as permanent pastures. Any modern carbonate precipitation in these interdunal areas has been stopped by drainage of the waters. Hence we can no longer expect to find pipe-clay or carbonates of any form precipitating at the surface in the interdunal areas, except where permanent or semi-permanent water occurs. The pipe-clay deposits are only to be found at depth and always covered by a modern soil.

(f) West Avenue Range.

Sample D33 is a white flaky surface material collected from a small flat area within the broad West Avenue Range. This material is very fine grained calcite encrusting and cementing quartz grains. It is almost certainly secondary and precipitated from surface run-off waters.

(g) West Avenue-Reedy Creek Range Interdunal Area.

Samples D34 to D37 were collected near the main road in the low swampy area between the West Avenue and Reedy Creek Ranges. White gypsum and carbonate coated algae were found on the surface of the soil. For 2 feet below this, black soil with a great deal of shell material was uncovered. At about 30 inches the soil became lighter grey in colour and contained a small amount of calcite, but this layer was thin and kunkar was uncovered at 36 inches. It is probable that all the carbonates found in this hole are secondary.

Samples D11 to D14 were collected about 12 miles further south in this same narrow interdunal area. Although a five foot depth was reached in the bore hole only quartz, clay minerals and shelly material were found.

(h) Reedy Creek-(E.and W.Dairy, Woakwine) Range Interdunal Area.

Drain L, a major cross-dune drain which continues through Lake Hawdon North and eventually empties into Lacapede Bay just east of Robe, is about 10 feet deep at Conmurra H.S. An excellent profile of sediments at this locality was provided in the drain cutting and Samples W10 (1-5) were collected here. The upper foot of light grey soil showed considerable calcite but contained predominant quartz and clay minerals. From 1 to 4 feet in depth there was a partially indurated material with much quartz and nodular calcite. A very white layer of typical pipe-clay occurred from 48 to 51 inches. Calcite, ($Ca_{88}Mg_{12}$) was the only mineral found in this pipe-clay besides minor quartz and a little shelly material. An 8 inch layer below the pipe-clay was a compact calcite-bearing material, possibly a kunkar horizon. From 63 to 97 inches a very sandy layer with minor calcite was encountered. The upper four feet in the section may have been affected by secondary changes and may in fact obscure a complex history of sea fluctuations. It is certain that a true pipe-clay layer does occur below the surface, but the actual thickness of the pipe-clay layer may have been reduced somewhat by compaction subsequent to sedimentation.

South of Conmurra H.S. and along the western flank of the Reedy Creek Range algal biscuits have been found in the process of formation. Mawson (1929) described the peculiar occurrence of these calcitic growths at Konetta H.S. On a recent field trip (1956), the writer collected many of these biscuits from the area described by Mawson. Since the water in this area is being drained away and the soil ploughed over, the biscuits will very soon disappear altogether. Certainly they were once more extensive than they are today and any further study of their formation will have to be made in the very near future if it is to observe the actual process of formation. A remarkable photograph of the surface covered with these calcite biscuits is presented in the paper by Mawson (1929). The biscuits are composed almost entirely of calcite although a little quartz and clay minerals are present as contaminants from the soil. These unique algal deposits occur south of Conmurra and appear to be concentrated in the widest portion of the Reedy Creek-(Dairy, Woakwine) Range interdunal flat near Konetta H.S. The formation of these deposits, though fascinating, is not completely relevant to this study.

Still further south than Conmurra H.S., samples W8 and W9 were collected. They showed kunkar at shallow depth overlain by a quartz sand which contained very minor calcite.

Sample W7 (1-4), taken in a paddock just north of Millicent was from a bore of about 2 feet deep. This is the southernmost sample taken in any interdunal area. The uppermost six inches were certainly ploughed over soil. The entire 2 foot section was in a dark grey soil containing quartz, clay minerals and minor calcite. The X-ray diffraction photographs were very sharp and all the calcite reflections very clear. It is impossible to ascertain of the origin of the carbonates, but they are probably secondary.

(i) Woakwine-Robe Range Interdunal Area.

The most westerly interdunal flat is populated by a series of salt and fresh water lagoons. Samples D 7 and D8 were taken on a small swamp covered with a white stringy mat of dried organic remains, just opposite the northwest corner of Lake St. Clair and 3 miles from Nora Creina Bay. The mat of organic fibres was gypsum encrusted algae. Presumably the plants had thrived in the water filled lagoon and become encrusted with the salts when the water evaporated. The mud under the mat in the lagoon was red-brown in colour at the surface, but a whitish-grey coloured mud, rich in calcite, was found in depth. Samples D9 and D10 were taken in the northeast part of Lake St. Clair. The surface was made up of salt crystals below which a white layer containing gypsum, halite, calcite, gastropod shells and other plant and animal remains was found. This layer is so water saturated that the surface shook with every step taken and sample collecting was hazardous. It appears that although lagoons in the Woakwine-Robe Range interdunal area fill with water and precipitate various salts each year, carbonates are not predominant and those that are present are probably formed by precipitation consequent on evaporation. If carbonates are to be found in depth in these lagoons they would have been formed under different conditions than exist there today.

The Naracoorte-Harper Range interdunal area also contains some lagoons which retain their water all or most of the year. The other interdunal flats contain swamps but no permanent lagoons.

(j) Summary

In none of the lagoons and swamps discussed in this section of the paper have carbonates been actually observed in the process of precipitation. However, pipe-clays have been found at depth in Bool Lagoon, in the East Avenue-West Avenue Interdunal flat and in the Reedy Creek-Dairy Range interdunal flat. The fact that pipe-clay was not discovered in the other interdunal flats may well be due to sampling methods, but it is interesting that the pipe-clay was only found in the widest, most continuous and best defined interdunal flats. These wide and well defined flats may well represent old "Coorongs" while the other flats may be similar to the flats and swamps flanking the modern Coorong. A very thorough study of the interdunal flats in the South East of

South Australia may well elucidate the complex history to which they have been subjected.

Dolomite was a constituent of the pipe-clay found in Bool Lagoon and in the East Avenue-West Avenue Range interdunal flat but not in the Reedy Creek-Dairy Range interdunal flat. Dolomite was also identified in the clays in the Ardune-East Avenue Range interdunal area. Varying amounts of calcite were found along with quartz and clay minerals in most of the other interdunal clays and calcite was the only carbonate mineral present in the pipe-clay in Drain L near Conmurra H.S.

The appearance of pipe-clay at depth in the well defined interdunal areas indicates that conditions suitable for the precipitation of carbonates have prevailed in the past in this region. Although calcite is the dominant carbonate mineral appearing in the interdunal areas it is interesting to note that dolomite has been found in two of the pipe-clays and in some clay rich soils.

We may summarize this section with a general statement. We can safely say that true pipe-clays, as observed in the modern Coorong, have formed in old interdunal areas in the southeast of South Australia. The present study suggests that these old pipe-clays are concentrated in the wide and extensive interdunal flats and are limited or non-existent in the small disconnected flats. Without intensive sampling it is impossible to say if the old pipe-clays have the same range of compositions as the modern ones. The present study suggests that they are roughly the same and that both one and two phase precipitates occur, as in the modern pipe-clays.

A single observation in the Reedy Creek-Dairy Range interdunal flat suggests that successive cycles of formation may sometimes be present. These could be observed if satisfactory sections could be obtained. It is suggested that a detailed study of the drain sections would be rewarding and that deep bore holes put down in the bottom of the drain cuts would be most instructive.

The presence of fossils in the old pipe-clays and in the sands above and below them, also suggests that a palaeontological study might indicate if the conditions of formation of the old pipe-clays were the same as the modern ones.

Samples Collected from the Interdunal Areas in the Upper South East Province

The third group of samples, discussed below, was collected in the northern half of the South East and are all located at least 10 miles inland from the Coorong. North of the Kingston-Naracoorte trainline the dunes converge and the interdunal areas become more difficult to define. Tracks giving access to the area are very limited and difficult to traverse. Samples were taken in low swampy areas in the hope of encountering pipe-clay at depth. Only one bore hole contained pipe-clay at depth. The samples may have been collected in areas where a great thickness of soil and sand have covered any pipe-clay that may have precipitated in the past, or it is possible that pipe-clay as such may never have precipitated in some of the narrow interdunal areas either in the north or southern sections of the South East province.

Bores U1 and U2 were put down approximately 10 miles directly inland from the southernmost extent of the water in the Coorong. Both bores showed about 18 inches of soil, sand and grey-green clay with very minor carbonate. U1 showed a very thin layer of pipe-clay at 20 inches below the surface which contained both calcite and dolomite, but calcite is the major phase. A kunkar like material was reached at 26 inches. Both bores were located in the first well defined interdunal area after the Coorong. The area is drained by Salt Creek and may have been connected with the Coorong in the recent past.

Bore U3, collected near Kercoonda H.S. contained 2 feet of black and grey clays with quartz sand, grading to lighter coloured sands at a depth of 42 inches. Carbonates were very minor, even in the lighter coloured sands at depth.

U4, D62 and D63 were collected about 6 miles northeast of U3 on Davy Denning Swamp, which contains permanent water. U4 contained a great deal of plant material. The surface sample showed some calcite, below which was 10 inches of black sand. From 10 inches to 2 feet a whitish grey mottled clay was found. Some calcite was present in this layer. At greater depths a yellow sand and clay were encountered. D62 and D63 are quartz sands which contain a very minor amount of calcite.

U5 and U6 were collected 4 miles north of U4. U5 contained mostly quartz, but when a fine fraction was floated off in water, the surface sample was seen to contain minor calcite and dolomite, with a little gypsum. The remainder of the bore sample, covering about 1 foot, showed very minor carbonate with the quartz sand. Only calcite was identified in the lower half of the hole. U6 was a sample of the slime growing in an old plough furrow in the same area as U5. The slime contained considerable fine-grained calcite on X-ray analysis.

U7, collected in water logged flats 2 miles northwest of U5 showed both calcite and dolomite in depth. The first 2 inches of soil showed much quartz and clay with minor calcite. This was followed by 2 inches of a grey sand containing minor calcite and dolomite. From 4 to 7 inches in depth the sand became more clay rich and lighter grey in colour. X-ray diffraction photographs showed very broad and diffuse carbonate reflections. The (112) of the calcite could not be resolved from the (112) reflection of dolomite. The reason for this lack of resolution is probably to be found in the type of clay mineral present, since some clays give interfering reflections lying between the calcite and dolomite (112) reflections.

U8 and U9, collected at Bonney's Camp, showed only very minor calcite in grey sands.

Bores U10 and U11 were put down into clay pans 3 miles east of Meningie. In both cases the upper inch was a white powder which was mostly gypsum. Below this was grey sand and clays. In U11 a pink gastropod-rich clay layer was encountered at 4 to 8 inches. The only carbonate mineral, calcite, found in these clay-pans was present in very minor amounts.

Bore U12 was put down in a low area on the eastern side of the main road 8 miles north of Meningie. The surface crust was a white powder containing halite and gypsum, followed by a 1 inch layer of black mud giving off a distinct H_2S odour. Grey and green clays extended from 1 to 48 inches, where a heavy influx of water was encountered. Calcite occurred in very minor amounts throughout the clays.

Only one true pipe-clay, other than that in the Coorong proper, was found in the upper South East province. However calcite and dolomite have been discovered in the muds and clays, and calcite in the algal slime on the swampy ground. This suggests that carbonates may be formed by secondary reaction in a soil by algal, or perhaps other plant action. This point has not been investigated further, but it could well be of importance in determining the formation of carbonates in swampy or water logged ground such as one finds in many parts of the South East.

Samples Collected from the Coorong and Lagoons South of the Coorong

The fourth group of samples from the South East to be discussed are those from the Coorong and the lagoons to the south of it. The lagoons are isolated remnants of the Coorong which in the recent past were directly connected with the Coorong and hence with the open sea. They have become isolated by the gradual accumulation of wind blown sand and precipitated pipe-clay. The deposits are anchored by plants such as sedges that grow on the banks and in the shallow portions of the lagoons. The lagoons are elongate north-south, in the same direction as the modern Coorong.

Samples have been collected in the Coorong itself and in three separate lagoons to the south. Kingston Lake, the most southerly lagoon, is only 10 miles north of Kingston. Kingston Lake is about 4 miles long and $\frac{3}{4}$ of a mile wide. Lagoon M 7 miles north of Kingston Lake also extends about 4 miles in length. The third lagoon sampled is 2 miles north of Lagoon M and is much smaller in area than either Kingston Lake or Lagoon M.

I propose to discuss the samples collected in the Coorong itself and then move south, ending with a discussion of the samples from Kingston Lake.

(a) The Coorong Samples

The Coorong samples, D59, 60, 61 were collected on the northern side of the old Coorong road as it crosses from the mainland to Younghusband Peninsula at the Causeway. During the winter season water may fill the Coorong well to the south of the Causeway. However the samples were collected in March 1956 when the water had receded quite a way, and although the sediments were still wet, the surface skin was dry.

The surface of the Coorong at this point was covered with dead algae (established by Dr. Jean Mayo, Genetics Department, University of Adelaide) and small pink gastropod shells. Below this were 2 inches of dirty grey pipe-clay which contained minor dolomite. Most of the pipe-clay sample was made up of calcite with minor halite, quartz, clay and shell fragments. From 2 to 8 inches a sandy and shelly layer contained mostly quartz and shells but a small amount of the fine-grained calcite was present also. A lighter coloured quartz and calcite layer extended to about 2 feet when a very dark-grey-brown mud appeared and remained to the limit of sampling.

South of the Causeway the Coorong narrows and soon becomes a series of small lagoons. Some of these lagoons produce salt which is mined commercially in good years, while others consist of carbonates, the salt being blown off.

Pipe-clay occurs well north of the Causeway, though only as a thin layer. Pipe-clay has actually been observed precipitating at Cantara and forms a very thin bottom layer here. Ten miles south of Salt Creek, Forbes (1955) collected a pipe-clay sample (A78.1) which contained predominant calcite, ($Ca_{84}Mg_{16}$), with minor dolomite, $Ca_{55}Mg_{45}$.

The most northerly observation of pipe-clay is in a small lagoon about 1 mile south of Salt Creek. In the Coorong itself it is doubtful if pipe-clay can be found any further north than 5 miles south of Salt Creek and here it is only a surficial layer.

(b) Lagoon 12 miles South of the Causeway

Samples D56, 57 and 58 were taken in a lagoon about 12 miles south of the Causeway. The top inch of the lagoon is a grey-brown impure pipe-clay. The sample contains a considerable amount of quartz and clays as well as both calcite and dolomite. Within a few inches the sediment grades from this dark brown impure pipe-clay through lighter grey pipe-clay to a white pipe-clay. The pipe-clay is made up almost entirely of dolomite and calcite, with very minor quartz, celestite, halite and clays. Intensity profiles of (112) reflections of the carbonates showed dolomite to be the major carbonate. A broad (112) reflection from magnesian calcite was asymmetric towards high 2θ values, probably due to interference from celestite. A much less intense third carbonate peak at 3.03Å is undoubtedly due to some shelly materials in the sample. The composition of the calcite was ($Ca_{81}Mg_{19}$) and the dolomite composition was $Ca_{55}Mg_{45}$. After 3 feet of pipe-clay a brown-grey layer composed of quartz, calcite and clays is found, which becomes more shelly with depth.

(c) Lagoon M Samples

The next lagoon to the south which was sampled has been called Lagoon M in this study. It has been sampled in several places. The northernmost samples, D54 and 55 showed 33 inches of pipe-clay consisting of calcite ($Ca_{81}Mg_{19}$) and dolomite $Ca_{55}Mg_{45}$, minor halite and quartz as well as the usual shelly materials. Below the pipe-clay was a grey-brown clay containing calcite, quartz and clay minerals.

In the southern end of this lagoon two separate bore holes were put down. The first is near the western margin of the lagoon. Samples D46 to 48 from this hole showed only 3 inches of pipe-clay containing calcite ($Ca_{81}Mg_{19}$) and dolomite $Ca_{55}Mg_{45}$. This pipe-clay graded into a light grey sandy and shelly layer (3 to 18 inches) which contained some calcite but was mostly quartz and clay minerals. Below this sandy layer a black non-calcareous mud was found.

In the very southern end of Lagoon M in an area covered with dead algae, about 150 yards further out into the lagoon than samples D46-48, Samples D49-52 were collected. The top 2 inches of this hole contained a very fine-grained layer composed of major dolomite and calcite as well as considerable amounts of quartz and halite. Much fine-grained organic matter was also present as well as shelly material. This pipe-clay contained calcite of composition ($Ca_{81}Mg_{19}$) and dolomite $Ca_{54}Mg_{46}$. From 2 to 6 inches the pipe-clay became lighter in colour, although the compositions of the carbonates remained constant within the limits of measurement. Between 6 and 12 inches a white and very sticky pipe-clay layer was found which was almost pure carbonates. Dolomite, $Ca_{54}Mg_{46}$ was not in as large a proportion as in the upper samples and instead, calcite of a composition ($Ca_{77}Mg_{23}$)was the dominant phase. From 12 to 18 inches a highly fossiliferous layer was encountered. In this layer the white pipe-clay cemented many pink gastropod shells which gradually changed to a brown-grey gastropod shell layer at 18 inches and continued to at least 3 feet.

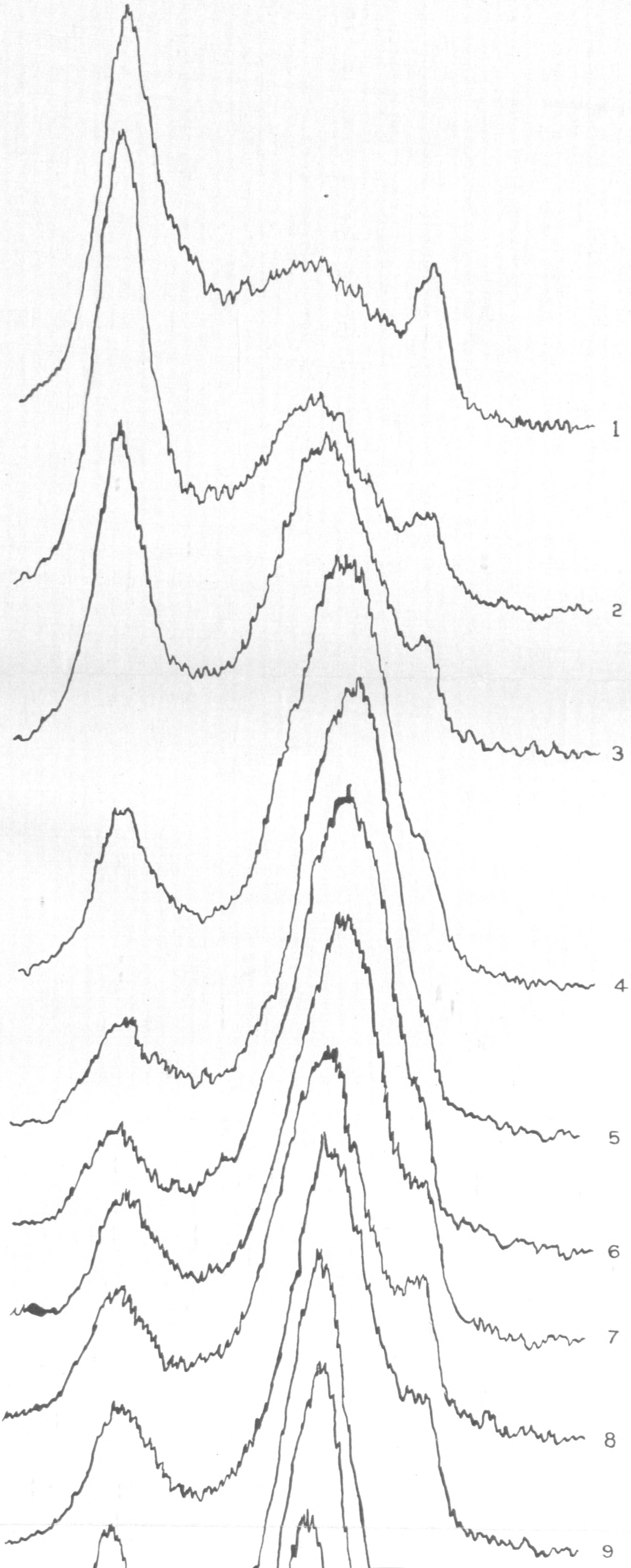
At the western edge of the southern end of Lagoon M an area of sun cracked pipe-clay was found. Salt crystals could be seen in hand specimens (e.g. D53). The pipe-clay contains calcite ($Ca_{88}Mg_{12}$) and dolomite $Ca_{55}Mg_{45}$ and far more quartz and organic material than in the centre of the lagoon. At 10 inches below the surface a similar pink gastropod layer was encountered to that found in other parts of the lagoon.

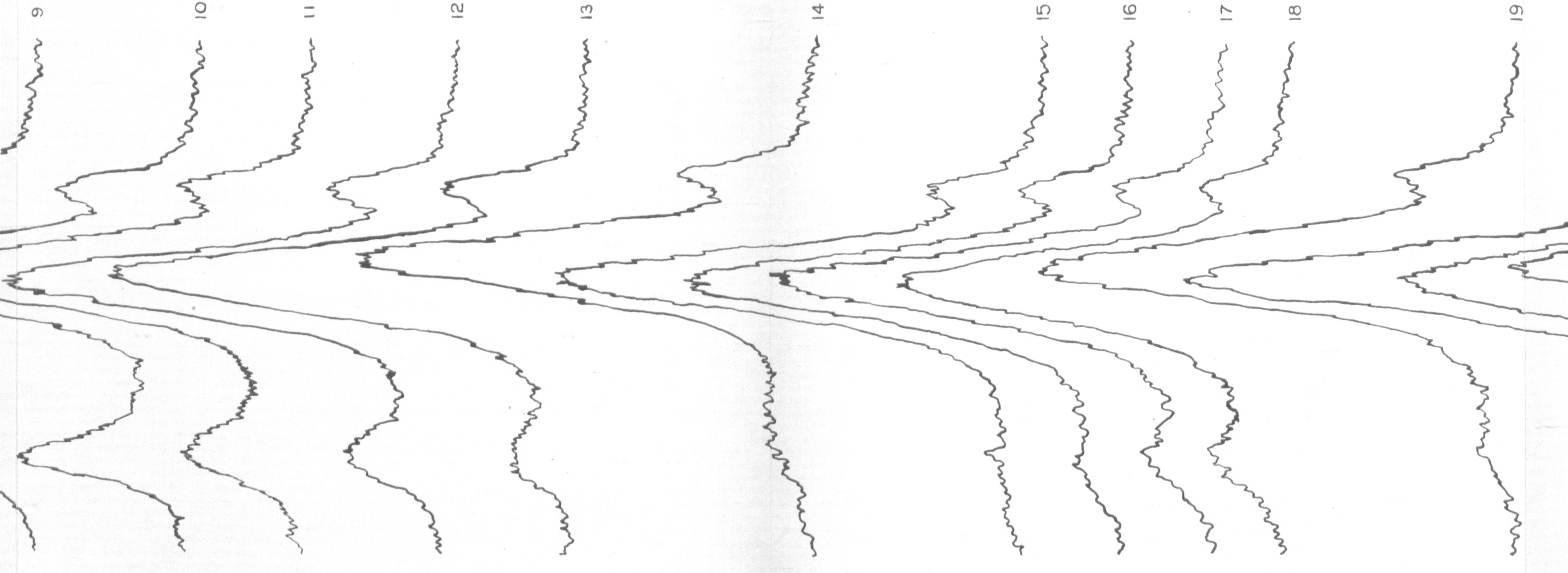
In a later field trip, in March 1957, another section was taken in the middle of this lagoon where at least 29 inches of pipe-clay was found. Samples were collected at every inch. The upper inch was grey pipe-clay. Dolomite, $Ca_{54}Mg_{46}$ was the dominant carbonate mineral. Calcite ($Ca_{81}Mg_{19}$) showed a very low and broad (112) reflection. Shell material of relatively pure calcite, celestite and halite were present in all samples taken in this bore. At 2 to 3 inches the pipe-clay became white in colour. Calcite of a composition ($Ca_{88}Mg_{12}$) gradually became the dominant carbonate phase while the percentage of dolomite, $Ca_{57}Mg_{43}$, decreased. At 8 inches in depth the calcite composition increased in Mg content to ($Ca_{84}Mg_{16}$) while the amount of dolomite relative to calcite increased. The calcite became still further Mg rich, ($Ca_{81}Mg_{19}$) at 11 inches. The dolomite composition was

Fig. 7

Intensity Profiles of Bore Hole S4

Samples 1-30

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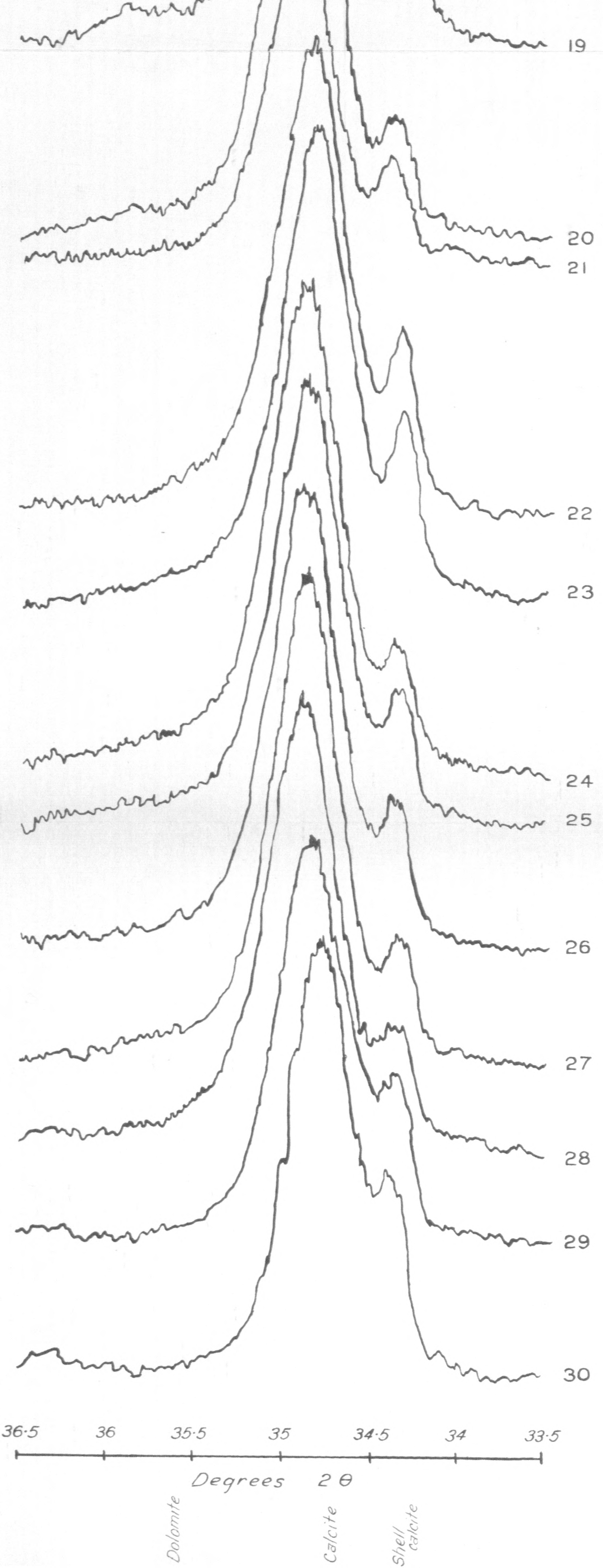
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Degrees 2θ
Dolomite
Calcite
Shell calcite

constant. The amount of dolomite relative to calcite gradually reduced until at 14 inches the dolomite reflection was scarcely able to be detected. The calcite at 14 inches had a composition of ($Ca_{88}Mg_{12}$), less Mg rich than the calcite in either the inch above or below. The composition of the calcite remains fairly constant at ($Ca_{84}Mg_{16}$) from 15 to 22 inches, except at 18 inches when the calcite again becomes more Mg rich at ($Ca_{81}Mg_{19}$) and the amount of dolomite $Ca_{57}Mg_{43}$ briefly increases relative to calcite. After the gradual increase of dolomite at 17 and 18 inches it decreases and from there to the bottom of the bore dolomite is not able to be detected. When dolomite finally does disappear at 19 inches the pipe-clay becomes very white and there seem to be less clay and quartz impurities. Coarse shell material does become a major phase, however. Calcite of composition ($Ca_{88}Mg_{12}$) is found at 23 inches but below that, in the very white pure layer, the composition is ($Ca_{84}Mg_{16}$). At 30 inches the pipe-clay becomes contaminated with a great deal of quartz and it starts to grade into the sandy layers below.

The intensity profiles of the (112) reflections of the carbonates in this very thick pipe-clay section are given in Fig.7. The changes discussed above are well illustrated in this figure. The gradual increase in magnesian calcite relative to calcian dolomite is very marked in the first few samples. The increase in dolomite relative to calcite at two points in depth is also plain. The fluctuation in composition of the calcite seems to parallel the increase in dolomite relative to calcite. That is, the more dolomite present, the more Mg rich the calcite becomes.

The samples taken in Lagoon M show, as a group, the highest Sr content. The full discussion of this point will be given in a later section.

(d) Kingston Lake

Kingston Lake is the best sampled locality in the whole of the South East. It is here that the carbonates were first observed in actual precipitation and the first bore hole samples were taken. These early bore hole samples have already been discussed (A78-6 to 13).

In March 1956 the author put a bore down in Kingston Lake (Samples D38-45) close to the western margin. The surface of the lagoon at this time was covered with a gypsum and carbonate encrusted layer of dead algae. Directly under the dead and stringy algae but not actually on an open surface, quartz grains could be seen. The grains were probably caught by the plants as they were blown inland from the dunes along the sea shore to the west. Organic material was found in all of the samples. The half inch of pipe-clay under the mat of plant fibres and their locked sand grains contained calcite ($Ca_{90}Mg_{10}$) and dolomite $Ca_{50}Mg_{50}$. The next inch showed a small amount of both calcite and dolomite with a great deal of anhedral quartz grains and shells. From 2 to 6 inches (Sample D41) a more compact layer was found which also consisted of both carbonates and quartz as well as shelly material. Dolomite, $Ca_{57}Mg_{43}$ was by far the dominant carbonate phase. The calcite had an estimated composition of $(Ca_{90}Mg_{10})$. Accurate measurement was not possible as the intensity of the calcite reflection was barely above background, and the presence of large amounts of shell material caused the profile to be broad and ill-defined. From 6 to 13 inches below the surface a loosely consolidated quartz sand occurred which contained a great many broken shell fragments as well as minor precipitated calcite and dolomite. The sand became darker with depth. At 33 inches the intensity of the calcite (112) reflection was greater than that of the dolomite (112) reflection but the sand had become lighter in colour again. The depth of the light grey coloured sand is unknown, but it was at least 8 inches thick by the time the bottom of the hole was reached.

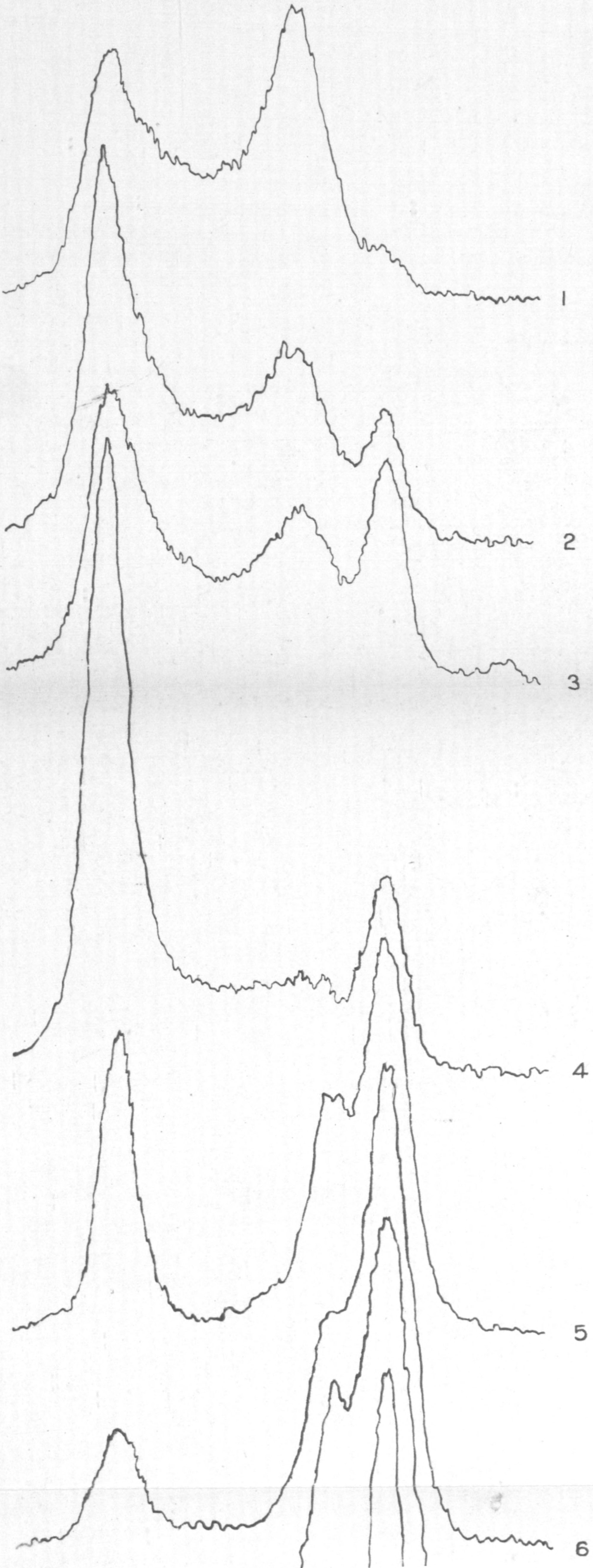
Three other bores were put down in various parts in Kingston Lake in March 1957 to determine the thickness of the pipe-clay in this lagoon. One bore, (S1), was put down in the approximate centre of the lagoon. Another bore, (S2), was sunk on the western edge of the lagoon where the sedges were just beginning to grow and the third bore, (S3), was put down in the plant covered area 10 yards beyond the bank marking the present edge of the lagoon. S3 was about 12 yards due west of S2.

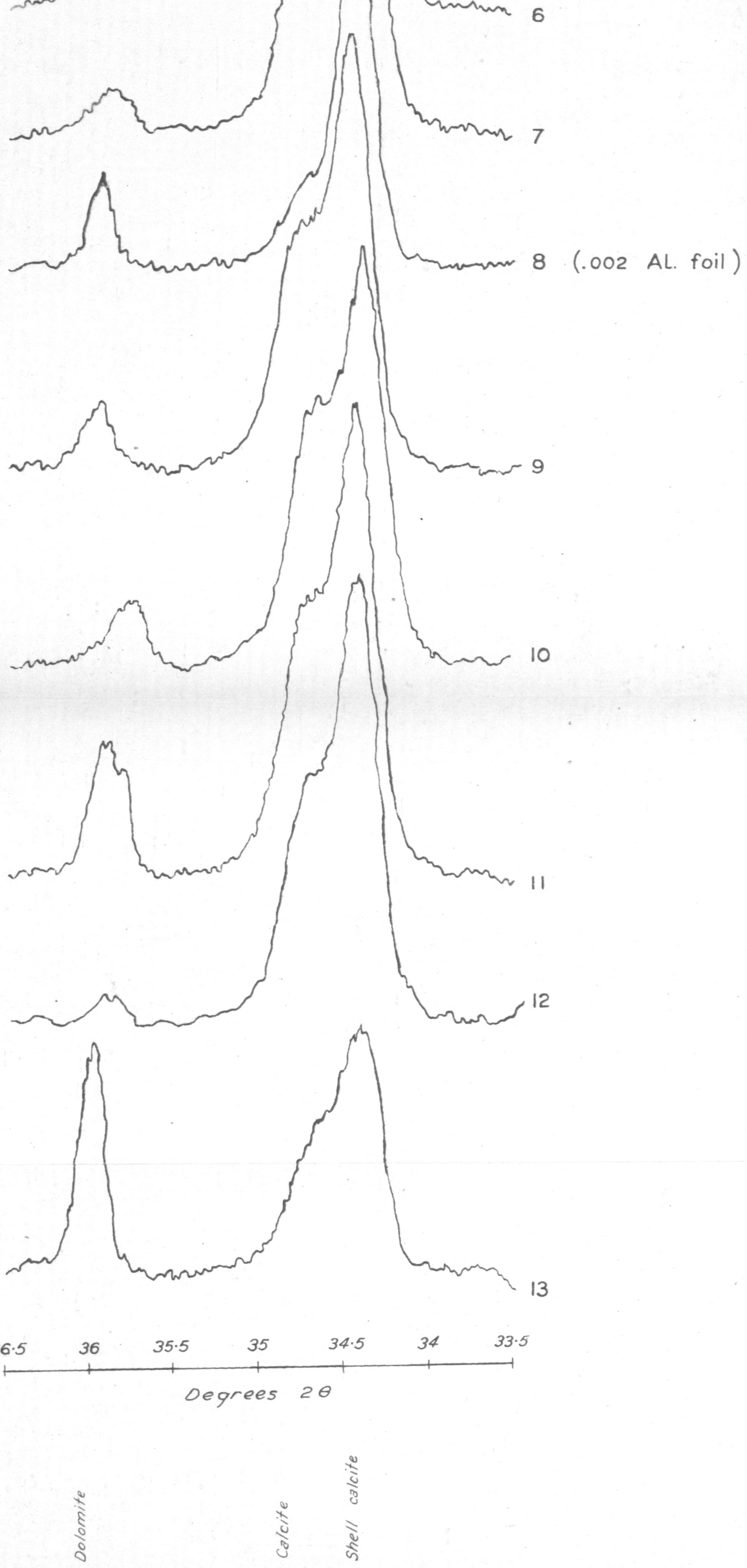
S1, the bore put down in the present centre of the lagoon, showed only 1½ inches of pure pipe-clay. The calcite

Fig. 8

Intensity Profile of Bore Hole S1

Samples 1-13

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Calcite
Shell calcite

had a constant composition of ($Ca_{84}Mg_{16}$) and the dolomite a composition of $Ca_{57}Mg_{43}$, within the limits of measurement, although the amount of dolomite relative to calcite changed slightly with depth. Fig.8 gives the (112) reflection intensity profiles of the samples taken in this bore hole. In the upper half inch the calcite (112) reflection is slightly more intense than that of dolomite. At 1 inch the calcite profile decreases and the dolomite increases, and at the bottom of the hole the amount of shelly material has increased markedly and the amount of dolomite has decreased again. Samples S1-4 to 12, covering 11 inches in depth are grey sands, showing discrete grey and white sand grains and a great deal of shelly material. At 14½ inches a black sulphurous mud was encountered. From the intensity profiles it appears that dolomite is the dominant precipitated carbonate in the upper part of the grey sand, and calcite is dominant in the lower part. It is interesting, however, that dolomite is again prominent in the muds below the sand layer.

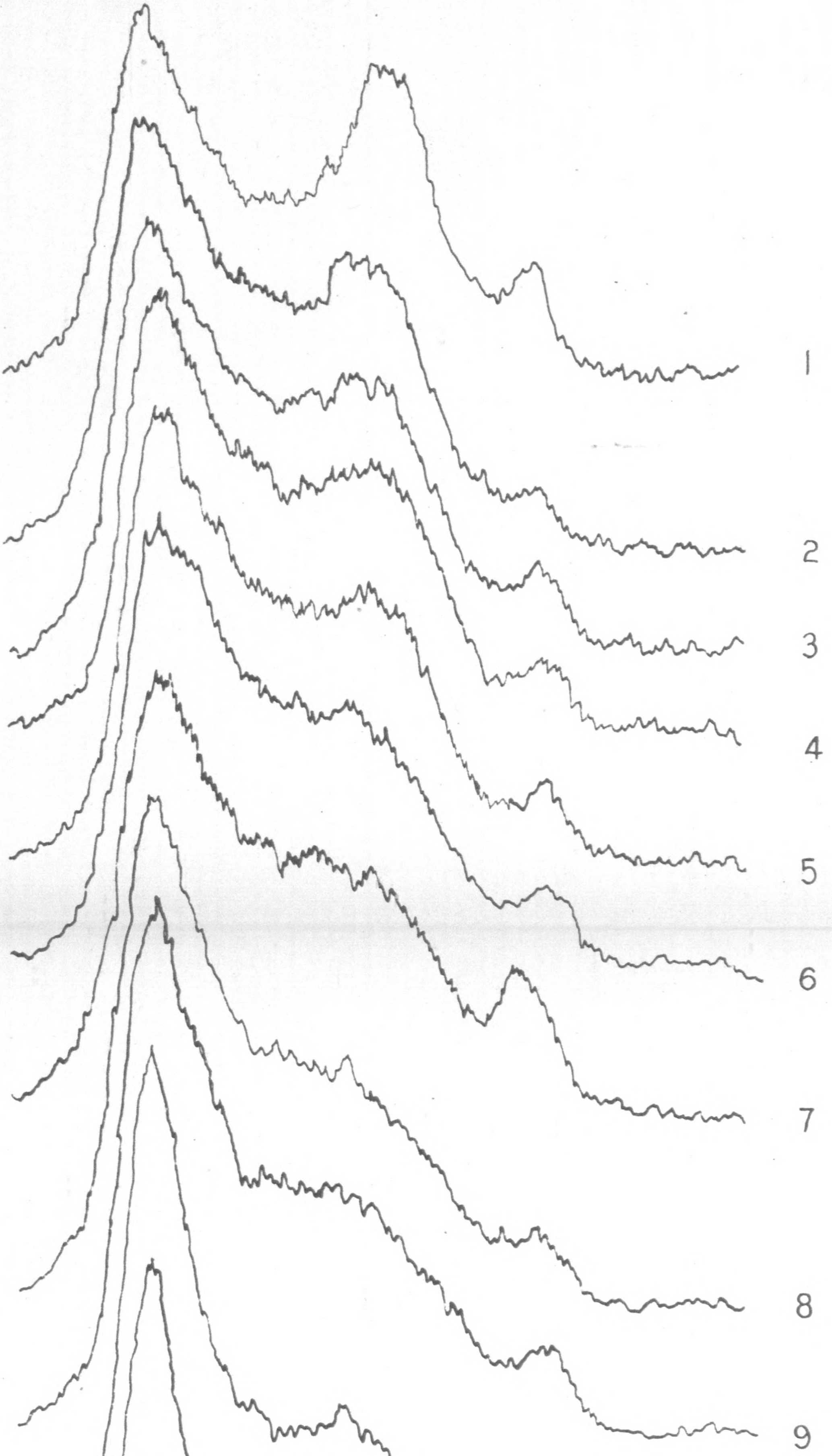
Bore S2, from the edge of the present lagoon shows a surface of sun cracked pipe-clay below which there is 5 inches of white pipe-clay then 2 inches of a transition zone where the amount of quartz in the pipe-clay increases gradually and finally at 7 inches becomes a grey sand layer. The grey sand layer becomes darker grey in depth and extends to at least 13 inches below the surface.

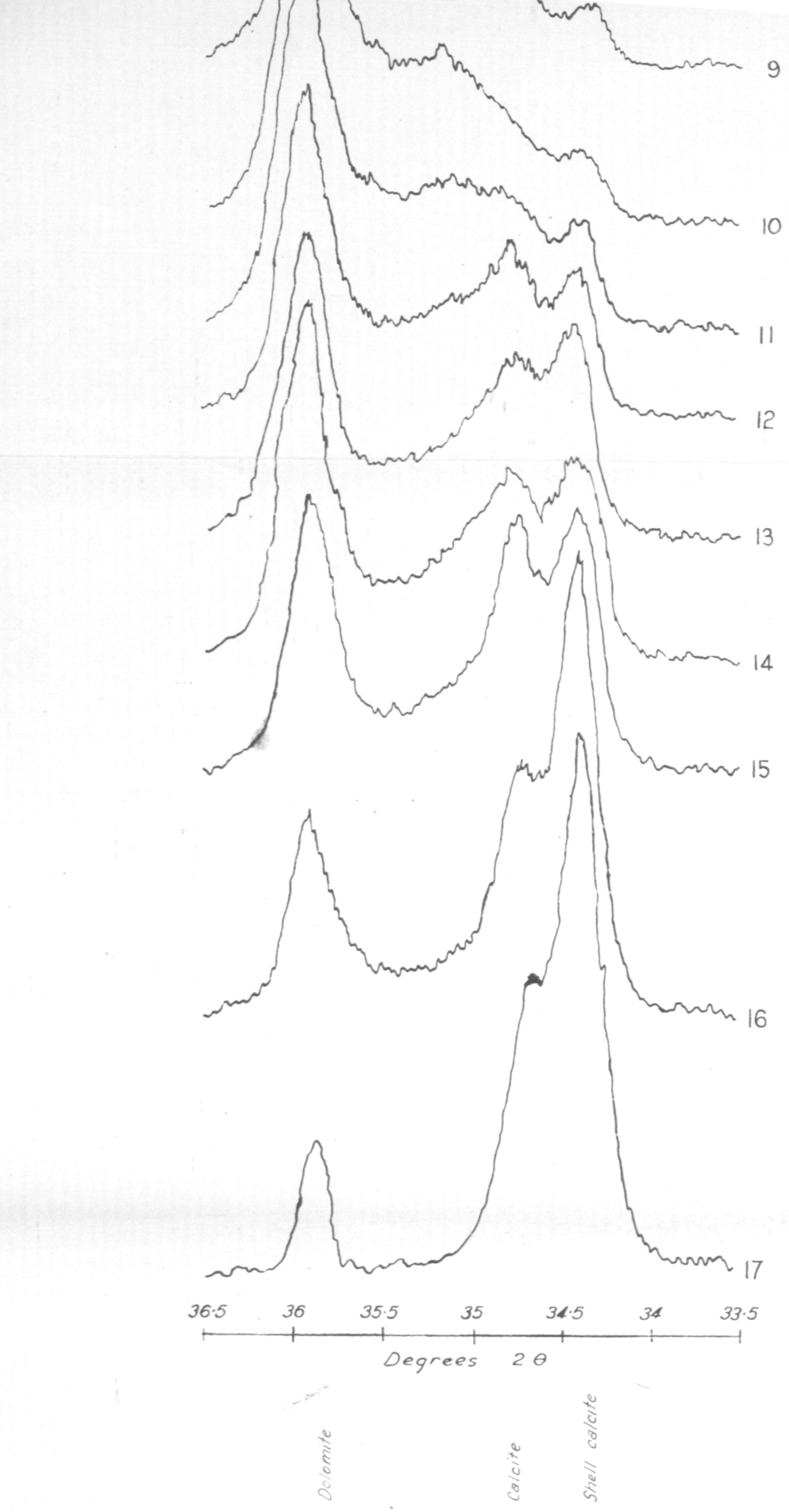
Intensity profiles of the samples from S2 are given in Fig.9. The topmost sample, the sun cracked pipe-clay, appears

Fig. 9

Intensity Profile of Bore Hole S2

Samples 1-17

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Dolomite
Calcite
Shell calcite

very similar to the topmost sample in S1. The underlying pipe-clay samples S2-2 to S2-10 show very broad profiles, precluding accurate measurement. The calcite profile decreases in intensity relative to the dolomite with depth. It also appears that the calcite peak is shifting towards the asymmetric dolomite peak in depth. The profile is so poor however, that it is impossible to determine anything quantitative about it. The poorness of the profile is undoubtedly due to the very low intensity (it rarely reaches twice that of background) and certainly due to interfering reflections from clay minerals in the pipe-clay. In the transition zone samples, S2-11 to S2-14, the magnesian calcite profile increases, as does the shell calcite profile. The dolomite profile decreases through this zone however and continues to decrease in the sands at the bottom of the hole. Shell calcite is the dominant carbonate phase in the grey sands and it appears that the precipitated calcite peak is shifting from more magnesian content in S2-11 to a more pure calcite in S2-17. The dolomite profile, in the transition zone where its position can be measured accurately, gives a composition of $Ca_{54}Mg_{46}$. The bottommost sample, however, has a dolomite of composition $Ca_{57}Mg_{43}$.

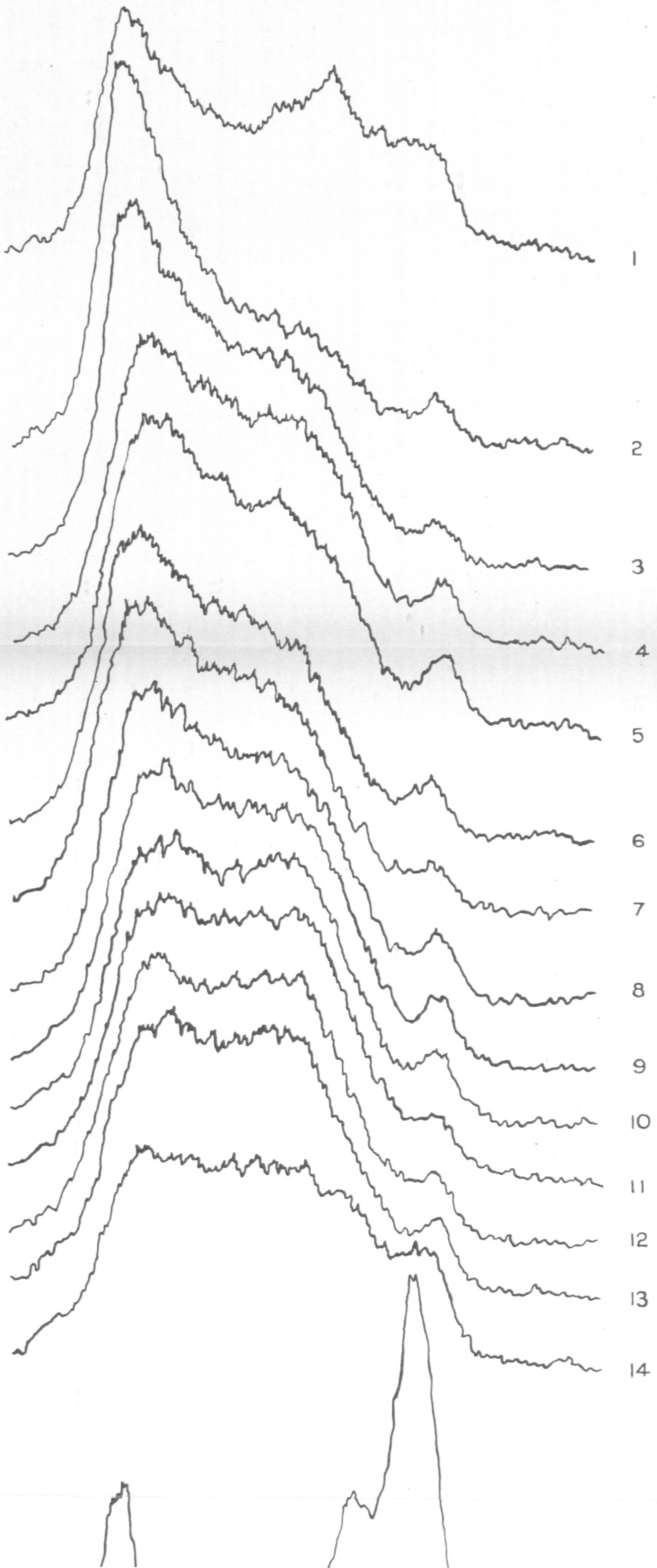
Sample bore S3 on the bank of the present lagoon shows in depth: 2 inches of black soil, 11 inches of impure pipe-clay, 1 inch transition zone and a grey sand to the bottom of the bore at 20 inches.

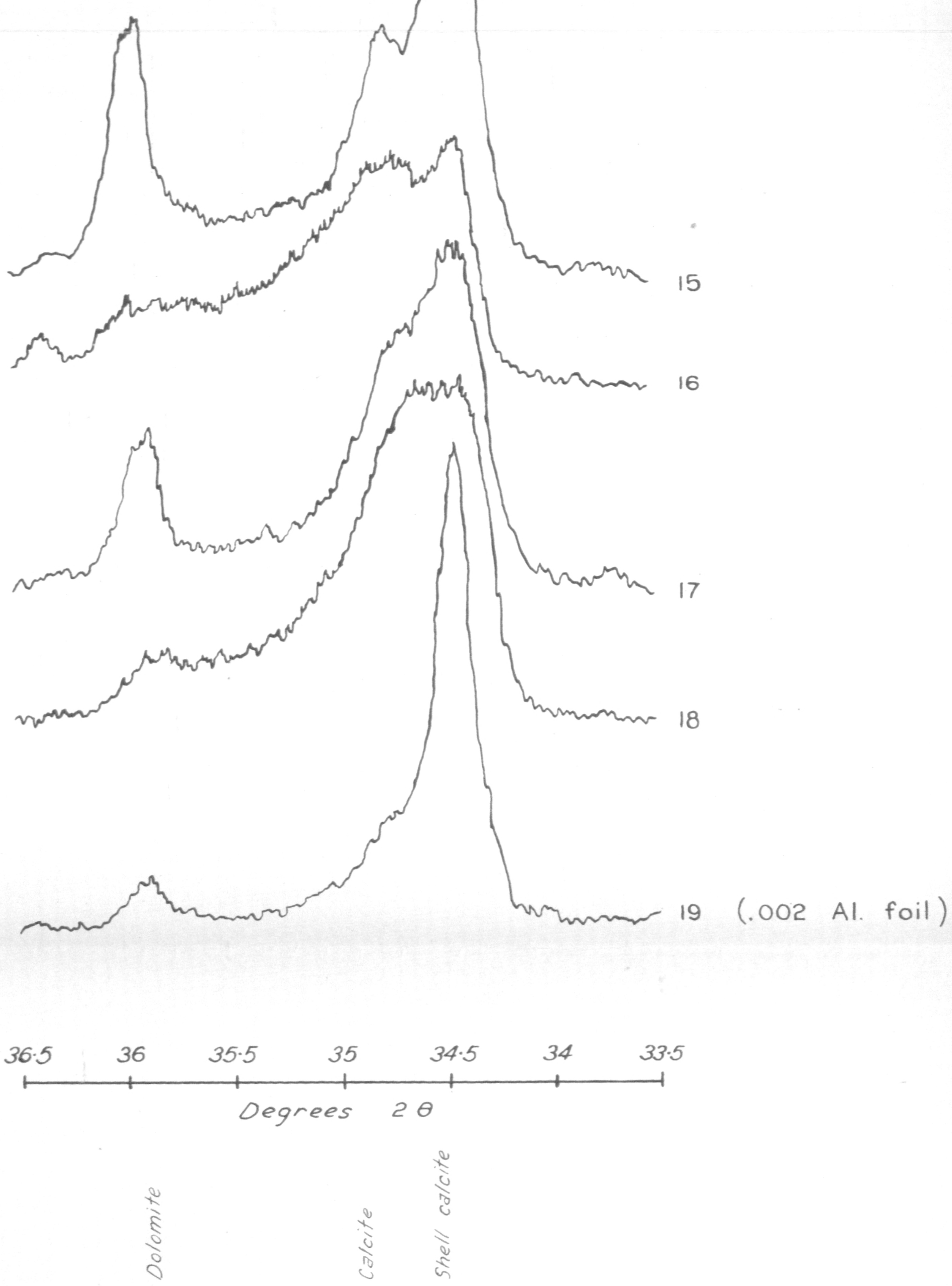
The intensity profiles are given in Fig.10. Again the top sample appears to have the same calcite/dolomite ratio

Fig. 10

Intensity Profile of Bore Hole S3

Samples 1-19

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Degrees 2 θ
Dolomite
Calcite
Shell calcite

and composition of carbonates, as the two other top samples S1 and S2, even though it is a black soil. The remaining pipe-clay profiles S3-2 to S3-14 are very broad and poorly resolved. It is impossible to distinguish a calcite or a dolomite profile. Celestite and a large amount of clay minerals, especially montmorillonite, have been identified in these samples. Since these minerals give reflections in between the calcite and dolomite reflections they would interfere. The interference would cause a broad intensity area rather than sharply defined individual profiles.

A remarkable break exists between the last pipe-clay sample S3-14 and the more sandy transition zone sample S3-15. The sands appear to have variable dolomite and calcite content with dominant shell calcite. In the bottom sample S3-19 both dolomite and calcite are minor components.

These three bore samples point up the difficulty in determining the composition of carbonates in pipe-clays unless the sample contains little clays and celestite. It appears that the uppermost samples from both the edge and the centre of the lagoon are quite similar in composition of the calcite and dolomite and the calcite/dolomite ratio.

Bore S3 is far too contaminated with other minerals, especially clays, to be able to give unequivocal data. Indeed, bore S2 shows quite broad intensity profiles, more so than the bore put down in the centre of the lagoon. However, we can obtain trends of the calcite/dolomite ratio within the pipe-clays of these three bores, if nothing else. In all three bore holes in the lagoon the amount of magnesian calcite decreased relative to dolomite with depth.

The variable thickness of pipe-clay in the lagoon may be due to many factors, not the least of which would be the wind which would blow the suspended carbonates toward the eastern side of the lagoon. Since the western edges would be protected by the plant stabilized bank the thicker section of pipe-clay is found there rather than in the centre portion of the lagoon. A bore has not been put down on the eastern side of the lagoon to test this suggestion. Such a bore would be most instructive.

(e) Discussion

Why should magnesian calcite decrease in depth in this lagoon when in Lagoon M the reverse is happening? Dolomite decreases and magnesian calcite increases with depth in Lagoon M. If magnesian calcite was so unstable that it was changing to dolomite and a purer calcite in time we would expect both lagoons to show decreasing magnesian calcite with depth.

The impervious nature of the pipe-clay precludes solution and redeposition effects within the section. The two gradual increases of dolomite in depth in Lagoon M can be explained as the result of gradually changing conditions of precipitation in the past which favored the precipitation of dolomite over calcite and which gradually changed back to favoring the precipitation of calcite over dolomite.

Since all the bores in Kingston Lake showed the same trend with depth it appears that the precipitation is fairly constant here. Local differences occurred only in the thickness of the pipe-clay sediment.

The topmost samples are very similar. For any particular lagoon it appears that the precipitation must have a constant composition for a given year. The precipitation in an adjoining lagoon is not necessarily identical, however, and may in the past have followed a different trend. In other words, each lagoon acts as a single system and precipitates according to the specific conditions prevailing in the lagoon at that time. The total amount of Mg precipitating either in the form of dolomite or in solid solution in the calcite varies with the lagoon but not the position in the lagoon.

It seems that there has been a general increase in the amount of Mg precipitating at times as evidenced by the increase in dolomite relative to calcite and the increasing Mg content in the coprecipitating calcites. The reasons for the increase in **Mg** precipitating may be due to an unusually high elevation of the pH of the lagoon waters. It is well known that $CaCO_3$ may precipitate from waters having a pH of 8.2 - 8.4 (McClendon, 1929) and that Mg salts precipitate at much higher pH. The normal pH of these lagoon waters is 8.2 and during active precipitating a pH of 9.2 has been recorded. The precipitation seems to be heaviest over areas of heavy plant growth. Baas-Becking (1934) has shown that plants can raise the pH of lake waters through photosynthesis to 9.3 during the day and the pH may fall as low as 8.0 at night. Certainly these lagoons in the South East of South Australia are producing dolomite at ordinary temperatures and pressures from waters very similar to the sea in composition (Alderman and Skinner, 1957). The extraction cycle of CO_2 by plants to raise the pH seems the only possible variable that can cause the observed effects.

The foregoing section contains a great mass of detail most of which is also presented in the Appendix and in the appropriate text figures. It is instructive to summarize the points developed, however, lest they are lost in the detail.

First, bore holes in the Coorong and the lagoons south of the Coorong show a topmost layer of pipe-clay containing varying amounts of quartz, clays and shell fragments as impurities. Within three feet of the surface the pipe-clay passes to sandy and shelly beds which still contain some precipitated carbonates. This suggests that if the Coorong were examined in detail, precipitating carbonates may be found where active current and wave action still occur, and where quartz sand and shell deposits are still building up. The differences in composition of the precipitated carbonates in the pipe-clay and the sand layers are either minor or non-existant. The change from pipe-clay to sands is gradual, as shown by the transition zone. A faunal study may well show how environment conditions have varied. It would be more instructive, however, to attempt to relate the modern Coorong features to the history revealed in the lagoons south of the Coorong.

The second point which emerges is that the precipitates vary with both time and place. It will be demonstrated in the following section that a modern place-variation exists which follows a logical pattern. It has not been possible to demonstrate such a logical pattern with time, however. Thus, pipe-clays in Kingston Lake show dolomite increasing over calcite with depth, while in Lagoon M the reverse is happening. The difference in thickness of sediment between Lagoon M and Kingston Lake is astonishing, but speculation is useless without further extensive sampling.

The third and possibly the most important point is that the more dolomite present in a pipe-clay, the higher the Mg content of the co-precipitated calcite. This point and its possible explanation have been discussed in the following section and will not be developed here. The reason for the changes causing the variations are of course speculative. Plant density and plant type (which control the pH of the waters through photosynthesis), water composition and temperature are the likely variables. How these change with time and place must await further work.

Samples of Pipe-clay collected in the process of precipitation

The term precipitating pipe-clay used in this study refers to the material actually observed precipitating from the saline waters and collected while still in suspension in the water.

One-half gallon samples of the waters containing the pipe-clay in suspension were collected and the solids were allowed to settle in the laboratory. The precipitates were separated by decanting the water and air drying them at room temperature.

Precipitating pipe-clay samples were collected from various localities in the Coorong south of the Causeway and from two lagoons south of the Coorong proper. Samples were collected from Kingston Lake over a period of two years, but the other precipitating pipe-clay samples were all collected during December 1956.

The amount of pipe-clay in suspension varies from place to place within a lagoon but it is visibly concentrated over areas of heavy plant growth. This shows up as an uneven or blotchy pattern in the milkiness produced by the pipe-clay in suspension. No attempt has been made to measure this variation accurately but the average precipitating pipe-clay sample collected contained 0.05 grams of solid in 100 cc. of water.

Composition of the Precipitating Pipe-clay

Magnesian calcite and calcian dolomite have been found in varying amounts in all of the precipitating pipe-clays. The two carbonates are by far the dominant constituents in all precipitates. Some halite precipitates during the drying of the samples but can be removed by washing with distilled water.

X-ray powder diffraction patterns of the washed and dried samples usually only showed the broad reflections of the two precipitating carbonates and less intense but well defined reflections from shell calcite. Occasionally a clay mineral can be identified and often a small amount of quartz also. Celestite, quartz and clays can be easily distinguished after the carbonates have been dissolved in dilute HCl.

The quartz and clay minerals appear to be contaminants, perhaps windblown from the nearby sand dunes. They are present in small amounts and never exceed 1% of the whole. Celestite, as discussed later, appears to be a precipitate from the saline waters, coming out of solution at the same time as the carbonates.

In the collection of the precipitating pipe-clay samples it was inevitable that some of the abundant animal and plant life in the waters would be collected also. Every sample contains some of the molluscs, ostracods, shrimps and gastropods as well as some of the plant spores growing in the waters. The animals have hard parts composed of almost pure calcite. This shell calcite shows up on the diffraction patterns of the precipitating pipe-clays as a third peak with a d(112) of approximately 3.03Å. This peak does not interfere with the peaks of the precipitating carbonates and is very easily identified.

The compositions of the carbonate minerals in the pipe-clay have been determined from their d(112) values. The magnesian calcites have a composition range of ($Ca_{77}Mg_{23}$) to ($Ca_{84}Mg_{16}$) corresponding to a d(112) of 2.97Å and 2.99Å respectively. The dolomite has a d(112) of 2.91Å and is constant within the limits of experimental error for all precipitating pipe-clays and corresponds to a dolomite composition of $Ca_{56}Mg_{44}$. Often, however, the dolomite reflection is too low in intensity or too asymmetric for accurate measurement.

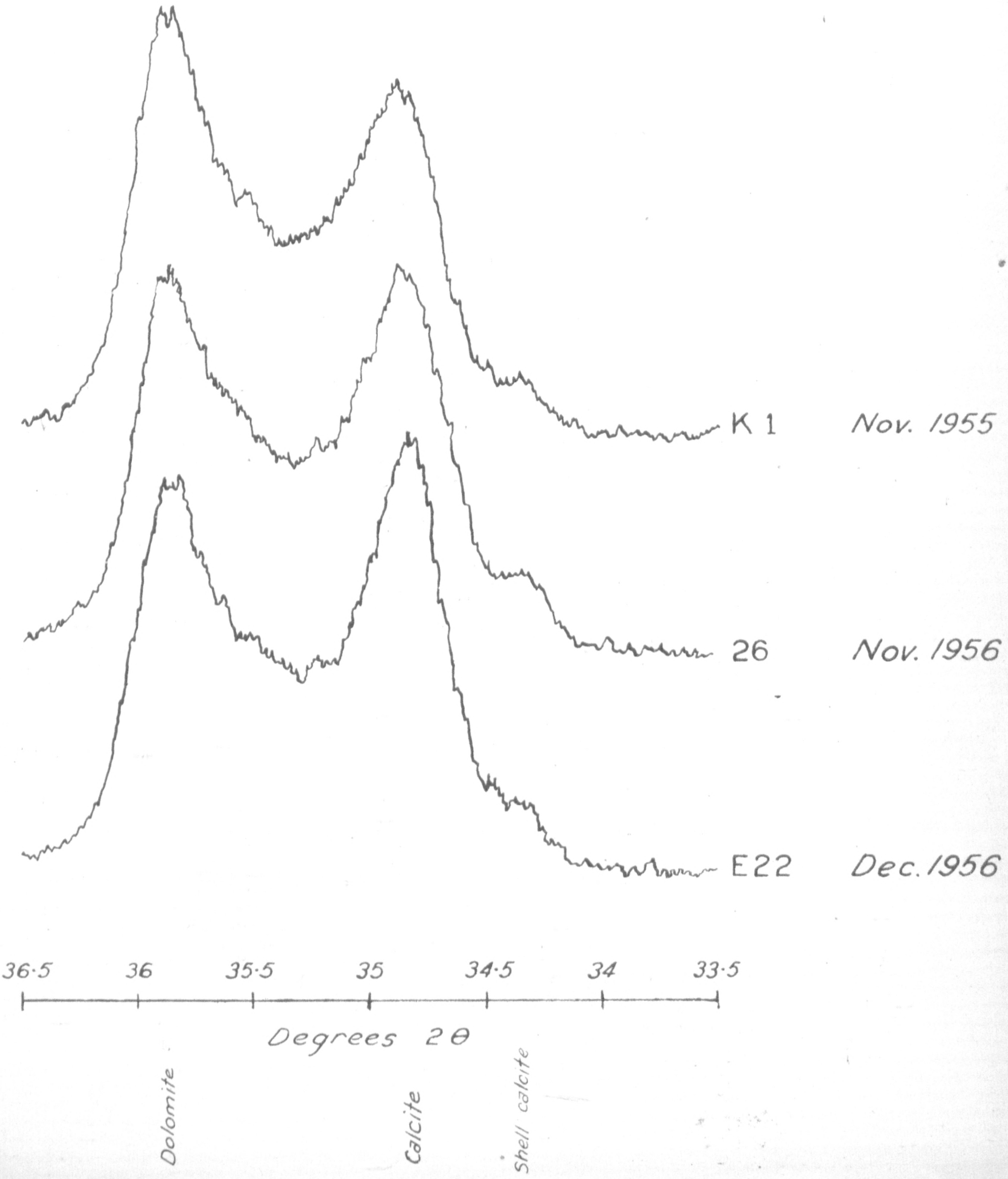
The magnesian calcite precipitating in a particular lagoon seems to have a constant composition no matter where or when the sample is collected. Kingston Lake which has been sampled for two years (1955 and 1956) provides a unique group of samples. Several precipitating pipe-clays were taken at different times and different places in the lagoon during the second year. In all of these samples the magnesian calcite has a composition of ($Ca_{84}Mg_{16}$). However, samples collected in the Coorong at the same time as those in Kingston Lake (December 1956) showed a calcite composition of ($Ca_{77}Mg_{23}$). Thus the magnesian calcites of the Coorong samples have a composition that is measurably different from the composition of the magnesian calcites precipitating in Lagoon M and Kingston Lake at the same time.

The intensity of the magnesian calcite and calcian dolomite (112) reflections is a direct expression of their amounts in the sample. The calcite/dolomite ratio is distinctive for a particular lagoon or particular position in the Coorong. This ratio remains constant during the year and

Fig. 11

Intensity Profile of precipitating pipe-clays.

Collected in Kingston Lake



from year to year within the limits of observation, but varies from lagoon to lagoon and from place to place in the Coorong. Fig.11 illustrates the constant composition and the calcite/dolomite ratio in Kingston Lake samples collected at different times. Kingston Lake and Lagoon M show well defined calcite and dolomite reflections of approximately equal intensity. The Coorong samples show much less intense dolomite reflections relative to calcite.

It is most interesting that precipitating pipe-clay samples from different localities do not have magnesian calcites of the same composition nor the same calcite/dolomite ratio. Another interesting relation can be pointed up by considering the precipitating pipe-clays in order of their geographic occurrence. Samples from Kingston Lake are the southernmost precipitating pipe-clay samples collected and consequently the furthest from the present open sea. Lagoon M is just 7 miles north of Kingston Lake but is a true lagoon and is not in any way connected with the open sea. The portion of the Coorong sampled is the southernmost portion and lies south of the Causeway. In a normal year Sample E12, the most northerly precipitating pipe-clay collected, would be at the southern most position of unrestricted flow of the Coorong waters. E12 was not observed in precipitation (see Appendix).

Fig.12 shows the localities of the precipitating samples discussed. Accompanying the map is Fig.13 which gives the diffraction patterns of the samples located on the map. The diffraction patterns are arranged in geographical succession

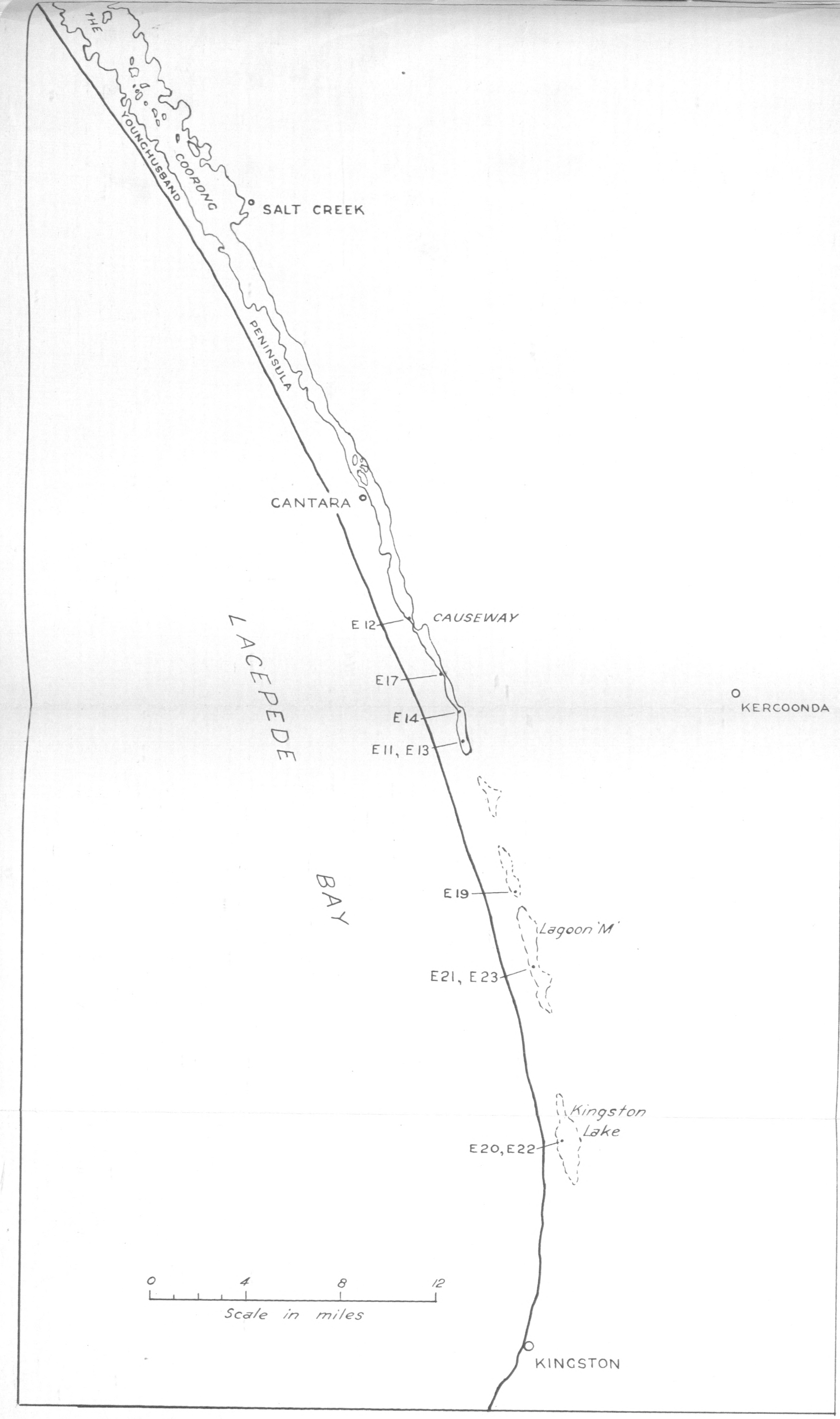
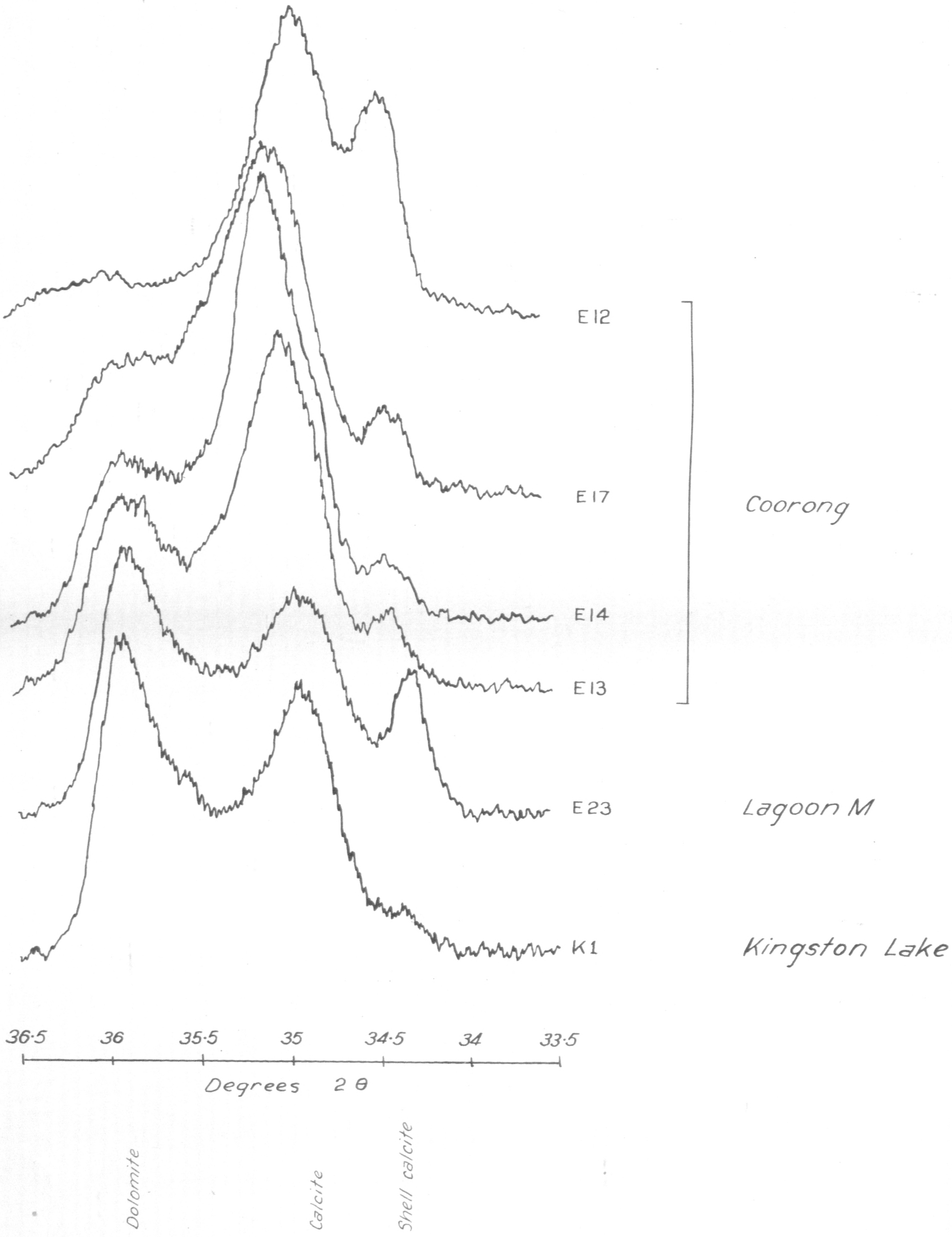


Fig. 12 *Map of Coorong and lagoons showing location of pipe-clay samples collected in active precipitation.*

Fig. 13

Intensity Profiles of precipitating pipe-clays



from north to south. The northernmost sample E 12, on the map is at the top of the group of profiles. Kingston Lake sample K1, being the southernmost sample is at the bottom of the group.

The increase of dolomite relative to calcite in the samples from north to south is striking. Sample E12 at the top has virtually no discernable dolomite. As we proceed further south with each sample in the Coorong there is a steady increase in the amount of dolomite relative to calcite, Still further south, in the isolated Lagoon M and Kingston Lake the dolomite to calcite ratio reaches a maximum.

Another interesting fact concerns the composition of the magnesian calcites. Kingston Lake samples have the lowest magnesium bearing calcites, ($Ca_{84}Mg_{16}$). The Coorong samples as a group have the highest magnesian content calcites ($Ca_{77}Mg_{23}$).

It would seem that as the amount of calcian dolomite decreases the magnesian calcite becomes more magnesium rich which is exactly opposite to the conclusion drawn from the bore hole samples. It is at present impossible to ascertain the precise amounts of calcian dolomite and magnesian calcite present in any particular sample (see discussion under X-ray Methods, Intensity). Only relative amounts of these two constituents can be determined. However, assuming that calcite and dolomite have (112) reflections of equal intensity, the southernmost lagoon samples are estimated to have a much more magnesium-rich total composition than the Coorong samples. Thus, the amount of magnesium coming out of solution in the carbonates at present precipitating from the saline waters appears to increase as we move south down the Coorong and becomes a maximum in the isolated lagoons. This point could only be tested by collecting large enough samples of the precipitating pipe-clay to allow bulk analyses to be made, or by making a series of water analyses. In this way the Ca/Mg ratio of the pipe-clay and of the saline waters could be determined and the variations should give a quantitative measure to the qualitative relations discovered in the present study.

The samples from Lagoon M and Kingston Lake show approximately equal calcite and dolomite intensity profiles. These samples represent the highest amount of dolomite relative to calcite observed in actual precipitation. Thus, conditions in the enclosed lagoons appear to be most favourable for the precipitation of dolomite.

The gradual decrease of dolomite relative to calcite in the Coorong samples must indicate gradually changing conditions, and specifically those conditions that favor the precipitation of the dolomite phase over the calcite phase as we move south. It is interesting that the amount of dolomite decreases as the distance from the open sea decreases. Sample E12, precipitating from water which is in direct connection with the sea contains little or no dolomite.

The marked and consistent relations between the calcite and dolomite discussed above indicate that the dolomite forming in the South East of South Australia is not secondary, that it is not forming by alteration of a precipitated magnesian calcite, but is a primary phase, and is co-precipitating with a magnesian calcite phase directly from saline waters.

STRONTIUM DISTRIBUTION

Celestite, $SrSO_4$, has been identified in many pipe-clay samples. Since Sr may, in small amounts, enter into solid solution with the rhombohedral carbonates it was necessary to determine if all the Sr was present as the sulphate. If Sr had entered into solid solution in calcite the X-ray method of determining the Mg content of the calcites could not have been used. The shift in (112) spacings would represent a change in cell size in response to two elements, Mg and Sr, each having opposite effects. Mg would act to shrink the cell, while Sr, larger in ionic size, would act to expand the cell and measurement of one variable could not have determined the precise composition of the calcite.

A number of pipe-clay samples were analysed for Sr using the X-ray fluorescent spectroscope of the C.S.I.R.O., Division of Soils. Dr. K. Norrish directed the writer in the mechanical details of the analysis and the method of calculation of results. The percent of Sr in each sample is given in the appendix along with the other data obtained for each sample.

Table 4 accompanying this section is a summary of the Sr data for the samples studied by the writer. The table is arranged by sample number, not geographic occurrence, although some attempt has been made to take up the groups of samples in the same order as they were discussed in the main body of the thesis. Hence, the A78 series samples are first, lower South East samples second and upper South East samples third. The main portion of samples in the Coorong and the lagoons are the next few columns. The samples of the precipitating pipe-clays and some of the waters collected in the Coorong and the lagoons are the last section.

The accuracy of the analyses is 5 to 10 percent of the component. The smaller amounts of Sr, i.e. less than 0.1 percent, are about 10% accurate and the higher amounts of Sr, i.e. greater than 0.1%, are about 5 to 7% accurate. It is felt that greater accuracy than this is not warranted, although, using the X-ray fluorescent spectroscope, greater accuracy could have been obtained if desired.

To determine if **Sr** had entered the carbonate structure it was necessary to take a weighed amount of a sample analysed for Sr by X-ray spectroscopy, dissolve the sample in dilute hydrochloric acid until the carbonate minerals were completely dissolved; weigh and analyse the residue to determine its constituents. In all the pipe-clays analysed in this manner the amount of Sr determined spectroscopically could be definitely accounted for by the amount of celestite in the residue. The method of analysis described above is crude but since the amount of Sr determined by the spectroscopic method in any sample was never more than 1%, the amount of Sr actually available to enter the calcite structure would be negligibly small. It was felt, therefore, that the determination of the Mg content of the calcite by measurement of the (112) spacing was valid for the pipe-clays and that all the Sr present should be considered as celestite.

Celestite may precipitate inorganically in marine sediments and it is known that Sr may substitute for Ca in anhydrite and in aragonite up to 4% Sr (Rankama and Sahama, 1950, p.479-480). It is also known that the tests of some radiolarians are $SrSO_4$. These radiolarians however, are found only in deep sea deposits. The celestite in the precipitating pipe-clays is almost certainly an inorganic precipitate, although organisms may play an important role in triggering the precipitation. Although it has not been definitely proven that the Sr is not present as animal tests, no skeletons could be detected in the residue after acid treatment under a magnification of 1250x.

One of the most interesting results of the X-ray spectroscopic study was the discovery that the pipe-clays contained much more Sr than the sands below them. In fact, the pipe-clays still in suspension when collected, as a group, have the highest Sr content. Also, pipe-clay samples near the surface were usually more Sr rich than deeper ones.

The range of Sr content in the samples studied was from a trace (less than 0.001%) to 1.12% Sr. The sands below the pipe-clay usually contained about 0.1% Sr, although occasionally, where a great many carbonates were present, the sands contained as much as 0.3% Sr. The pipe-clays contained from 0.3 to 1.12% Sr.

The lower South East samples contained less Sr than those of the upper South East, although it should be pointed

TABLE 4

Sr Content of all Samples Studied

Sample No.	Sr %	Sample No.	Sr %	Sample No.	Sr %	Sample No.	Sr %
SAMPLES COLLECTED PRIOR TO PRESENT STUDY							
A78.1	.56	A78.11	.09	A78.18	.23	A78.26	.08
.2	not done	.12	.09	.19	.30	.35	.23
.6	.34	.13	.09	.20	.30	.36	.24
.7	.15	.14	.09	.22	.14	.37	-
.8	.06	.15	.34	.23	.25	.38	.13
.9	.06	.16	.28	.24	.08		
.10	.08	.17	.24	.25	.07		
LOWER SOUTH EAST SAMPLES							
W1-1	.01	W2-4	.28	W6-2	.28	W8-2	-
1-2	.08	2a	-	6-3	.18	9	.04
1-3	.06	3-1	-	6-4	-	10-1	-
1-4	.10	3-2	-	7-1	-	10-2	.03
1-5	.03	4	-	7-2	-	10-3	.15
2-1	.24	5-1	-	7-3	-	10-4	.07
2-2	.23	5-2	-	7-4	-	10-5	.05
2-3	.28	6-1	.21	8-1	-		
UPPER SOUTH EAST SAMPLES							
U1-1	.05	U4-1	.05	U7-2	.17	U10-5	.03
1-2	.01	4-2	.02	7-3	.31	11-1	.01
1-3	.01	4-3	.12	7-4	.43	11-2	.27
1-4	.04	4-4	.06	8	-	11-3	.38
2-1	.03	5-1	.28	9-1	-	11-4	.32
2-2	.10	5-2	.22	9-2	-	12-1	.13
3-1	.13	5-3	.02	10-1	.18	12-2	.13
3-2	.01	5-4	.02	10-2	.13	12-3	.03
3-3	.04	6	.29	10-3	.16	12-4	.01
3-4	.01	7-1	.26	10-4	.25	12-5	.03

TABLE 4 (cont.)

Sample No.	Sr %	Sample No.	Sr %	Sample No.	Sr %	Sample No.	Sr %
INTERDUNAL, COORONG AND LAGOON SAMPLES							
D7	not done	D21	.15	D35	.02	D49	.44
8	.24	22	.01	36	.02	50	.44
9	.12	23	.03	37	.04	51	.49
10	.18	24	.02	38	.24	52	.23
11	.01	25	.05	39	.40	53	.53
12	.01	26	.08	40	.23	54	.23
13	.12	27	.20	41	.24	55	.38
14	.02	28	.18	42	.08	56	not done
15	.05	29	.01	43	.09	57	not done
16	.17	30	.01	44	.13	58	.20
17	.20	31	.13	45	.10	59	.49
18	.15	32	.20	46	.27	60	.24
19	.01	33	.08	47	.24	61	.17
20	-	34	.19	48	.60	62	.02
						63	.16
KINGSTON LAKE SAMPLES							
S1-1	.60	S2-1	.48	S2-14	.27	S3-9	.62
1-2	.40	2-2	.58	2-15	.24	3-10	.80
1-3	.365	2-3	.58	2-16	.20	3-11	.71
1-4	.27	2-4	.56	2-17	.15	3-12	.745
1-5	.16	2-5	.57			3-13	.66
1-6	.16	2-6	.46	S3-1	.51	3-14	.40
1-7	.26	2-7	.54	3-2	.40	3-15	.24
1-8	.31	2-8	.47	3-3	.66	3-16	.465
1-9	.31	2-9	.36	3-4	.64	3-17	.26
1-10	not done	2-10	.425	3-5	.61	3-18	.31
1-11	.13	2-11	.35	3-6	.67	3-19	.18
1-12	.16	2-12	.28	3-7	.89		
1-13	.10	2-13	.23	3-8	.78		
LAGOON M SAMPLES							
S4-1	.49	S4-8	.66	S4-15	.615	S4-22	.31
4-2	.51	4-9	.30	4-16	.29	4-23	.28
4-3	.46	4-10	.30	4-17	.32	4-24	.31
4-4	1.12	4-11	.59	4-18	.53	4-25	.31
4-5	.38	4-12	1.12	4-19	.30	4-26	.32
4-6	.45	4-13	.95	4-20	.25	4-27	.29
4-7	.46	4-14	.93	4-21	.28	4-28	.29
						4-29	.30
						4-30	.315

TABLE 4 (cont.)

SAMPLES OF PRECIPITATING PIPE-CLAYS

Sample No.	Sr%	Sample No.	Sr %	Sample No.	Sr %
K1	.44	E12	.37	E19	.56
26	.70	E13	.57	E20	.28
27	not done	E14	.60	E21	1.12
E11	.37	E17	.55	E22	.53
				E23	.70
				54	.42

out that fewer samples were collected from the lower South East than from the upper section, and hence this observation may not be significant.

From Table 4 we see that samples A78-1, 6 and 15 contain the highest amounts of Sr in this group. These samples are all surface samples of pipe-clay and all contain both calcite and dolomite. The bore hole put down in Lake Hawdon North, samples A78-15 to 26 shows considerable Sr content in the upper pipe-clay layers but the Sr content lessens in depth.

The samples of the W group from the lower South East all contain less than 0.28% Sr. Bore W2 put down six miles west of Naracoorte shows the highest Sr content throughout the section of dark grey soil. Bool Lagoon bore W6 shows 0.28% Sr in a pipe-clay layer between 6 and 12 inches. Both these bores contain carbonates. It is interesting that other pipe-clay samples from this group W1-4 and W10-3 show the highest Sr percent in their particular bores. The sands and siliceous soils collected in the lower South East showed no detectable Sr. The obvious conclusion to be drawn here is that Sr is preferentially concentrated with carbonates.

The upper South East samples (U1 - U12) collected inland from the Coorong, show somewhat higher Sr as a group than the lower South East samples. The highest Sr content 0.43%,is recorded in U7-4, a pipe-clay sample which contains both calcite and dolomite. Two inches of grey sand above this pipe-clay also shows quite a high Sr content (0.31%). It is notable that bore U11 in the clay pan near Meningie shows high Sr content throughout and the highest, 0.38% Sr, in a gypsum-rich clay layer 2 to 4 inches in depth. Other reasonably high Sr samples, U5-1 and U6, are surface scums both of which show carbonates on X-ray analysis. U10-4, another clay pan bore contains 0.25% Sr and gypsum but no carbonates were detected on X-ray analysis.

The D series samples collected along the Naracoorte-Kingston train line show minor Sr compared to the Coorong and lagoon samples. Samples D39 to D48, D49, D51 and D59, the pipe-clay layers of Kingston Lake, Lagoon M and the Coorong respectively, all show high Sr values. However, D48, a carbonate-cemented sand underlying the pipe-clay of Lagoon M (samples D46, 47) in another section of the lagoon, shows the highest value recorded in the D group of samples, 0.60% Sr.

The more extensive and precise sampling of Kingston Lake in the three bores S1, S2 and S3 showed high Sr content in the pipe-clay layers represented by the following samples: S1-1 to S1-3, S2-1 to S2-10, S3-1 to S3-14. The sands under the pipe-clay layers contained relatively more Sr than most previously discussed sands.

Lagoon M bore, S4, is consistently high in Sr. Samples S4-4 and S4-12 show over 1% Sr. These two samples appear to be highs in two general Sr increases. Samples S4-13 and S4-14 show 0.9% Sr and five other samples representing inch sections in the bore show over 0.5% Sr. It is also noteworthy that the pipe-clay in active precipitation in Lagoon M, sample E21, showed 1.12% Sr.

The highs of Sr in the Lagoon M bore do not seem to have any direct correlation with the precipitation of carbonate minerals. There is no observable corresponding increase or decrease in the amount of carbonate minerals or any preference for one phase over the other when the Sr content increases. The overall trend of the calcite and dolomite precipitation does not appear to change with Sr increase. In all cases where the Sr is high both magnesian calcite and calcian dolomite are precipitating and the only variation in the calcite/dolomite ratio corresponds to the position of the sample in depth as discussed previously. The only conclusion one can make concerning Sr relative to calcite and dolomite is that the conditions under which the celestite precipitates are obviously also favourable for the precipitation of the carbonate minerals as well.

The precipitating pipe-clay samples show high Sr content in all cases. The highest, E21, has already been mentioned as collected in Lagoon M, as is sample E23 (0.70% Sr). Three separate precipitating pipe-clays have been collected from Kingston Lake. Sample 26 contains 0.70% Sr and K1, 0.44% Sr. Sample E22 collected in December 1956 from Kingston Lake contains 0.53% Sr and shows a large number of spore cases which have been shown to be composed of magnesian calcite and calcian dolomite.

The variation in Sr content in samples from the same lagoon can be explained in a number of ways: by changes in the exact locality of the specimen, influence of plants, pH, salinity, temperature, time of day (though this should be expressed in the variables already mentioned) and the weather. However, unless many more samples are collected under known conditions an unequivocal description of the conditions most favourable for the precipitation of celestite cannot be given. Obviously, just such data are necessary to define the precipitation of the carbonates also. The precipitation of celestite is an allied effect most probably intimately associated with the carbonate precipitation, and probably due to the same causes. The possible variables are discussed in the next Chapter.

The group of Coorong precipitating pipe-clays show somewhat less Sr than the lagoonal precipitating pipe-clays. It should be pointed out that sample E12 from the Coorong is the only pipe-clay sample which does not contain dolomite. The relative amount of dolomite to calcite in the Coorong samples is less than the amount of dolomite relative to calcite in the lagoons. Calcite is the dominant precipitating carbonate phase in all the Coorong samples.

Strontium in the Water Samples

Since we are only giving Sr content data on the precipitated pipe-clay, or suspended solids, we have not actually

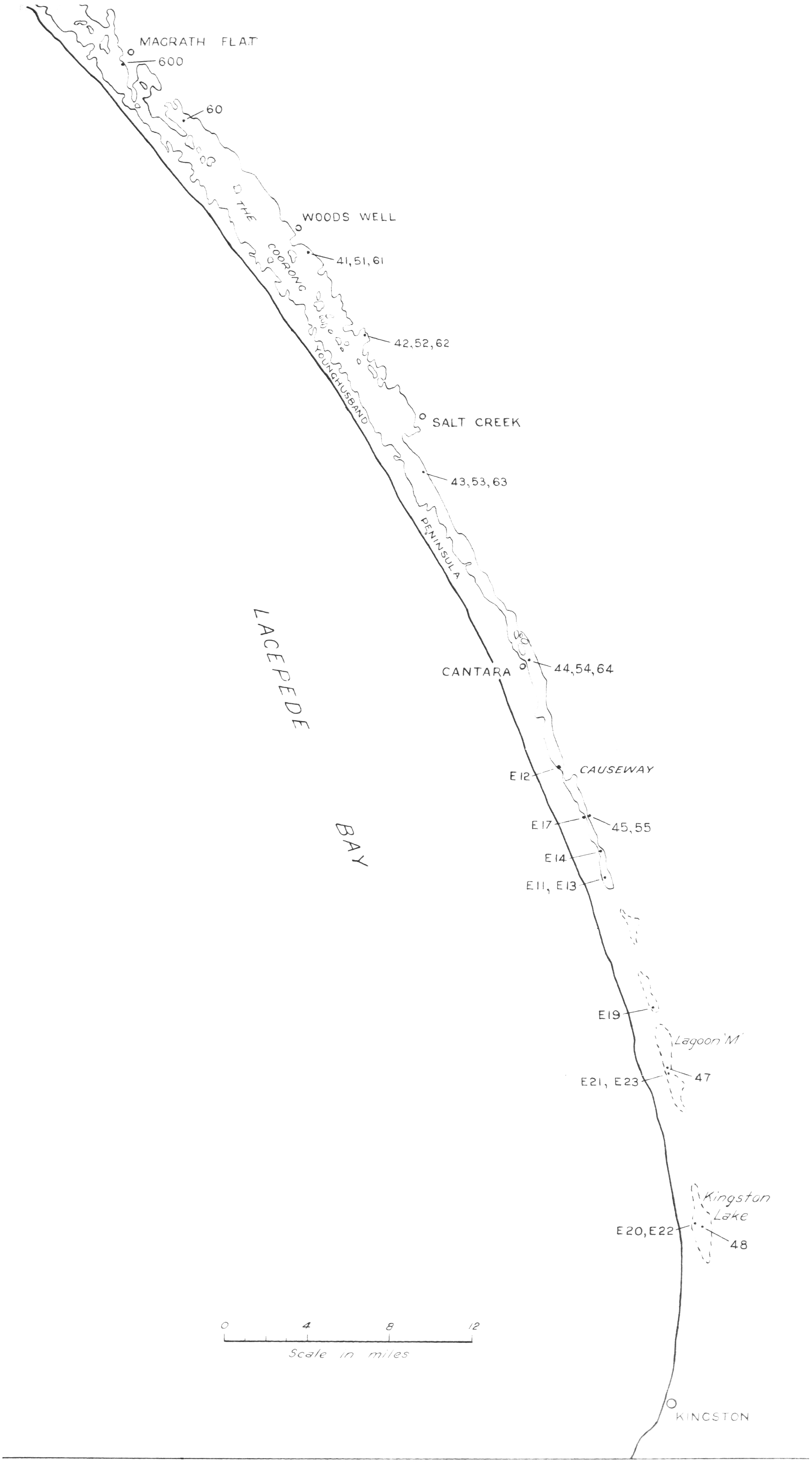


Fig. 14 Map of Coorong and lagoons showing location of pipe-clay samples collected in active precipitation, also water samples.

given the Sr content of the water from which the solids precipitate. Because a particular precipitating pipe-clay contained less Sr it may be inferred that the water from which it precipitated contained less Sr. This inference can easily be tested in the waters from the Coorong and lagoons of the South East. The Sr content of the water from several localities was obtained in November 1957 by X-ray fluorescent spectroscopic analysis of the residue of the waters after evaporation. The evaporation was carried out in the laboratory. The predominant constituent of all these water samples was, of course, halite.

The figure quoted for the Sr content of the waters is actually the percentage of Sr in the total dissolved solids. In this way variations due to salinity are eliminated. It is of course self-evident that the total Sr will increase with increasing salinity, unless a Sr salt precipitates from solution.

Fig.14 shows the localities where water samples were collected. It is unfortunate that 1957 has been a dry year and Kingston Lake, Lagoon M and the southern end of the Coorong dried up in October instead of January, 1958. For comparison, the precipitated pipe-clay samples E12 to E23 collected in December, 1956 along the Coorong and in the two lagoons, have been included in Fig.14 as well.

On the first trip in early October water samples 41 to 48 were collected. Three weeks later no water was found in the lagoons and only four water samples 51 to 54 could be collected in the Coorong. Similarly, three weeks later in mid-November only the four samples, 61 to 64 from the Coorong had any water and the most southerly or fourth locality (64) was precipitating halite from a concentrated brine. Two samples were collected further north in the Coorong on this trip. Sample 600 was taken at Magrath Flat and 60 collected four miles south of Magrath Flat, in a large shallow bay in the Coorong.

Samples 41 to 44, 51 to 54 and 61 to 64 were collected at the same localities at three-week intervals. By collecting samples at identical localities the Sr content of the water could be measured and observations could be made on any changes before and after any precipitation which might take place. Due to the dry year precipitation was not observed in the lagoons. However, sample 54 from Cantara was collected on November 2nd when the water was slightly cloudy with white pipe-clay in the process of precipitation. X-ray analysis of the solids showed both magnesian calcite and calcian dolomite were precipitating with three times as much calcite as dolomite. This precipitating pipe-clay at Cantara is very similar to the pipe-clay which precipitated in the southern portion of the Coorong last year (1956).

Table 5 presents the Sr content of the water samples collected to date in 1957. The range of Sr content is from 0.016% Sr to 0.102% Sr with most samples showing about 0.02% Sr. Comparing the three water samples from identical localities,

TABLE 5

Sr content of water samples

Sample No.	Sr %	Salinity %
41	.016	3.99
51	.0195	4.29
61	.0182	4.95 *
42	.023	4.04
52	.0184	4.40
62	.020	5.34 *
43	.022	4.53
53	.0184	5.79
63	.0182	6.60 *
44	.040	10.0
54	.0332 ppt. (.42%)	14.14
64	.0225	28.61 *
45	.065	6.85
47	.102	3.1
48	.031	5.3
60	.0193	6.47 *
600	.0196	3.00 *

* Salinity measured by evaporation of known quantity of water in laboratory. Other salinities done by Mines Department.

41, 51, 61; 42, 52, 62; and 43, 53, 63 it appears that all the Sr percentages are similar. Considering the evaporation method used and the possibilities of not having a truly even mixture of the salts for the spectrographic analysis the results must be considered identical. In these samples then, no systematic variation can be demonstrated due to locality or time of sampling. The fourth locality, Cantara, where three samples have also been collected, 44, 54, 64, shows somewhat higher initial Sr content which has decreased over the period of six weeks to the same level as the other Coorong samples. Sample 64 was collected from shallow, very saline water and 54 contained pipe-clay in suspension. The Sr percent of the precipitating pipe-clay was 0.42%.

It is interesting that the highest Sr content of the waters analysed is 0.102% Sr from Lagoon M where last year a sample of precipitating pipe-clay contained 1.12% Sr. The most northerly samples 60 and 600 show about the same amount of Sr as other Coorong samples collected on the same trip.

Odum (1951) demonstrated that the Sr content of sea water varies with salinity; the higher the salinity the higher the relative amount of Sr. Table 5 gives the salinities of the water samples as well as the Sr content. From the water samples collected in the South East there does not appear to be any significant relation between salinity and Sr content. Lagoon M with the highest Sr content has one of the lowest salinities. In any of the localities where three samples have been taken the salinity has increased with time but the Sr content does not show significant variation.

The Sr content of the water is very small compared to the pipe-clay samples. The Sr in solution comes out at the same time as the carbonates precipitate. The method of precipitation of the Sr is linked to the carbonate precipitation and a general discussion of the entire problem including the $SrSO_4$ precipitation, is given as part of the summary.

Discussion and Summary

Turkian and Kulp (1956) give average figures for Sr content in various rocks of the earth's crust. Limestones, for instance, average 610 ppm Sr, (0.061% Sr). They also point out that the Sr content increases with time. The most recent limestones have the highest Sr content.

Most of the samples from the South East of South Australia showed higher Sr contents than 0.06%. The sands below the pipe-clays contained between 0.03 and 0.20% Sr. Pipe-clays from the Coorong and the lagoons to the south of it contained from 0.30 to 1.1% Sr, with the most frequent amount being 0.55%. Precipitating pipe-clays showed a range of 0.40 to 1.1% Sr with the most frequent amount being 0.70%. Quite obviously the South East is a Sr-rich province, since most of the pipe-clay samples contain nearly 10 times the amount of Sr found by Turkian and Kulp in limestones of the past. The South East appears therefore to be outstanding for its high

Sr content as well as its carbonate precipitation. That the two are connected seems obvious but their individual responses to the various physical changes that occur is unknown.

Briefly summarising the data of the Sr content in samples collected in the South East of South Australia a few points should be listed.

1. The carbonate deposits forming in the South East today contain about 10 times as much Sr as the average figure found for limestones throughout the world, of all ages.
2. The lower South East samples contained much less Sr than the upper South East samples.
3. The higher Sr contents are associated with the precipitated carbonates, calcite and dolomite, and not with shell fragments or the sands below the pipe-clays.
4. High Sr seems to be found most often with dolomite and calcite, only occasionally without any carbonates present. Where carbonates are absent, gypsum is present. In this case it is probable that the Sr is present in solid solution in the gypsum.
5. The amount of Sr in a pipe-clay sample appears to vary independently from the calcite and dolomite variations.
6. There is no apparent relation between the Sr content of a pipe-clay and the depth, as there is in the calcite to dolomite ratio.
7. The Sr occurs in celestite, $SrSO_4$, and is believed to be inorganically precipitated.

8. The environment favourable for the precipitation of celestite is also favourable for the precipitation of calcium and calcium-magnesium carbonates. The two effects however, do not appear to respond to variations in the physical conditions in the same way.

9. There does not seem to be a consistent relation between salinity and Sr content of the waters. Within the Coorong the salinity increases as we move south, but the amount of Sr relative to the total salts remains essentially constant. This is contrary to the effect to be expected from Odum's (1951) work. During the summer months evaporation slowly increases the salinity of the water in the Coorong. At any given locality then, there is a progressive increase in salinity during the summer. There is no parallel increase in the amount of Sr relative to the other salts. There is of course, an increase in the total Sr in the waters due to the increase in the total salts in solution.

10. Lagoon M, an isolated body of water fed by surface run-off, is a very high Sr region. The waters in Lagoon M contain approximately 5 times as much Sr in solution, relative to other salts, as the waters in the Coorong and other lagoons. The pipe-clay in Lagoon M is also much richer in Sr than other lagoons and the Coorong. The high Sr in the pipe-clay must surely be a direct result of the high Sr content of the waters. The

reason for the high Sr content of the waters in Lagoon M is not known, but is certainly worthy of further investigation.

DISCUSSION OF PIPE-CLAY FORMATION

Results and conclusions have been discussed in detail at the close of individual chapters in the body of the thesis. Nevertheless, it is instructive to briefly ennumerate the main points again. First, it has been established that the pipe-clay in the South East of South Australia consists essentially of very fine-grained magnesian calcite and calcian dolomite in varying proportions. Celestite, quartz, clays, shells and plant remains are the other materials present. Secondly, it has been established that pipe-clay has formed extensively in the past in the South East, and that the method of formation is probably the same as that observed in the modern Coorong and associated lagoons.

Regular and significant variations in the calcite/dolomite ratio and in the calcite compositions have been demonstrated, both geographically and stratigraphically. No complete explanation for these variations has been found.

Calcite and dolomite have been observed in direct precipitation from the waters of the Coorong and lagoons south of it. The composition and relative amounts of the two precipitating carbonates shows a regular variation with geographic location. These two points, in particular the first, suggest that Mawson (1929) and Forbes (1955) were incorrect in suggesting that the dolomite in the pipe-clay was formed by metasomatic replacement of calcite soon after precipitation. For the same reason it is considered unlikely that the dolomite forms by exsolution from magnesian calcite.

The precipitation of the carbonates occurs in waters which closely approximate sea-water in the relative amounts of the various salts present, but which show a wide variation in the salinity. Precipitation occurs in waters with a salinity range from about half that of sea-water (Kingston Lake, Alderman and Skinner 1957) to at least four times that of sea-water (14.14%, observed by Professor A.R. Alderman at Cantara Causeway, November 1957). The precipitation has been repeatedly observed when water-plant growth is most vigorous and has been specifically noted to be concentrated over areas of heavy plant growth in the waters. The obvious conclusion to be drawn from these observations is that the plants in some way cause or trigger the precipitation of the carbonates. Alderman and Skinner (1957) ascribe the cause to elevated pH due to active photosynthesis of the plants.

Although the precise conditions and mechanisms for the precipitation of calcite and dolomite from the waters of the South East cannot be defined, the factors controlling the precipitation of carbonates from aqueous solution can be presented.

The general theory and chemisty of $CaCO_3$ precipitation from aqueous solution are lucidly given by Johnston (1915, 1916) and Johnston and Williamson (1916a, 1916b). Of these four papers, the joint discussion in the Journal of Geology (1916b) is the most pertinent.

The solubility of calcite in aqueous solution, in the presence of solid calcite, is defined by $[Ca^{++}]\ [CO_3^{=}]$ =

constant at a fixed temperature. $[Ca^{++}]$ designates the concentration of the Ca^{++} ion and $[CO_3^{=}]$ the concentration of the carbonate ion. This equation is independent of the other salts in solution.

The concentration of the $CO_3^{=}$ ion depends on the partial pressure of CO_2 gas in the atmosphere in contact with the solution. The CO_2 in solution is hydrated to H_2CO_3 and the concentration of the H_2CO_3 can therefore be expressed as

$$[H_2CO_3] = cP_{CO_2}$$

where c is a constant and P_{CO_2} is the partial pressure of CO_2. This equation is temperature dependent. The solubility of CO_2 decreases with increasing temperature. The equation is also affected by the other salts present in solution and on their concentrations. This effect is small however, as pointed out by Johnston (1915), and hence salinity variations do not greatly affect the amount of H_2CO_3 in solution.

The H_2CO_3 dissociates as follows:

$$H_2CO_3 \longrightarrow HCO_3^{-} + H^{+}$$

$$HCO_3^{-} \longrightarrow CO_3^{=} + H^{+}$$

and hence the $CO_3^{=}$ becomes available for precipitation of $CaCO_3$. The above relations give to the following mass action equations,

$$\frac{[HCO_3^{-}]\,[H^{+}]}{[H_2CO_3]} = \text{constant}$$

$$\frac{[CO_3^{=}]\,[H^{+}]}{[HCO_3^{-}]} = \text{constant.}$$

It is obvious then, that none of the quantities $[HCO_3^-]$, $[H_2CO_3]$, $[CO_3^=]$ or $[H^+]$ can be varied independently. A variation in any of these would change the others according to the equations given. Similarly, a measure of one of the variables, say $[H^+]$ (e.g. from pH), allows the others to be calculated when the various constants are known.

The main variables that must be considered then, are the temperature and $[H_2CO_3]$. The effect of increasing temperature is to slightly increase the solubility of calcite (i.e. increase the product $[Ca^{++}]\,[CO_3^=]$ but to greatly reduce the solubility of CO_2 in water (i.e. reduce $[H_2CO_3]$). Thus, if a solution saturated in CO_2 is subjected to a sudden temperature increase, $CaCO_3$ will precipitate. If the temperature rise is gradual and the solution is always in contact with the atmosphere, a sudden change in $[H_2CO_3]$ is unlikely to occur, as any excess CO_2 in solution will escape to the atmosphere. For this reason it is considered unlikely that temperature fluctuations could cause the carbonates to precipitate in the Coorong. The main variable that is of importance, as pointed out by Johnston and Williamson, is the sudden reduction of $[H_2CO_3]$ by organic or inorganic means. For instance, plants abstract H_2CO_3 from the water, causing an excess of $CO_3^=$, and at a certain level calcium carbonate precipitates to balance the equation $[Ca^{++}]\,[CO_3^=]$ = constant.

The production of free ammonia by decaying matter or by bacteria will also cause $CaCO_3$ to precipitate by reducing $[H^+]$ (increasing pH) and hence, increasing $[CO_3^=]$.

As previously discussed, the carbonate precipitation in the Coorong and lagoons appears to be associated directly with plant activity. Preliminary measurements have shown that there is a rise of pH (i.e. a decrease in $[H^+]$ and hence an increase in $[CO_3^=]$) corresponding to the daytime activity, and it is logical to ascribe the precipitation of the carbonates to this cause. The plants abstract H_2CO_3 from the waters by photosynthesis during the daytime. The abstraction is more rapid than solution of CO_2 from the atmosphere and hence an equilibrium is not reached and a corresponding pH rise is observed. At a pH as yet undetermined, and possibly temperature and salinity dependent, carbonates precipitate. Under some conditions a pH as low as 8.46 (McClendon, 1918) causes calcite to precipitate from saline solution. In the case of the Coorong and lagoons, the pH is rarely as low as this, and consequently some degree of super-saturation must occur. At what pH the super-saturated solution precipitates is as yet unknown.

It is known (see for example, Atkins 1930) that $MgCO_3$ does not precipitate from solution until a much higher pH than $CaCO_3$ does. The real reason for this is the great difference in the degree of hydrolysis between the calcium and magnesium carbonates in aqueous solution. Atkins (1930) found that pure dolomite in water produced a pH intermediate between calcite and magnesite, and on this basis suggested that pH was the controlling factor in dolomite precipitation. This cannot be the whole explanation, for purely on the basis of ionic equilibria in solution, as presented here, $CaCO_3$ should first precipitate, leaving $MgCO_3$ in solution. The two major factors which are not accounted for in this theory are (a) solid solution of $MgCO_3$ in $CaCO_3$, which modifies all the equations presented, and (b) the degree of super-saturation necessary for precipitation to occur. The first factor is a calculable one, and tends to slightly alter the constants in the mass action equations presented. As Johnston and Williamson suggested, the effect is not large. The second factor, the degree of super-saturation, is less tangible and is almost certainly dependent of the temperature, salinity and composition of the solution. It cannot be evaluated at present, but it is felt that the answer to the Coorong carbonate precipitate may be concealed in it.

It has been previously noted that precipitation occurs over a wide range of salinity. Plants such as Ruppia maritima Linn., which abound in the Coorong and lagoons, can tolerate very wide salinity variations, and hence the prime cause of the precipitation is present through a wide range of conditions. A floral study of the Coorong and lagoons would almost certainly reveal plants other than Ruppia maritima which contribute to the precipitation.

Precipitation occurs repeatedly during the spring and early summer months. The reason this is possible is that the amount of Ca in solution is vastly greater than the Ca precipitated as $CaCO_3$. Only a minute fraction of the Ca present is actually balanced against $CO_3^=$, since sulphate and chloride ions are the most prevalent ones in solution. The percentage of the H_2CO_3 which dissociates to $CO_3^=$ is very small (Johnston and Williamson, 1916b). It is the $CO_3^=$ which is the controlling factor in the precipitation and since this is replenished each evening, the precipitation can occur repeatedly.

Celestite, $SrSO_4$, is also observed to precipitate with the carbonates. $SrSO_4$ dissociates to Sr^{++} and $SO_4^=$ in solution and its solubility is defined by $[Sr^{++}][SO_4^=]$ = constant. Hydration of the $SO_4^=$ radicle means that $[SO_4^=]$is dependent on $[H^+]$ (or pH), and at a certain pH, $SrSO_4$ will precipitate. This pH has not been determined, but is apparently in the same range as the pH necessary for the dolomite and magnesian calcite precipitation. It should be noted that since neither Sr nor $SO_4^=$ are being replenished, in contrast to the $CO_3^=$, repeated precipitation of $SrSO_4$ cannot occur unless the salinity of the water increases continuously. At constant salinity a single precipitation should theoretically remove all the <u>available</u> $SrSO_4$. If the salinity increases progressively by evaporation, this will continuously raise $[Sr^{++}]$ in the solution and allow repeated precipitations of $SrSO_4$ by pH fluctuations, which control $[SO_4^=]$.

The total amount of $SrSO_4$ that can come out of solution is fixed by the total amount in solution at the time of the first precipitation, provided that no addition occurs from external sources. Thus, water high in Sr relative to other salts will precipitate more $SrSO_4$ than the same volume of water, with the same salinity, but lower Sr relative to other salts. This appears to be the explanation of the generally high Sr content of the pipe-clays in Lagoon M compared to other localities. The reason for the enrichment of Sr in the waters is not known though. Also, given two equal volumes of water with the same relative salt compositions but differing salinity, the water with the higher salinity will precipitate more $SrSO_4$. This may be the explanation of the Sr increases at certain levels in the Lagoon M bores. If we assume that a constant volume of water fills that lagoon and if the salinity of this water varies from year to year, higher Sr will be observed in the more saline years. On the other hand, as previously pointed out, $[CO_3^=]$ controls the amount of carbonate precipitating, and since $[CO_3^=]$ is relatively insensitive to salinity changes, the volume of carbonates precipitated will be fairly constant under fluctuating salinities. It is possible that a history of salinity fluctuations may be able to be read in the pipe-clays from their Sr contents.

The most plausible explanation for the salinity variations seems to the writer to lie in the amount of water entering the lagoon through rainfall. If we assume that the salts reaching the lagoon are cyclic-salts from the sea, it seems reasonable to suggest that the lagoon would receive approximately the same amount of salts each year. In a dry year the cyclic-salt will be dissolved in a small amount of water which may just fill the lagoon. In a wet year the same amount of salts will be distributed over a much greater volume of water which may not only fill the lagoon, but also overflow into surrounding swamps and be lost to the lagoon. Thus a dry year would mean higher salinity and hence higher Sr in the pipe-clay.

It is hoped that many of the questions raised by this investigation of the modern carbonate sediments in the South East of South Australia will be answered in the near future by continued systematic study.

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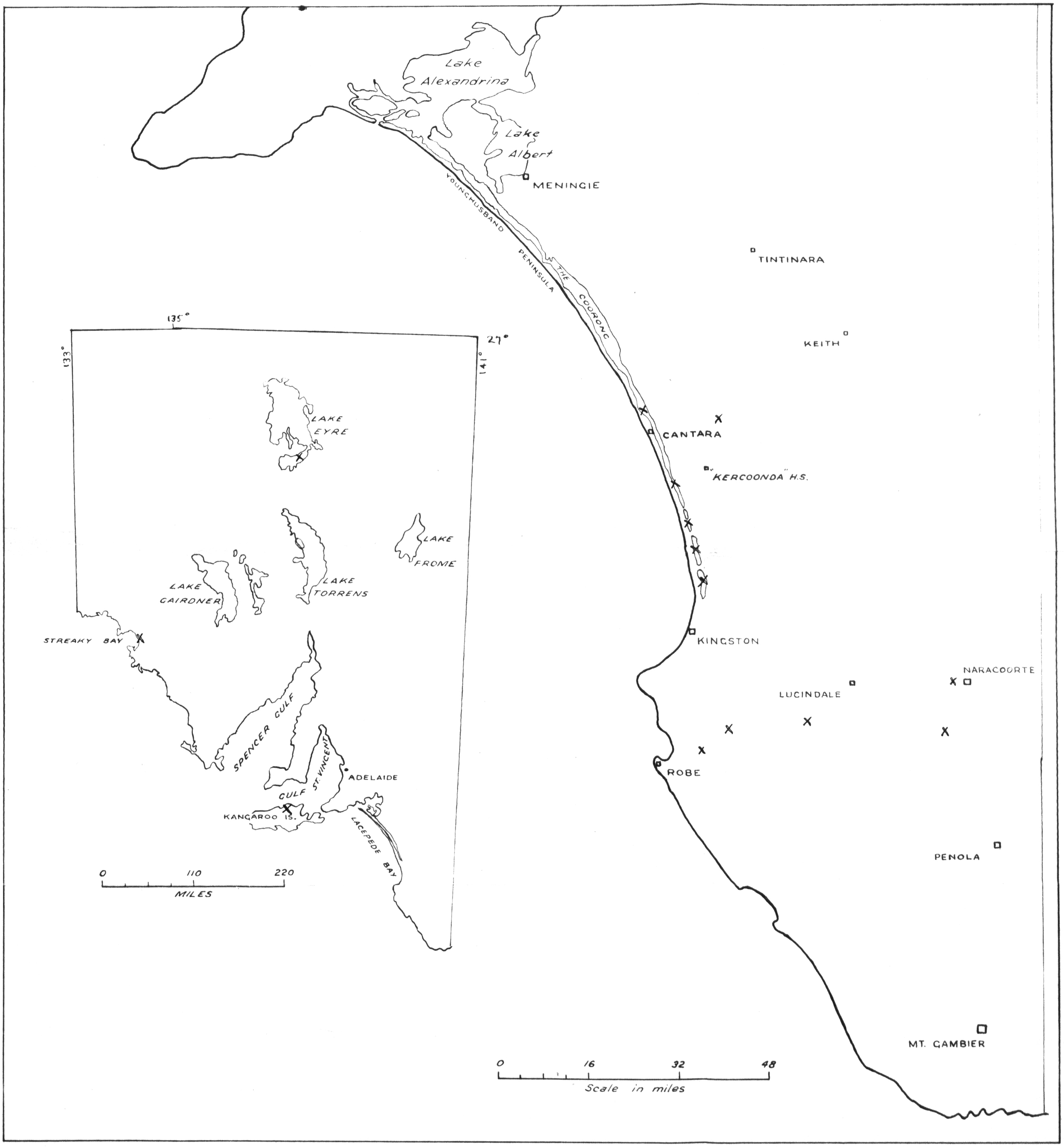

Fig. 2 Pipe-clay localities in South Australia. (x)

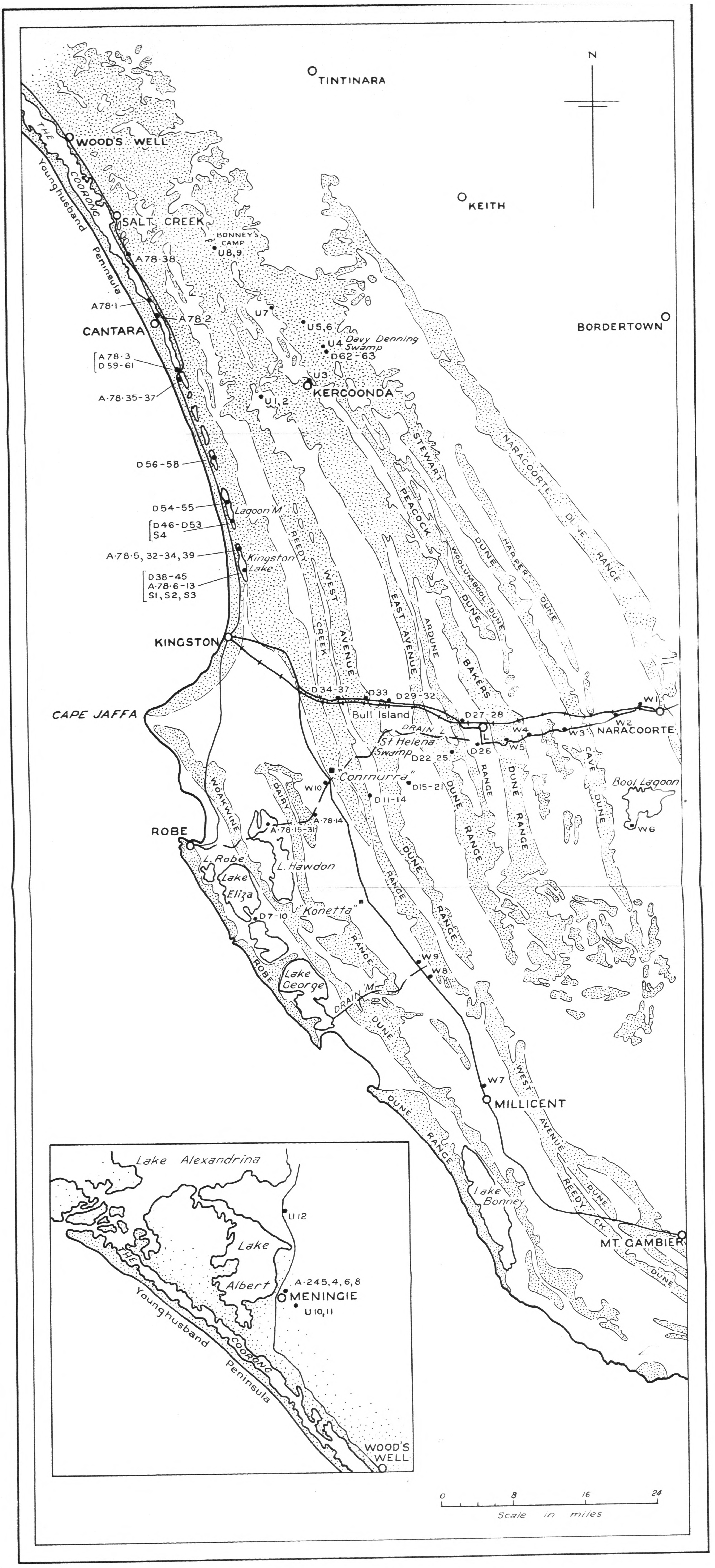

Fig. 1 Topographic map of the South-East of South Australia showing the location of samples.

APPENDIX

COMPILATION OF DATA ON ALL SAMPLES DISCUSSED

Abbreviations used in this table:

Cal ($Ca_{95}Mg_5$) - Calcite present, composition in brackets.

Dol $Ca_{50}Mg_{50}$ - Dolomite present, composition not in brackets.

Cal ($Ca_{95}Mg_5$)(d) - Composition determined using X-ray diffractometer.

qz - quartz, hal - halite, gyp - gypsum, cl - clays, cst - celestite, sh - shell material.

(tr) - trace of component, pl - plant material.

o - surface sample

D.M. - Department of Mines

$R\bar{3}$ - Structural Dolomite, determined by X-ray analysis.

as D54 - Same bore hole as D54 at different depth.

Part anal - Partial chemical analysis.

Sample No.	Location	Depth (inches)	Description	Constituents	Sr %	Comments
A245-4, 6,8 (CSIRO)	Meningie clay pans just E. of town	0	white powder	gyp,hal	not done	called pipe-clay
A78.1	10 m.S.E.Salt Creek	0	pipe-clay	Cal($Ca_{84}Mg_{16}$) Dol $Ca_{55}Mg_{45}$ qz,hal,cl,cst,pl,sh	.56	Part anal.Forbes (1955)
A78.2	13 m.S.E.Salt Creek	0	sand	Cal, qz, sh,pl		
A78.6	Kingston Lake near W. edge	0-2	pipe-clay	Cal($Ca_{91}Mg_{9}$)(d) Dol $Ca_{56}Mg_{44}$(d) qz,sh,cl,pl	.34	Dol. $R\bar{3}$ can be separated by taking finest grain size. Minor sh.Part anal. Forbes (1955)
A78.7	as A78.6	2-4	pipe-clay	Cal, Dol, qz,sh,cl	.15	Dol. dominant. Part anal. Forbes (1955)
A78.8	as A78.6	4-8	quartz sand	Cal($Ca_{95}Mg_{5}$) Dol (tr), qz, cl, sh, pl	.06	Part anal. Forbes (1955)
A78.9	as A78.6	8-12	quartz sand	Cal, Dol (tr), qz, cl, sh, pl.	.06	Part anal. Forbes (1955)
A78.10	as A78.6	12-18	quartz sand	Cal, Dol (tr), qz, cl, sh, pl.	.08	Part anal. Forbes (1955)
A78.11	as A78.6	18-24	sand	Cal, Dol (tr), qz, sh, cl	.09	

A78.12	as A78.6	24-27	sand	Cal, qz, sh, cl	.09	Part anal. Forbes (1955)
A78.13	as A78.6	27-29	dark grey sand	Cal, qz, sh, cl	.09	Gastropods obvious. Part anal. Forbes (1955)
A78.14	Drain L, 4 m.W. Conmurra H.S.	0	shelly sand	Cal, Dol (tr), qz, cl, sh, pl	.09	
A78.15	Lake Hawdon North	0-2	pipe-clay	Cal($Ca_{84}Mg_{16}$) (d) Dol (tr), qz, cl, cst, hal, gyp	.34	Part anal. Forbes (1955). EDTA anal. Hutton, CaO 33.34, MgO 12.40, CO_3 47.09, SO_4 .03, FeO .02. (112)reflection of Cal highly asymmetric toward higher 2θ
A78.16	as A78.15	2-4	grey pipe-clay	Cal($Ca_{98}Mg_2$)(d) Dol $Ca_{56}Mg_{44}$ (d) qz,cst,gyp,hal,cl.	.28	Broad reflections, Dol. dominant. Part anal. Forbes (1955)
A78.17	as A78.15	4-10	pipe-clay	Cal($Ca_{98}Mg_2$) (d) Dol $Ca_{56}Mg_{44}$ (d) qz,cst,gyp,hal,cl,sh.	.24	Dol. R$\bar{3}$ dominant. Part anal. Forbes (1955). Anal. D.M., SiO_2 6.86, Al_2O_3 1.21, Fe_2O_3 .29, CaO 34.77, MgO 11.22, CO_2 39.39, SO_3 .27, NaCl 1.01, H_2O 2.67, Organic carbon .34. Total 98.03.
A78.18	as A78.15	10-18	pipe-clay	Cal (as A78.17), Dol, qz, cl, hal, cst	.23	Part anal. Forbes (1955)
A78.19	as A78.15	18-24	pipe-clay	Cal($Ca_{95}Mg_5$)(d), qz, cl, hal, cst	.30	Cal. only detected. Part anal. Forbes (1955).

A78.20	as A78.15	24-30	dark grey pipe-clay	Cal, Dol (tr), qz, cl, hal, cst	.30	Part anal. Forbes (1955)
A78.22	as A78.15	30-39	dark grey pipe-clay	Cal, qz, cl, hal	.14	Part anal. Forbes (1955). No dol. detected.
A78.23	as A78.15	39-42	well indurated pipe-clay layer	Cal($Ca_{95}Mg_5$), qz, cl, cst	.25	Part anal. Forbes (1955). No dol. detected.
A78.24	as A78.15	42-44	dark pipe-clay	Cal, qz, cl	.08	
A78.25	as A78.15	44-46	light grey pipe-clay	Cal, qz, cl	.07	
A78.26 -31	as A78.15	46-70	green-grey clay	Cal, qz, cl	.08	Sulphur smell.
A78.35	Lagoon 5 m.S.E. Causeway	0	sand	Cal ($Ca_{88}Mg_{12}$), qz,cl	.23	Part anal. Forbes (1955)
A78.36	as A78.35	0-36	sand	Cal, qz, cl	.24	
A78.37	Lagoon 5 m.S.E. Causeway	0	surface crystal	gyp		
A78.38	as A78.35 further north	0	surface evaporite	Cal (tr), qz, cl, hal	.13	halite predominates
W1-1	2.4 m. W. Naracoorte on main road	0-12	brown soil	qz, Cal (Ca_{100}), pl, cl	.01	
W1-2	as W1-1	12-24	brown and red clay	Cal (Ca_{100}), qz, pl, cl, sh	.08	

W1-3	as W1-1	24-36	grey clay	Cal(Ca_{100}), qz, pl, cl, sh	.06	
W1-4	as W1-1	36-48	pipe-clay	Cal($Ca_{91}Mg_9$), qz, cl, hal	.10	Sharp reflections
W1-5	as W1-1	48-60	impure pipe-clay	Cal ($Ca_{91}Mg_9$), qz, cl, hal	.03	
W2-1	6.1 m. W. Naracoorte	0-10	grey soil	Cal ($Ca_{95}Mg_5$), qz, gyp, cst, sh, cl	.24	Broad reflections. Shell material abundant.
W2-2	as W2-1	10-18	black soil	Cal ($Ca_{95}Mg_5$), qz, cl, sh, cst	.23	Shells prominent.
W2-3	as W2-1	18-24	grey brown soil	Cal ($Ca_{95}Mg_5$), qz, cl, sh, cst, pl	.28	Abundant shell and plant material.
W2-4	as W2-1	24-30	grey brown soil	Cal($Ca_{95}Mg_5$), qz, cl, sh, cst	.28	Much shell material. Spicules remain after HCl treatment.
W2a	near W2-1	-	white nodules in soil	Cal ($Ca_{95}Mg_5$), qz, cl	-	Sharp reflections. Quartz grains, CO_3 cement. Secondary kunkar nodules.
W3-1	Stewart-Woolumbool Interdunal area 12.5 m. W. Naracoorte	0-12	sand	qz, cl, pl	-	
W3-2	as W3-1	12-24	red clay	qz, cl, pl	-	Sandy clay.
W4	Small flat area 19.5 m. W. Naracoorte	0-18	grey sand	qz, cl, pl	-	

W5-1	Baker-Ardune Interdunal area	0-16	sand	qz, cl, pl	-	
W5-2	as W5-1	16-30	grey and red clay	qz, cl, pl	-	Plants abundant.
W6-1	Bool Lagoon	0-6	black shelly soil	qz, Cal (Ca_{100}), cl, Dol $Ca_{50}Mg_{50}$	.21	Black soil with small white cal. nodules.
W6-2	as W6-1	6-18	grey clay grading into pipe-clay	Cal ($Ca_{94}Mg_{6}$), Dol $Ca_{50}Mg_{50}$, qz, cl, cst	.28	
W6-3	as W6-1	18-24	lighter grey pipe-clay	$\left.\begin{array}{l}\text{Cal}\\\text{Dol}\end{array}\right\}$ as W6-2. qz, cl	.18	
W6-4	as W6-1	24-30	dark grey pipe-clay	$\left.\begin{array}{l}\text{Cal}\\\text{Dol}\end{array}\right\}$ as W6-2. qz, cl.	-	Depth of layer unknown. Water encountered.
W7-1	N. of Millicent	0-10	black soil	Cal (Ca_{100}), cl, qz,pl	-	X-ray film shows sharp reflections.
W7-2	as W7-1	10-15	dark grey clay	Cal ($Ca_{95}Mg_{5}$), qz, cl,pl	-	as W 7-1.
W7-3	as W7-1	15-22	dark grey clay	Cal ($Ca_{95}Mg_{5}$), qz, cl,pl	-	as W7-1.
W7-4	as W7-1	22-24	grey soil	Cal, qz, cl, pl	-	Kunkar encountered at 24".
W8-1	N. of cross roads Robe-Turner-Beachport	0-10	sand	qz, cl, pl	-	
W8-2	as W8-1	10-15	red and grey clay	qz, cl, pl	-	Kunkar encountered at 15".

W9	1.9 m.N. Drain M.	0-8	sand	qz, cl, pl, Cal	.04	Kunkar at 8".
W10-1	Drain L at Conmurra	0-12	grey clay	qz, Cal ($Ca_{95}Mg_5$), cl Dol (tr)	-	Considerable cal. but predominantly qz. and clay minerals.
W10-2	as W10-1	12-48	Kunkar	Cal ($Ca_{95}Mg_5$), Dol (tr), qz, cl, pl	.03	Hard and compact layer. Much cal. and qz.
W10-3	as W10-1	48-51	pipe-clay	Cal ($Ca_{88}Mg_{12}$), qz, cl	.15	
W10-4	as W10-1	51-63	kunkar	Cal($Ca_{95}Mg_5$), qz, cl, pl	.07	Two kunkar layers in this bore hole.
W10-5	as W10-1	63-97	sand with shells	qz, Cal, cl, sh, pl.	.05	Shells abundant.
U1-1	10 m.E. of S. extent of water in Coorong	0-9	black soil	qz, cl, pl	.05	
U1-2	as U1-1	9-15	light grey sand	qz, cl, Cal(tr), pl	.01	
U1-3	as U1-1	15-20	grey-green clay	qz, cl, Cal(tr), pl	.01	Minor calcite.
U1-4	as U1-1	20-22	pipe-clay	Cal ($Ca_{98}Mg_2$), Dol (tr), qz, cl, hal, pl	.04	Carbonates are white powdery cement. Sandy layer below kunkar encountered at 26".
U2-1	near U1-1	0-12	black clay	Cal (tr), qz, cl, pl,	.03	Spore cases with CO_3 covering.
U2-2	as U2-1	12-18	grey-green clay	Cal (tr), qz, cl, pl	.10	Kunkar encountered at 18".

U3-1	near Kercoonda H.S.	0-2	black sandy clay	qz, cl, pl, Cal (tr)	.13	
U3-2	as U3-1	2-3	grey clays	qz, cl, pl, Cal (tr)	.01	
U3-3	as U3-1	3-14	brown-grey sand	qz, cl, pl, Cal (tr)	.04	Probably contains iron
U3-4	as U3-1	14-42	light grey sand	qz, cl, pl, Cal (tr)	.01	Thickness of this layer unknown
U4-1	6 m.N.E. of U3 on Davy Denning Swamp	0-1	surface scum	qz, Cal ($Ca_{98}Mg_2$), pl	.05	Chara and plant material abundant.
U4-2	as U4-1	1-10	black sand	qz, cl, pl, Cal (tr)	.02	
U4-3	as U4-1	10-24	white and grey mottled clay	qz, cl, Cal (tr)	.12	
U4-4	as U4-1	24-30	yellow sand and clay	qz, cl, pl, Cal (tr)	.06	
U5-1	4 m. N. of U4	0-¼	surface scum	Cal (Ca_{100}), Dol $Ca_{50}Mg_{50}$, qz, pl, cl, gyp, cst	.28	Carbonates in fine white powder.
U5-2	as U5-1	¼-6	clay and sand	qz, cl, Cal(tr), cst,pl	.22	
U5-3	as U5-1	6-12	grey sand and clay	qz, Cal (tr), cl, pl	.02	
U5-4	as U5-1	12-18	grey sand, mottled clay	qz, Cal (tr), cl, pl	.02	
U6	4 m. N. U4	0-½	slime in plough furrow	Cal ($Ca_{95}Mg_5$), qz, cl, cst	.29	Much plant and animal remains.

U7-1	2 m. N.W. of U5	0-½	surface scraping dried out grey scum	Cal, Ca (tr), qz, cl, cst	.26	
U7-2	as U7-1	½-2	black soil	Cal ($Ca_{95}Mg_5$), qz, cl, cst, pl	.17	
U7-3	as U7-1	2-4	grey sand	Cal ($Ca_{95}Mg_5$), Dol $Ca_{55}Mg_{45}$ qz, cl, pl, cst	.31	Carbonates minor
U7-4	as U7-1	4-7	white clay sand	Cal, Dol, qz, cl, pl, cst	.43	Broad reflections of the carbonates. Not able to get accurate measurements.
U8	Bonney's Camp	0	sand	qz, Cal (tr), cl, pl	-	
U9-1	near U8	0-2	grey sand	qz, Cal (tr), cl, pl	-	
U9-2	as U9-1	2-6	white sand	qz, cl, pl	-	
U10-1	clay pan 3 m. E. Meningie	0-1	white clay	qz, gyp	.18	
U10-2	as U10-1	1-4	black soil	Cal, qz, cl, pl	.13	
U10-3	as U10-1	4-8	light grey sand	qz, gyp, cl, pl	.16	
U10-4	as U10-1	8-24	white sand	qz, gyp, cl, pl, cst	.25	
U10-5	as U10-1	24-30	sand	qz, Cal (tr), pl, cl	.03	
U10-6	as U10-1	30-34	yellow clay	qz, Cal (tr), pl, cl	.01	
U11-1	clay pan ½ m. S. of U10	0-2	white clay	qz, gyp, cst, pl, cl	.27	

U11-2	as U11-1	2-4	clay and sand	Cal ($Ca_{95}Mg_5$), Dol (tr), pl, cst, qz	.38	
U11-3	as U11-1	4-8	gastropod-rich light grey clay layer	qz, gyp, Cal (tr)	.32	
U11-4	as U11-1	8-12	grey sand	qz, gyp, Cal (Ca_{100}), pl	.32	
U12-1	E. side main road 8 m. N. Meningie	0-½	salt surface layer	hal, gyp	.13	
U12-2	as U12-1	½-1	black mud H_2S smell.	gyp, cl, qz	.13	
U12-3	as U12-1	1-3	grey clay	Cal(tr), qz, cl, hal	.03	
U12-4	as U12-1	3-36	grey-green clay	Cal (tr), qz, cl	.01	
U12-5	as U12-1	about 48	Under water. Clay as U12-4	qz, Cal (tr), cl, gyp	.03	
D7	small flat area opposite Lake St. Claire 3 m.E. Nora Creina	-	plant dried and encrusted with salt	gyp	-	
D8	as D7	-	light grey soil below dried plant	Cal ($Ca_{90}Mg_{10}$), qz, cl, pl, hal	.24	Coarse qz. grains, in part cemented by fine calcite.
D9	Lake St.Claire	-	surface salt layer	gyp, qz, hal	.12	

D10	Lake St. Claire. Soil layer below salt		grey mud	Cal $(Ca_{90}Mg_{10})$, qz, gyp, hal, sh, pl	.18	Many gastropods, plant material.
D11	minor drain in Reedy Creek - W. Avenue Interdunal area	48-60	black mud	qz, pl, cl.	.01	Plant material abundant.
D12	as D11	36-48	brown sand	qz, cl, pl.	.01	Grinds flaky. Clays abundant.
D13	as D11	18-36	black compact soil	qz, cl, pl.	.12	Abundant plant remains.
D14	as D11	0-18	black compact soil	qz, cl, pl	.02	Abundant plant remains.
D15	minor drain in W. Avenue-E. Avenue Interdunal area	0-2	black compact soil	qz, cl, pl, sh	.05	Colourless spicules remain after HCl treatment.
D16	as D15	4-8	white cement with black patches, anhedral colourless grains	Cal, qz, cl, pl	.17	Cement effervesces in HCl.
D17	as D15	8-20	pipe-clay	Cal $(Ca_{91}Mg_{9})$ (d) Dol $Ca_{54}Mg_{46}$ (d) qz, sh, pl, cl, cst.	.20	Dolomite R$\bar{3}$ from very fine white material acting as a cement.
D18	as D15	20-32	pipe-clay	Cal $(Ca_{88}Mg_{12})$, Dol (tr), hal, qz, cl, sh, pl.	.15	Large white gastropods. Increase of cementing material relative to coarse grains and gastropods.
D19	as D15	32-44	pipe-clay	Cal $(Ca_{95}Mg_{5})$ (d) Dol (tr)	.01	As D18, contains more qz. and shelly material. Almost at water level.

D20	Further north, on same drain as D15	36-42	well indurated sand.	qz, cl.	-	
D21	as D20	72-80	white soil	qz, cl.	.15	Almost at water level in drain.
D22	E. Avenue-Ardune Interdunal area. Near Swamp	0-6	black soil	qz, cl.	.01	
D23	as D22	6-18	black soil	Cal (tr), Dol (tr), qz, cl.	.03	
D24	as D22	18-30	light grey soil	Cal (tr), Dol (tr), qz, cl.	.02	
D25	as D22	30-38	light grey and black patchy soil	Cal, qz, cl.	.05	Light patches predominantly clays. Broad reflections due to clays.
D26	Ardune-Baker Interdunal area	0-6	top soil in paddock	Cal $(Ca_{95}Mg_5)$ (d), qz.	.08	Bed-rock or kunkar at 8". Flint nodules in bed-rock.
D27	E. Avenue-Ardune Interdunal area. At railroad line	0-8	light grey unconsolidated soil	Cal, Dol (tr), qz, cl, cst, pl.	.20	
D28	as D27	8-15	white, sandy, lumpy soil	Cal $(Ca_{91}Mg_9)$, Dol(tr), qz, cl.	.18	Carbonates extremely fine-grained. Composition of cal. from solids still suspended after 5 min. Bedrock 15".
D29	E. Avenue-W. Avenue Interdunal area. Near Bull Island	0-9	dark grey soil	qz, cl, Cal (tr)	.01	Clays predominate. Minor carbonate.
D30	as D29	9-14	dark grey soil	qz, cl, Cal (tr)	.01	

D31	as D29	14-19	nodular, light grey soil	Cal $(Ca_{88}Mg_{12})$(d) Dol $Ca_{50}Mg_{50}$, qz, cst, cl, sh.	.13	Dolomite $R\bar{3}$ dominant carbonate. Carbonates act as a cement.
D32	as D29	19-	white and grey patchy, well indurated layer	Cal (tr), Dol $Ca_{50}Mg_{50}$ (d)	.20	Indurated pipe-clay. Dolomite dominant.
D33	small flat area in W. Avenue Range.	0	white flaky surface layer	Cal $(Ca_{95}Mg_{5})$(d), qz, cl, hal.	.08	Calcite composition determined on solids suspended 5-15 minutes.
D34	East of W. Avenue Range. Low swampy area	-	white, encrusted algae	gyp, hal, cl.	.19	
D35	as D34	0-9	loosely consolidated black soil, much organic matter and shelly material	qz, cl.	.02	Large shells.
D36	as D34	9-24	black mud	qz, cl.	.02	
D37	as D34	30-36	light grey, fossiliferous, indurated layer	Cal $(Ca_{95}Mg_{5})$(d), qz, cl.	.04	Kunkar at 36".
D38	Kingston Lake	-	chara (dried)	hal,cal,dol,gyp,cst.	.24	Salts encrust chara fibres.
D39	as D38	0-½	light grey pipe-clay	qz, gyp, hal, cl, Cal $(Ca_{90}Mg_{10})$(d), Dol $Ca_{50}Mg_{50}$	.40	Large size grains below Chara fibres. Caught from windblown drift.
D40	as D38	½-1½	small amount grey carbonate cementing grains, shell, organic debris	Cal, dol, qz, cst, cl, hal, pl.	.23	H_2S smell.

D41	as D38	1½-6	white carbonate cementing grains, shells. Well indurated	Cal $(Ca_{90}Mg_{10})$ (d) Dol $Ca_{57}Mg_{43}$ (d) qz, cst, cl.		Chem. anal. D.M. SiO_2 19.42, Al_2O_3 1.21, Fe_2O_3 0.25, CaO 28.61, MgO 9.42, CO_2 32.50, SO_3 0.43, NaCl 4.29, H_2O 1.84, Organic 0.17. Gastropods obvious. Dolomite appears dominant carbonate in 5-15 minute suspension. Dolomite $R\bar{3}$.
D42	as D38	6-13	loosely consolidated sand	Cal $(Ca_{88}Mg_{12})$, Dol $Ca_{55}Mg_{45}$, qz, hal, cl.	.08	Many shell fragments. White, black and colourless grains.
D43	as D38	13-26	dark sand	Cal, Dol (tr), hal, qz, cl.	.09	Very broad carbonate reflections.
D44	as D38	26-33	dark sand, much plant and shell material	Cal $(Ca_{88}Mg_{12})$ (d), Dol $Ca_{50}Mg_{50}$, qz, hal, gyp, cl.	.13	
D45	as D38	33-41+	light grey carbonates cementing shells, plant material and anhedral qz grains. Predominantly a sand	Cal $(Ca_{95}Mg_5)$, Dol $Ca_{50}Mg_{50}$ hal, qz.	.10	Cal. predominates over dol. Thickness of layer unknown. Spicules remain after HCl leach. Chem.anal.D.M. SiO_2 29.00, Al_2O_3 2.28, Fe_2O_3 0.40, CaO 31.78, MgO 1.34, TiO_2 nil, CO_2 26.05, SO_3 0.63, NaCl 5.18, H_2O 2.26, organic 0.57. Total 99.49.
D46	Lagoon M, S.end, near W. edge	0-1	pipe-clay	Cal $(Ca_{81}Mg_{19})$, Dol $Ca_{55}Mg_{45}$, qz, hal, gyp, cl, cst, sh.	.27	Some shells on surface.

D47	as D46	1-3	pipe-clay	Cal $(Ca_{81}Mg_{19})$, Dol Ca_{55} Mg_{45}, qz, hal, gyp, cl, cst	.24	Pipe-clay grades into sand below.
D48	as D46	3-18	sand with some white powdery cement. Shell and plant material	Cal $(Ca_{91}Mg_{9})$, qz, hal, cst, cl.	.60	Shells and shell fragments plentiful. Cst obvious after carbonates dissolved in HCl.
D49	Lagoon M. Further N. than D46 and towards centre of lagoon	0-2	pipe-clay	Cal $(Ca_{81}Mg_{19})$ (d) Dol $Ca_{54}Mg_{46}$ (d) qz, hal, cst, cl.	.44	Dol. $R\bar{3}$, dominant carbonate. Sharp reflections. Spicules remain after HCl leaching.
D50	as D49	2-6	whiter pipe-clay than D49	Cal $(Ca_{81}Mg_{19})$ (d) Dol $Ca_{54}Mg_{46}$ (d) qz, hal, cst, cl.	.44	More consolidated. Fewer shell fragments than D49.
D51	as D49	6-12	white, sticky pipe-clay	Cal $(Ca_{77}Mg_{23})$ (d) Dol $Ca_{50}Mg_{50}$ (d), qz, cst, cl, hal.	.49	Typical pipe-clay. Very pure.
D52	as D49	12-18	pink pipe-clay	Cal $(Ca_{88}Mg_{12})$, qz, hal, cl, cst.	.23	Pink gastropod shells. Become darker in depth. At 36" they are grey-brown colour.
D53	W. edge of Lagoon M.	0	white skin with salt crystals and shrinkage cracks	Cal $(Ca_{88}Mg_{12})$, Dol $Ca_{55}Mg_{45}$, qz, cl, hal, cst.	.53	Shrinkage cracks, ½" wide. Dried out version of what is in centre of lake. 10" below surface, pink gastropod layer appears.
D54	Lagoon M. 3 m.N. of D53.	33+	grey brown clay.	Cal $(Ca_{88}Mg_{12})$, qz, gyp, cl, hal, sh.	.23	Clay at base of pipe-clay section, D55.

D55	as D54	0-33	pipe-clay	Cal ($Ca_{81}Mg_{19}$), Dol $Ca_{55}Mg_{45}$, qz, cl, hal, cst.	.38	Dolomite R$\bar{3}$.
D56	Lagoon 5 m.N. of Lagoon M, and 12 m. S. of Causeway	0-1	brown-grey, impure pipe-clay. Grades to pure pipe-clay below.	Cal ($Ca_{95}Mg_{5}$), Dol $Ca_{50}Mg_{50}$, qz, cl, cst, gyp, hal, pl, sh.	-	Chara and salt obvious on surface. Plentiful qz. and cl.
D57	as D56	1-34	pipe-clay	Cal ($Ca_{81}Mg_{19}$), Dol $Ca_{55}Mg_{45}$, qz, cst, hal, gyp, sh.	-	Dol. dominant. Cst obvious. Some Shelly material.
D58	as D56	34+	shelly, brown clay, shell content increases with depth.	Cal ($Ca_{88}Mg_{12}$), qz, hal, sh.	.20	Shells examined by D. Taylor. Suggest salt water, shallow conditions, since shells not large. Pelagic ostracods, semi-pelagic foraminifera, molluscs, and algae spore cases.
D59	Coorong. N. side of Causeway	0-2	grey-brown pipe-clay	Cal ($Ca_{88}Mg_{12}$), Dol $Ca_{50}Mg_{50}$, qz, hal, gyp, cst.	.49	Surface of Coorong covered with Chara and pink gastropods. Sample mostly cal. and cl.
D60	as D59	2-8	grey-brown, loosely consolidated sand	Cal ($Ca_{88}Mg_{12}$), qz, hal, gyp, sh.	.14	Small fossils abundant. Many shell fragments as well as plant material.
D61	as D59	8-24	highly fossiliferous sand, light-brown colour	Cal ($Ca_{95}Mg_{5}$), qz, hal, gyp.	.17	Gastropods predominate. Some plant material. Grey-brown mud at 24".
D62	Swamp N.E. of Kercoonda	0	sand	qz,sh,Cal(tr), cl.	.02	
D63	as D62	0	black sand	qz, Cal(Ca_{100}), cl.	.16	Shell obvious. Plant material, algae, spore cases.

S1-1	Kingston Lake, centre	0-½	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d) Dol $Ca_{57}Mg_{43}$ (d) qz, cl, cst, sh.	.60	Water welled up to 18". Cal. and dol. equal proportions. Note high Sr.
S1-2	as S1-1	½-1	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d) Dol $Ca_{57}Mg_{43}$ (d) qz, cl, cst, sh.	.40	Dol. dominant. Shell calcite increased.
S1-3	as S1-1	1-1½	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d) Dol $Ca_{57}Mg_{43}$ (d) qz, cl, cst, sh.	.365	Pipe-clay ends with this sample. 1½ inch thick in this bore.
S1-4	as S1-1	1½-2½	white sandy-shelly layer	Dol $Ca_{54}Mg_{46}$ (d) qz, cl, cst, sh.	.27	Cal. not measurable. Dol. dominant. Shell calcite prominent. See Fig.8.
S1-5	as S1-1	2½-3½	darker grey sand	Dol $Ca_{57}Mg_{43}$ (d) Cal ($Ca_{81}Mg_{19}$) (d) qz, cl, cst, sh.	.16	Shells obvious. Cal. increased, reflection interfered with by shell calcite.
S1-6	as S1-1	4½-5½	grey sand	Cal ($Ca_{81}Mg_{19}$) (d) Dol $Ca_{57}Mg_{43}$ (d) qz, cl, cst, sh.	.16	Dol. diminishing. Shell cal. interfered with ppt. cal. No clearly defined peak.
S1-7	as S1-1	4½-5½	grey sand	Cal ($Ca_{81}Mg_{19}$) (d) Dol $Ca_{57}Mg_{43}$ (d) qz, cl, cst, sh.	.26	Dol. minor. Shell calcite predominant.
S1-8	as S1-1	5½-6½	grey sand	Cal ($Ca_{81}Mg_{19}$) (d) Dol $Ca_{57}Mg_{43}$, qz,sh.	.31	Dol. and cal. minor. Very shelly layer, so shell cal. major.
S1-9	as S1-1	6½-7½	grey sand	Cal, Dol, qz, cl, cst, sh.	.31	Shell cal. dominant, but not as many shells as previous sample. Dol. very low intensity, cal. interfered with, reflection not measured.

S1-10	as S1-1	7½-8½	grey sand	Cal, Dol, qz, cl, cst, sh.	not done	Very similar to S1-9.
S1-11	as S1-1	8½-11½	grey sand	Cal, dol, qz, cl, cst, sh.	.13	Dol. increased. (112) reflection may be split. Cal. somewhat obscured by shell cal.
S1-12	as S1-1	11½-14½	grey sand	Cal, dol, qz, cst, cl, sh.	.16	Dol. intensity low. Cal. interfered with by shell cal.
S1-13	as S1-1	14½-18+	black muds	Dol $Ca_{54}Mg_{46}$ (d), Cal, qz, cst, cl, sh.	.10	H_2S smell. Bottom of mud not reached. Shell content diminished. Cal. reduced but dol. increased.
S2-1	Kingston Lake. Edge of actual lagoon	0-½	sun-cracked pipe-clay	Cal ($Ca_{81}Mg_{19}$) (d), Dol $Ca_{54}Mg_{46}$ (d) qz, cl, cst, sh, pl.	.48	Cal. and dol. equal. Broad reflections, asymmetric towards each other. Minor shell content.
S2-2	as S2-1	½-1	pipe-clay	Cal ($Ca_{77}Mg_{23}$) (d), Dol $Ca_{57}Mg_{43}$ (d), qz, cl, cst, sh, pl.	.58	Cal. decreased. Broad Cal (112). Note Sr%.
S2-3	as S2-1	1-1½	pipe-clay	Cal, dol, qz, cl, cst, sh, pl.	.58	Broad reflections. Unsuitable for measurement. Note Sr%.
S2-4	as S2-1	1½-2	pipe-clay	Cal, dol, qz, cl, cst, sh, pl.	.56	as S2-3.
S2-5	as S2-1	2-2½	pipe-clay	Cal, dol, qz, cl, cst, sh, pl.	.57	as S2-3.
S2-6	as S2-1	2½-3	pipe-clay	Cal, dol, qz, cl, cst, sh, pl.	.46	As S2-3. Cal. reduced over previous samples.

S2-7	as S2-1	3-3½	pipe-clay	Cal, Dol, qz, cl, cst, sh, pl.	.54	As S2-3. Cal. reduced still further than S2-6.
S2-8	as S2-1	3½-4	pipe-clay	Cal, Dol, qz, cl, cst, sh, pl.	.47	as S2-3. Cal. reduction again.
S2-9	as S2-1	4-4½	pipe-clay	Cal, Dol, qz, cl, cst, sh, pl.	.36	Very similar to S2-8.
S2-10	as S2-1	4½-5	pipe-clay	Dol $Ca_{57}Mg_{43}$ (d), Cal, qz, cl, cst, sh, pl.	.425	Dol. increased, cal. very minor.
S2-11	as S2-1	5-5½	pipe-clay, passing to a sandy layer	Dol $Ca_{54}Mg_{46}$ (d), cal, qz, cl, cst, sh, pl.	.35	Dol.(112) intensity reduced. Cal. broad, low area. Transition from pipe-clay to sands.
S2-12	as S2-1	5½-6	sandy pipe-clay	Dol $Ca_{54}Mg_{46}$ (d), Cal ($Ca_{88}Mg_{12}$) (d), qz, cl, cst, pl, sh.	.28	Cal. gives defined reflection. Shells increase.
S2-13	as S2-1	6-6½	sandy pipe-clay	Dol $Ca_{54}Mg_{46}$ (d) Cal ($Ca_{88}Mg_{12}$) (d) qz, cl, cst, pl, sh.	.23	Cal. and shell cal. both increase.
S2-14	as S2-1	6½-7	sandy pipe-clay	Dol $Ca_{54}Mg_{46}$ (d) Cal ($Ca_{88}Mg_{12}$) (d)	.27	as S2-13.
S2-15	as S2-1	7-8	grey shelly sand	Dol $Ca_{57}Mg_{43}$ (d) Cal ($Ca_{88}Mg_{12}$) (d) qz, cl, cst, pl, sh.	.24	Cal, dol, shell cal. all about equal proportions.

S2-16	as S2-1	8-9	light grey sand	Dol $Ca_{57}Mg_{43}$ (d) Cal $(Ca_{88}Mg_{12})$ (d) qz, cl,cst, pl, sh.	.20	Shell cal. dominant. Cal. greater than dol.
S2-17	as S2-1	9-13	dark grey sand	Cal $(Ca_{91}Mg_{9})$ (d) Dol $Ca_{57}Mg_{43}$ (d) qz, cl, cst, pl, sh.	.15	Shell cal. dominant. Cal. much greater than dol.
S3-1	Kingston Lake. In bank, 10 yds. due W. of S2.	0-1	black soil	Cal $(Ca_{88}Mg_{12})$ (d) Dol $Ca_{57}Mg_{43}$ (d) qz,cl, cst, pl, sh.	.51	Cal. and dol.(112) reflections low and broad. Asymmetric towards each other. Note Sr.
S3-2	as S3-1	1-2	black soil	Dol $Ca_{57}Mg_{43}$ (d) cal, qz, cl, cst,sh,pl.	.40	Cal. very low. Dol. increased. Montmorillonite lines interfere with carbonate measurement.
S3-3	as S3-1	2-3	shelly pipe-clay	Cal, Dol, qz, cl,cst, sh, pl.	.66	Dol. diminished. Broad low area of Cal, cst, and cl. reflections
S3-4	as S3-1	3-4	pipe-clay	Cal, Dol, qz, cl, cst, sh, pl.	.61	Broad intensity area between cal. and dol. reflections. Cal. less than dol. Note Sr.
S3-5	as S3-1	4-5	pipe-clay	Cal,Dol, qz, cl, cst, sh, pl.	.61	as S3-4. Clay reflection interferes with carbonate measurement.
S3-6	as S3-1	5-6	pipe-clay	Cal, Dol, qz, cl, cst, sh, pl.	.67	as S3-5. Note Sr.
S3-7	as S3-1	6-7	pipe-clay	Cal, Dol, qz, cl,cst, sh, pl.	.89	as S3-4. Note Sr.
S3-8	as S3-1	7-8	pipe-clay	Cal, Dol, qz, cl, cst, sh, pl.	.78	as S3-7. Cal. increased. Note Sr.
S3-9	as S3-1	8-9	pipe-clay	Cal, Dol, qz, cl, cst, sh, pl.	.62	as S3-8.

S3-10	as S3-1	9-10	whiter pipe-clay	Cal, Dol, qz, cl, cst, sh, pl.	.80	Less shelly layer than S3-9. Cal. and dol. equal. Broad area of intensity between cal. and dol.
S3-11	as S3-1	10-11	whiter pipe-clay	Cal, Dol, qz, cl, cst, sh.	.71	As S3-10. Note Sr.
S3-12	as S3-1	11-12	pipe-clay	Cal, Dol, qz, cl, cst, sh.	.745	as S3-10. Note Sr.
S3-13	as S3-1	12-13	pipe-clay	Cal, Dol, qz, cl, cst, sh.	.66	as S3-10. Note Sr.
S3-14	as S3-1	13-14	pipe-clay getting sandy - transition	Cal, Dol, qz,cl,cst,sh.	.40	as S3-10.
S3-15	as S3-1	14-15	light brown sand	Cal ($Ca_{88}Mg_{12}$) (d) Dol $Ca_{54}Mg_{46}$ (d) cl,qz,cst,sh,pl.	.24	Break between these two samples. Shell cal. dominant. Cal. and dol. equal, distinct reflections.
S3-16	as S3-1	15-16	light brown sand	Dol (tr), Cal, qz, cst, pl, sh, cl.	.465	Dol. very low, asymmetric towards higher 2θ. Shell and ppt. cal. equal intensity.
S3-17	as S3-1	16-17	light brown sand	Dol $Ca_{57}Mg_{43}$ (d), Cal, cl, qz, cst, sh, pl.	.26	Dol. increased. Ppt. cal. interfered by shell cal. Shell cal. dominant.
S3-18	as S3-1	17-20	grey sand	Dol (tr), Cal, qz, cl, cst, sh, pl.	.31	Dol. very low. Ppt. cal. and shell cal. one broad reflection. Ppt. cal. probably less Mg than upper samples.
S3-19	as S3-1	20-22	dark grey sand	Cal, Dol (tr), qz, cl, cst, sh, pl.	.18	Dol. very low. Shell cal. brought on scale with .002 al. foil. Very shelly layer.

S4-1	Lagoon M, centre	0-1	grey pipe-clay	Cal $(Ca_{81}Mg_{19})$ (d) Dol $Ca_{54}Mg_{46}$ (d) qz,cl,cst, sh, pl.	.49	Dol. dominant. Cal. broad, low. Shell cal. sharp equal intensity with ppt. cal.
S4-2	as S4-1	1-2	white pipe-clay	Cal $(Ca_{81}Mg_{19})$ (d) Dol $Ca_{57}Mg_{43}$ (d), qz, cl, cst, sh, pl.	.51	Cal. increased intensity but still broad reflections. Shell cal. minor.
S4-3	as S4-1	2-3	pipe-clay	Cal $(Ca_{84}Mg_{16})$ (d) Dol $Ca_{57}Mg_{43}$ (d), qz, cl, cst, sh, pl.	.46	Dol. decreased. Cal. and dol. intensities equal shell cal. minor.
S4-4	as S4-1	3-4	pipe-clay	Cal $(Ca_{88}Mg_{12})$ (d) Dol $Ca_{57}Mg_{43}$ (d), qz, cl, cst, sh, pl.	1.12	Dol. much decreased. Shell cal. small. Ppt. cal. dominant broad reflection - Sr. higher.
S4-5	as S4-1	4-5	pipe-clay	Cal $(Ca_{88}Mg_{12})$ (d) Dol $Ca_{57}Mg_{43}$ (d), qz, cl, cst, sh, pl.	.38	Dol. still less. Ppt. cal. reflection strong and broad.
S4-6	as S4-1	5-6	pipe-clay	Cal $(Ca_{88}Mg_{12})$ (d) Dol $Ca_{57}Mg_{43}$ (d) qz, cl, cst, sh, pl.	.45	as S4-5.
S4-7	as S4-1	6-7	pipe-clay	Cal $(Ca_{88}Mg_{12})$ (d) Dol $Ca_{57}Mg_{43}$ (d) qz, cl, cst, sh, pl.	.46	Both dol. and cal. reflections broad. Cal. 3x dol.
S4-8	as S4-1	7-8	pipe-clay	Cal $(Ca_{84}Mg_{16})$ (d) Dol $Ca_{57}Mg_{43}$ (d) qz, cl, cst, sh, pl.	.66	Slight composition changes of cal. Note Sr.

S4-9	as S4-1	8-9	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d) Dol $Ca_{57}Mg_{43}$ (d)	.30	Dol. reflection asymmetric toward lower 2θ. Due to presence of other reflection.
S4-10	as S4-1	9-10	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d) Dol $Ca_{57}Mg_{43}$ (d) qz, cl, cst, sh, pl.	.30	Cal. and dol. reflections more distinct.
S4-11	as S4-1	10-11	pipe-clay	Cal ($Ca_{81}Mg_{19}$) (d) Dol Ca_{57} Mg_{43} (d) qz, cl, cst, sh, pl.	.59	Dol. reflection quite asymmetric. Cal. composition more Mg. rich. Note Sr. increase.
S4-12	as S4-1	11-12	pipe-clay	Cal ($Ca_{81}Mg_{19}$) (d) Dol $Ca_{57}Mg_{43}$ (d) qz, cl, cst, sh, pl.	1.12	Dol. diminishing. Note high Sr. 2nd in this bore.
S4-13	as S4-1	12-13	pipe-clay	Cal ($Ca_{81}Mg_{19}$) (d) Dol $Ca_{54}Mg_{46}$ (d) cl, qz, sh, cst, pl.	.95	Dol. reflection broad, low. Note Sr.
S4-14	as S4-1	13-14	pipe-clay	Cal ($Ca_{88}Mg_{12}$) (d) Dol (tr), cl, sh, qz, cst, pl.	.93	Dol. very small. Note Sr.
S4-15	as S4-1	14-15	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d), Dol (tr), cl, sh, qz, pl, cst.	.615	Dol. barely visible. Note Sr.
S4-16	as S4-1	15-16	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d), Dol (tr), cl, sh, pl, qz, cst.	.29	

S4-17	as S4-1	16-17	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d) Dol $Ca_{57}Mg_{43}$ (d) cl, cst, qz, pl, sh.	.32	Dol. increased. Note accurate composition.
S4-18	as S4-1	17-18	pipe-clay	Cal ($Ca_{81}Mg_{19}$) (d) Dol $Ca_{57}Mg_{43}$ (d) cl, cst, pl, sh, qz.	.53	Dol. increased. Note Sr.
S4-19	as S4-1	18-19	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d) Dol (tr), cl, cst, qz, sh, pl.	.30	Dol. disappearing.
S4-20	as S4-1	19-20	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d) Dol (tr), cl, cst, pl, sh, qz.	.25	Dol. very minor. This inch very white and pure pipe-clay.
S4-21	as S4-1	20-21	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d) cl, cst, qz, sh, pl.	.28	Dol. disappeared. Very pure white layer.
S4-22	as S4-1	21-22	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d), cl, cst, qz, sh, pl.	.31	Very white, pure pipe-clay.
S4-23	as S4-1	22-23	pipe-clay	Cal ($Ca_{88}Mg_{12}$) (d) cl, cst, qz, sh, pl.	.28	Very white pure pipe-clay.
S4-24	as S4-1	23-24	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d), cl, cst, qz, sh, pl.	.31	as S4-23.
S4-25	as S4-1	24-25	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d) cl, cst, qz, sh, pl.	.31	as S4-23.

S4-26	as S4-1	25-26	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d) cl, cst,qz, sh, pl.	.32	as S4-23.
S4-27	as S4-1	26-27	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d) cl, cst, qz, sh, pl.	.29	as S4-23.
S4-28	as S4-1	27-28	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d) cl, cst, qz, sh, pl.	.29	as S4-23.
S4-29	as S4-1	28-29	pipe-clay	Cal ($Ca_{84}Mg_{16}$) (d) cl, cst, pl, sh, qz.	.30	
S4-30	as S4-1	29-30	sandy pipe-clay	Cal ($Ca_{88}Mg_{12}$) (d) qz, cst, pl, cl, sh.	.315	transition to sands below.
		Date				
K1	Kingston Lake	Nov.55	water cloudy with white sediment	Cal ($Ca_{84}Mg_{16}$) (d) Dol $Ca_{56}Mg_{44}$ (d) cl, qz, cst, sh.	.44	Sharp carb. reflections asymmetric toward each other. Some shell calcite.
No.26	Kingston Lake	Nov.56	water cloudy with sediment.	Cal ($Ca_{84}Mg_{16}$) (d) Dol $Ca_{56}Mg_{44}$ (d) cl, qz, cst, sh.	.70	Sharp carb. reflections asymmetric toward each other. Cal. broadest of two reflections. Note Sr.
No.27	Kingston Lake	Nov.56	water contained very little sediment	Cal ($Ca_{84}Mg_{16}$) (d) Dol $Ca_{56}Mg_{44}$) (d) cl, qz, cst, sh.		Taken day after No.26. Very small ppt.

E11	16.4 m. N. of quarry on old Coorong Road	Dec.56	water milky with sediment	Cal $(Ca_{77}Mg_{23})$ (d) Dol. $Ca_{57}Mg_{43}$ (d) cl, qz, cst, sh.	.37	Sample taken in centre of Coorong. Dol. low.
E12	Causeway	Dec.56	not ppt. sample taken from bottom	Cal $(Ca_{84}Mg_{16})$ (d) cl, qz, cst, sh.	.37	No dol. Plants in area started to die. Sharp cal. and shell cal. reflection.
E13	15.8 m. N. of quarry on old Coorong Road	Dec.56	sediment more concentrated at edges	Cal $(Ca_{81}Mg_{19})$ (d) Dol $Ca_{57}Mg_{43}$ (d) cl, qz, cst, sh.	.57	Taken close to sample E11. Dol. low.
E14	18 m. N. of quarry on old Coorong Road	Dec.56	patchy sediment in water	Cal $(Ca_{77}Mg_{23})$ (d) Dol $Ca_{56}Mg_{44}$ (d) qz, cl, cst, sh.	.60	Sediment concentrated over plants. Dol. low. Shell cal. peak shifted.
E17	20.5 m. N. of quarry on old Coorong Road	Dec.56	slight amount of sediment in water	Cal $(Ca_{78}Mg_{22})$ (d) Dol $Ca_{56}Mg_{44}$ (d) qz, cl, cst, sh.	.55	
E19	Lagoon 10.4 m. N. of quarry on old Coorong Rd.	Dec.56	water clear	Cal $(Ca_{81}Mg_{19})$ (d) Dol $Ca_{56}Mg_{44}$ (d) qz, cl, cst, sh.	.56	Sample collected from sediment on grass fronds. Dol. low.
E20	Kingston Lake	Dec.56	slight ppt. water murky	Cal $(Ca_{84}Mg_{16})$ (d) Dol $Ca_{56}Mg_{44}$ (d) qz, cl, cst, sh.	.28	Small sample, probably not representative.
E21	Lagoon M.	Dec.56	water milky at edge	Cal $(Ca_{78}Mg_{22})$ (d) Dol $Ca_{56}Mg_{44}$ (d) qz, cl, cst.	1.12	Note high Sr. Cal. low interfered with by cst.

E22	Kingston Lake	Dec.56	water milky	Cal $(Ca_{84}Mg_{16})$ (d) Dol $Ca_{56}Mg_{44}$ (d) qz, cl, cst.	.53	Most of sample spore cases coated with cal. and dol.
E23	Lagoon M.	Dec.56	water milky near edge where plants thick	Cal $(Ca_{84}Mg_{16})$ (d) Dol $Ca_{56}Mg_{44}$ (d)	.70	Cal. low. Note Sr.
54	Cantara	Nov.57	water lightly milky	Cal $(Ca_{81}Mg_{19})$ (d) Dol $Ca_{56}Mg_{44}$ (d) qz, cl, cst, sh, pl.	.42	Only precipitating pipe-clay from 1957-8 dry year.