

## Chapter 19

### GEOCHEMISTRY OF GROUNDWATERS IN THE OTWAY BASIN OF SOUTHWESTERN VICTORIA

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#### ABSTRACT

The groundwaters of Tertiary and Upper Cretaceous rocks of the Otway Basin are subdivided into six groups, using the "chloride ratios" as a means of geochemical classification.

The distribution of each group is outlined, and the genesis of the groundwaters is discussed.

#### INTRODUCTION

In recent years sufficient information has been obtained about the geochemical characteristics of groundwaters in the Victorian part of the Otway Basin to formulate some general principles concerning their distribution and genesis. This information has been derived from three main sources:—from wells sunk by the Mines Department as part of a programme of deep drilling in search of useful groundwater; from wells sunk by petroleum exploration companies; and from private wells producing groundwater mainly for agricultural purposes. Water analyses used in this study were carried out by the Chemical Branch of the Mines Department, State Laboratories, Melbourne.

The private wells are relatively shallow and produce water from the Newer Volcanics and the Port Campbell Limestone. The deeper wells of the Mines Department have produced water mainly from the sandy aquifers of the Mepunga Formation and the Dartmoor Sand Member of the Dilwyn Formation, the Pebble Point Formation, and the Timboon Sand Member of the Paaratte Formation. In these deep wells electric logs and pumping tests were used to select the intervals containing the best quality water. Aquifers were developed by means of slotted casing. The deepest and most saline groundwaters, especially from the Waarre Sandstone and the mudstones and arkoses of the Otway Group were sampled by normal techniques using packers in cemented casing perforated at the aquifer levels.

The stratigraphic nomenclature used here is that proposed by Bock and Glenie (1965). The names and numbers given to the wells are those used by the Victorian Mines Department. See Fig. 19-1 for well localities.

#### ACKNOWLEDGEMENTS

The writer acknowledges with thanks the help provided by many members of the Geological Survey of Victoria, especially Messrs. R. C. Glenie, W. A. Esplan, P. R. Kenley and C. R. Lawrence, in the preparation of this paper.

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CHLORIDE RATIOS AND A CLASSIFICATION OF GROUNDWATERS IN THE OTWAY BASIN

The main geochemical characteristics of the groundwaters in the sands of the Mepunga Formation and the Dartmoor and Timboon Sand Members of the Wangerrip Group have already been described in terms of four main classes, with sub-classes based on chlorinity and alkalinity (Johns, 1968). These main classes are based on the concentrations of sodium and magnesium ions (in equivalents per million) per hundred equivalents per million of chloride *i.e.*, on the "chloride ratios" of sodium and magnesium. This system of classification is related to that used by Back (1966) in which "hydrochemical facies" are defined in terms of the concentration of sodium ions as a percentage of the total cations in equivalents per million. However, a classification based on chloride ratios of cations appears to have several advantages when the chloride ion is a major constituent of all the groundwaters, as in the Otway Basin.

Using chloride ratios, especially those of the main cations and of sulphate ions, the role of oceanic salts in the genesis of many groundwaters in Victoria can be demonstrated (Anderson, 1940, 1941). The oceanic salts may be derived from connate water remaining in the sediments since their last contact with ocean water or other saline water, or from cyclic salts in rainwater which has been concentrated by evaporation and transpiration before entering the aquifer (Anderson, 1945).

Cation exchanges between the aquifer and groundwater may be more easily understood when the ionic concentrations in the water analyses are quoted as chloride ratios (Johns, 1968). Similarly, sulphate reduction by the action of anaerobic bacteria in the sediments, or sulphate accumulation as a result of local changes in the conditions of sedimentation, can readily be shown despite wide variations in the composition of the groundwater.

Analyses of the different types of groundwater found in the Otway Basin are given in Table 19-1 with the ionic concentrations expressed in parts per million (p.p.m.). In the hypothetical combinations of ions in some of these water analyses the predominant salts are sodium and magnesium chlorides, in other waters they are sodium bicarbonate and sodium chloride, and in others again they are sodium and calcium chlorides, and so on.

In Table 19-2, the same water analyses are expressed in chloride ratios so that some of the many variables can be considered independently of others. Using the somewhat arbitrary limits of sodium and magnesium chloride ratios as in the previous study, which was limited to the sand aquifers, six geochemical classes of groundwater can be recognized in the main aquifers of the Otway Basin in Victoria. These classes are defined as follows:—

Class	Sodium-Chloride Ratio	Magnesium-Chloride Ratio
A	< 80	>> 20
B	80-95	>> 20
C	> 95	>> 20
D	> 95	>> 20
E	80-95	>> 20
F	< 80	>> 20

For comparison, the sodium-chloride ratio of ocean water is about 87 and the magnesium-chloride ratio about 20.

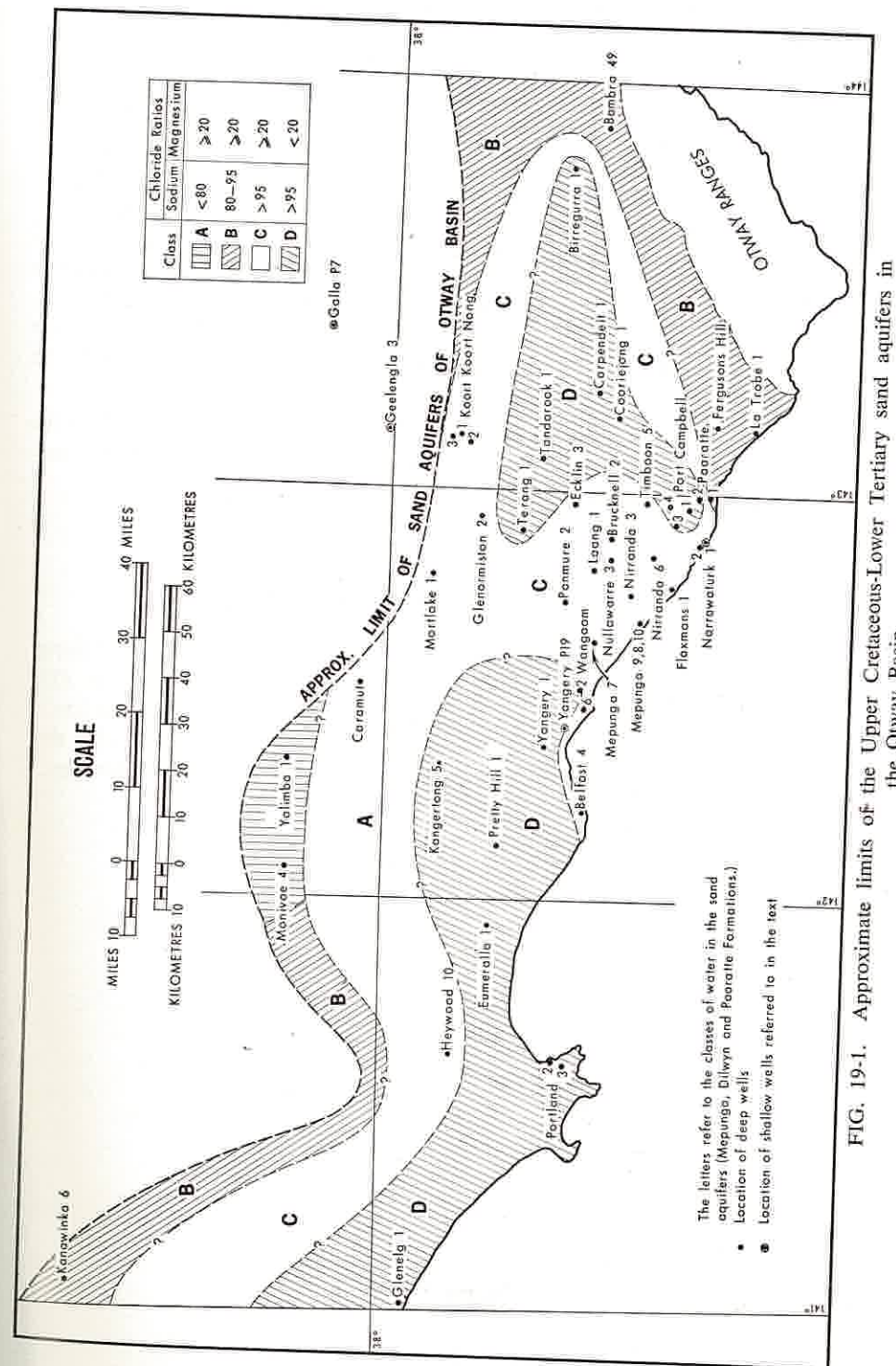


FIG. 19-1. Approximate limits of the Upper Cretaceous-Lower Tertiary sand aquifers in the Otway Basin



Some of these classes of water are characteristic of particular aquifer types while others are found in more than one aquifer (see Table 19-3). These geochemical classes are not intended to reflect the usefulness of any of the waters for particular purposes.

In each of these classes there may be wide variations in the chlorinity, and hence in the total content of dissolved solids. Two waters belonging to the same class but having different chlorinities can be represented by the class symbol followed by the chlorinity expressed to the nearest whole number e.g. B6 and B43. Such variations in chlorinity in sedimentary aquifers largely reflect the salinity of connate water in the sediments and the extent to which it has been flushed from them. The connate water may be derived from sea water or other saline water in which the sediments were deposited, or with which they have had subsequent contact. On the other hand, in aquifers such as the Newer Volcanics in Victoria the chloride content must have been derived mostly from cyclic salts in rain water which has been concentrated by evaporation and transpiration before infiltration.

Within each class of water there may also be variations in the alkalinity (the total concentration of bicarbonate and carbonate ions in equivalents per million). These variations are recognized as sub-classes as follows:—

Sub-Class	Alkalinity
k . . . . .	<4 e.p.m.
l . . . . .	4-7 e.p.m.
m . . . . .	7-12 e.p.m.
n . . . . .	>12 e.p.m.

Waters having similar cation-chloride ratios and chlorinities but with different alkalinities may be distinguished, for example, by the symbols D7m and D7k. Along with the pH, the alkalinity gives a measure of the total concentration of carbonic acid available for reaction within a given aquifer and is more useful than the bicarbonate-chloride ratio since the alkalinity is independent of the chlorinity.

TABLE 19-1  
Representative water analyses from the main aquifers in the Otway Basin, Victoria.

Well Reference (Vic. Mines Dept.)	Aquifer	Sample Depth feet	Parts per Million											pH	
			Total Solids	Na+K (Calc)	Ca	Mg	Fe (Sol)	Cl	HCO <sub>3</sub>	CO <sub>3</sub>	SO <sub>4</sub>	NO <sub>3</sub>	SiO <sub>2</sub>		Hardness (CaCO <sub>3</sub> )
Galla P. 7 . . . . .	Basalt (earlier) . . . . .	56-71	6,254	1,470	141	435	0.5	3,127	680	Nil	361	—	40	2,140	7.8
Yalimba No. 1 . . . . .	? Mepunga Formation . . . . .	633	2,416	570	120	130	0.3	1,223	265	9	97	9	9	834	7.5
Narrawaturk No. 1 . . . . .	Port Campbell Limestone . . . . .	35	4,070	1,030	216	128	—	1,738	653	Nil	282	Nil	—	1,067	7.2
Paaratte No. 1 . . . . .	Dartmoor Sand . . . . .	1,625- 2,000	348	40	44	13	1.0	70	146	12	16	5	165	8.2	
Geelengla No. 3 . . . . .	Basalt (later) . . . . .	34	980	125	37	80	—	146	428	Nil	18	—	422	8.1	
Yangery P. 19 . . . . .	Tuff/Limestone . . . . .	61-165	1,020	195	73	29	0.6	196	398	8	47	—	303	7.8	
Belfast No. 4 . . . . .	Dartmoor Sand . . . . .	1,747- 2,636	1,085	285	24	27	0.4	305	399	Nil	30	14	172	7.6	
Port Campbell No. 1 . . . . .	? Timboon Sand . . . . .	4,463- 4,475	4,590	1,510	22	3	—	1,160	1,694	184	19	—	66	8.8	
Glenelg No. 1 . . . . .	Dartmoor Sand . . . . .	2,323	1,330	420	5	4	0.5	306	544	38	3	12	29	8.5	
Port Campbell No. 3 . . . . .	Waarre Sandstone . . . . .	4,608- 4,620	17,209	5,980	506	115	—	9,986	496	10	238	—	1,737	8.3	
Eumeralla No. 1 . . . . .	Otway Group . . . . .	5,822- 6,034	19,166	4,000	3,110	13	—	11,170	366	Nil	487	14	7,820	7.9	



TABLE 19-2

The same water analyses as in Table 19-1, with ionic concentrations expressed in chloride ratios.

Well	Chloride Ratios (e.p.m. per 100 e.p.m. chloride)						Class of Water	Chlorinity (e.p.m.)	Alkalinity	
	Na+K	Ca	Mg	HCO <sub>3</sub>	CO <sub>3</sub>	SO <sub>4</sub>			e.p.m.	Sub-class
Galla P. 7 .....	73	8.0	40.6	12.7	0.0	8.5	A	88	11.2	m
Yalimba No. 1 .....	71	17.0	31.0	13.0	0.9	4.9	A	34	4.7	l
Narawaturk No. 1 ..	91	22.0	21.0	22.0	0.0	11.9	B	50	10.7	m
Paaratte No. 1 .....	92	112.0	54.0	121.0	20.0	17.0	B	2	2.8	k
Geelengla No. 3 .....	131	45.0	160.0	170.0	0.0	9.0	C	4	7.0	m
Yangery P. 19 .....	154	66.0	43.0	118.0	4.9	18.0	C	66	6.8	l
Belfast No. 4. ....	140	14.0	25.0	67.0	0.0	7.9	C	10	6.5	l
Port Campbell No. 1	201	3.4	0.8	85.0	19.0	1.2	D	33	28.0	n
Glennelg No. 1 .....	210	2.9	3.8	110.0	15.0	0.7	D	9	10.2	m
Port Campbell No. 3	92	9.0	3.4	2.9	0.0	1.8	E	282	8.4	l
Eumeralla No. 1. ....	55	50.0	0.3	1.9	0.0	3.2	F	314	6.0	l

## GROUNDWATER GEOCHEMISTRY VICTORIA

TABLE 19-3

Distribution of the classes of groundwater in the main aquifers of the Otway Basin, Victoria

Aquifer	Class of Water					
	A	B	C	D	E	F
Newer Basalts						
Later flows and tuff ....			+			
Earlier flows .....	+					
Heytesbury Group, associated with basalt or tuff .....	+		+			
Heytesbury Group, (Port Campbell Limestone) .....		+				
Nirranda Group (Mepunga Formation)	+	+	+	+		
Wangerrip Group—						
Dilwyn Formation (Dartmoor Sand)	?	+	+	+		
Pebble Point Formation .....			+	+		
Paaratte Formation (Timboon Sand)		?	+	+		
Waarre Sandstone .....			+	+	+	
Otway Group (mudstone/arkose) .....				?	+	+

In many types of aquifer the alkalinity never exceeds about 7 e.p.m. (sub-classes k and l). The only carbonic acid available in these aquifers is derived from the atmosphere and from bacterial activity in the soil at the intake area, and is limited in amount (Foster, 1950). However, in some of the Otway Basin aquifers, additional carbonic acid is provided from within the aquifer by the decomposition of carbonaceous matter in the sediments. The thermal decomposition of amino acids derived from proteins, and of fatty acids derived from lipids which would originally have been present in the carbonaceous sediments, proceeds at temperatures which are only moderately elevated. Free acids, especially carbonic acid, would therefore be produced within the sediments and would gradually be released into the groundwater. In fact, cores taken from the Wangerrip Group sediments in the Otway Basin almost invariably contain free acid. The pH of the finer-grained carbonaceous sediments in a 1 to 5 water suspension at room temperature, is often as low as 2.5.

In general, the groundwater alkalinity increases progressively from Class A to Class D. In Classes C and D the formation of sodium bicarbonate, which is much more soluble than calcium or magnesium bicarbonate, allows the alkalinity to exceed 7 e.p.m. and to rise to about 70 e.p.m. where the necessary carbonic acid is available.

The pattern of the areal distribution of groundwater in Classes B, C and D in the Lower Tertiary-Upper Cretaceous sand aquifers of the Otway Basin (Figure 19-1) is similar to that found in comparable aquifers in other sedimentary basins in England (Thresh, 1912; Ineson and Downing, 1963), Belgium (Delecourt, 1939) and the Gulf coastal plain of U.S.A. (Cederstrom, 1946; Foster, 1950; Back, 1966).



In particular, the cation exchange reactions which produce softening of the water as it moves down-dip from the intake area, and the formation of sodium bicarbonate-rich waters seem to be characteristic of these sand aquifers (Johns, 1968). In the Otway Basin, however, Class A waters which are usually found only in certain basalts and non-marine sediments are also found in the Mepunga Formation (?) near Hamilton.

#### Class A

In these waters the sodium-chloride ratio is considerably less, and the magnesium-chloride ratio is greater than in sea water (see Table 19-2). Magnesium-chloride is present in relatively high concentrations when compared with waters of different classes but similar chlorinities. The hypothetical salts in the water from basalt in Galla P.7 well are as follows:—

Calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$ . . . . .	7.1 e.p.m.
Magnesium bicarbonate, $\text{Mg}(\text{HCO}_3)_2$ . . . . .	2.9 e.p.m.
Magnesium sulphate, $\text{MgSO}_4$ . . . . .	7.5 e.p.m.
Magnesium chloride, $\text{MgCl}_2$ . . . . .	24.2 e.p.m.
Sodium chloride, $\text{NaCl}$ . . . . .	63.9 e.p.m.

In the Otway Basin these hard waters occur in the earlier basalts of the Newer Volcanics and in sands or limestones in close association with these basalts. The chloride content of the basalts is probably all derived from cyclic salts of oceanic origin in which the sodium-chloride ratio is about 87. Since the sodium-chloride ratio is decreased and the magnesium and calcium-chloride ratios increased in these Class A groundwaters relative to sea water, it appears likely that some of the sodium ions have been removed from solution and magnesium (and possibly calcium) ions added by a process of cation exchange hardening. The feldspars, ferromagnesian minerals and their clay weathering-products could provide a source of exchangeable magnesium and calcium ions.

Class A waters also contain calcium and magnesium bicarbonates derived from the aquifer by the action of carbonic acid, but their alkalinity is usually low. The sulphate-chloride ratio is usually about the same as in sea water, i.e. about 10, which suggests that most of the sulphate is also of cyclic origin. The chlorinity varies from a few e.p.m. up to more than 150 e.p.m., depending, presumably, on the drainage efficiency of the intake areas for the basalts.

#### Class B

For these waters the sodium-chloride ratio is approximately the same as in sea water (between 80 and 95), but the magnesium and calcium-chloride ratios are greater (see Table 19-2). Much of the dissolved matter is of oceanic origin with some calcium and magnesium bicarbonates being added as a result of the action of carbonic acid within the aquifer. The oceanic salts are derived mainly from connate water remaining in the sediments since deposition, and partly from cyclic salts. The alkalinity is usually less than 7 e.p.m. and most of the chlorinities are less than 50 e.p.m. The sulphate-chloride ratio is commonly about 10, as in sea water. Occasionally the sulphate-chloride ratio is about 20 (Table 19-2, Paaratte No. 1) which suggests that there may have been some areas where sulphates were concentrated relative to chlorides during the deposition of the sediments.

Class B waters are commonly found in the Port Campbell Limestone where that aquifer is not associated with basalt or tuff. The hypothetical salts in water from Narrawaturk No. 1 well are,

Calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$ . . . . .	10.7 e.p.m.
Calcium sulphate, $\text{CaSO}_4$ . . . . .	0.1 e.p.m.
Magnesium sulphate, $\text{MgSO}_4$ . . . . .	5.8 e.p.m.
Magnesium chloride, $\text{MgCl}_2$ . . . . .	4.7 e.p.m.
Sodium chloride, $\text{NaCl}$ . . . . .	44.9 e.p.m.

Class B water is also found in the (?) Mepunga Formation and the Dartmoor Sand Member aquifers near the edges of the Otway Basin (Fig. 19-1). This is the predominant water type in limestone aquifers elsewhere, as in the Murray Basin, in which there are very few minerals involved in cation-exchange reactions and in which the amount of carbonic acid available for reaction is limited.

#### Class C

The sodium, magnesium and calcium-chloride ratios in Class C waters are all greater than in sea water due to the presence of sodium, calcium and magnesium bicarbonates, and sometimes sulphates, derived from the aquifer (Table 19-2). These moderately hard waters are present in several aquifers in the Otway Basin (Table 19-3). They occur frequently in the later basalts of the Newer Volcanics, and in associated tuffs. The nitrate concentrations in many of these waters in basalt and tuff are unusually high. Where the basalts and tuffs overlie or are adjacent to outcrops of the limestone of the Heytesbury Group the groundwater in the limestone aquifer changes from Class B, as is usually found in limestone, to Class C.

The alkalinity is usually less than 8 e.p.m. and the chlorinity less than 10 e.p.m. The presence of sodium bicarbonate as well as calcium and magnesium bicarbonates in the groundwater of the later basalts probably results from the direct action of carbonic acid on the fresh feldspars in the basalt. The earlier basalts may have undergone more weathering in the presence of sodium chloride of cyclic origin, so producing Class A waters instead of Class C.

Class C waters are also common in the sand aquifers of the Lower Tertiary and Upper Cretaceous, especially to the east of Warrnambool, further away from the intake areas than the Class B waters (Fig. 19-1). Carbonic acid derived from the gradual decomposition of carbonaceous matter which is present in most of these sediments sometimes enables the alkalinity to rise to more than 30 e.p.m. The chlorinity varies from a few e.p.m. to more than 60 e.p.m., with variations in depth as well as in different areas of the basin (Johns, 1968). The deeper waters tend to be more saline. The hypothetical salts in groundwater from Belfast No. 4 well are as follows:—

Calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$ . . . . .	1.2 e.p.m.
Magnesium bicarbonate, $\text{Mg}(\text{HCO}_3)_2$ . . . . .	2.2 e.p.m.
Sodium bicarbonate, $\text{NaHCO}_3$ . . . . .	3.1 e.p.m.
Sodium sulphate, $\text{Na}_2\text{SO}_4$ . . . . .	0.6 e.p.m.
Sodium chloride, $\text{NaCl}$ . . . . .	8.6 e.p.m.

The sodium bicarbonate in these waters from the sand aquifers may be produced by the action of carbonic acid on the alkali feldspar in some of the sediments, by hydrolysis of clay minerals with a high proportion of exchangeable sodium ions (Taylor, 1928), and by cation exchange reactions between calcium and magnesium ions in the water and absorbed sodium ions on the sediments



(Johns, 1968). There is some evidence for such cation exchanges in the appearance of sodium sulphate in solution. However, the concentrations of calcium and magnesium ions remaining in the groundwater suggest that this explanation proposed by Foster (1950) for the high concentrations of sodium bicarbonate in some very soft waters may not be satisfactory for Class C waters.

#### Class D

These are soft waters in which the sodium-chloride ratio is greater than 95, but the magnesium-chloride ratio is less than 20 (Table 19-2). Magnesium and probably calcium ions which were present in the groundwater nearer the intake areas (Class A, B and C) have been removed from solution and replaced by sodium ions as a result of cation exchanges within the aquifer. Class D waters are found only in the deeper parts of the Otway Basin in the Mepunga Formation and the various formations of the Wangerrip Group (Fig. 19-1). These sediments were deposited under conditions which varied from marine to paralic, littoral, deltaic and lagoonal (Bock and Glenie, 1965). In each case the sediments would have been deposited in waters containing dissolved solids largely of oceanic origin with differing degrees of dilution by fresh water depending on local conditions. Sodium ions would therefore be expected to be a major constituent of the exchangeable cations as is usual among sediments deposited in oceanic waters (Cederstrom, 1946). Such sediments are later capable of softening hard groundwater containing high concentrations of calcium and magnesium ions, as was shown by Thresh (1912) in the London Basin.

The salts in groundwater from the Paaratte Formation (Timboon Sand Member especially) of Port Campbell No. 1 well are as follows:—

Calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$ , . . . . .	1.1 e.p.m.
Magnesium bicarbonate, $\text{Mg}(\text{HCO}_3)_2$ , . . . . .	0.3 e.p.m.
Sodium bicarbonate, $\text{NaHCO}_3$ , . . . . .	26.5 e.p.m.
Sodium carbonate, $\text{Na}_2\text{CO}_3$ , . . . . .	6.1 e.p.m.
Sodium sulphate, $\text{Na}_2\text{SO}_4$ , . . . . .	0.4 e.p.m.
Sodium chloride, $\text{NaCl}$ , . . . . .	32.7 e.p.m.

The alkalinity of Class D waters is commonly greater than 7 e.p.m. (*i.e.* in sub-classes m and n) due to the presence of high concentrations of sodium bicarbonate and carbonate. Foster (1950) demonstrated that hard water containing calcium and magnesium bicarbonates could be converted to soft sodium bicarbonate water with a greatly increased alkalinity after contact with lignite, calcium carbonate and sodium-rich ion-exchange resin. As calcium and magnesium ions were removed from solution by the ion-exchange resin more calcium bicarbonate could be dissolved as a result of the action of lignite on the calcium carbonate, and then this calcium bicarbonate could likewise be removed and replaced by more sodium bicarbonate. The final concentrations of calcium and magnesium ions in solution were reduced and the sodium concentration greatly increased compared with the original solution.

The conditions for such reactions to occur exist in parts of the Lower Tertiary-Upper Cretaceous aquifers. However, the hydrolysis by carbonic acid of clay minerals having exchangeable sodium ions (*i.e.* replacement of sodium by hydrogen ions) may also play a part in the production of high concentrations of sodium bicarbonate and carbonate, as in Class C.

The chlorinity of Class D waters varies from about 2 e.p.m. to more than 300 e.p.m., with variations in depth and in different areas of the basin. These variations reflect different chlorinities in the environment of deposition of the sediments and different degrees of flushing of connate water by less saline groundwater. The degree of flushing depends on the porosity and permeability of the sediments, the structure of the basin, and on the distance from the intake area. Relatively impermeable sediments, or permeable sediments in closed structures usually contain water of high chlorinity.

There are also variations in other ionic concentrations with depth in the Mepunga Formation and the Wangerrip Group although these variations are usually within one class of water only. However, at the top of these sediments Class C waters may sometimes be found above Class D waters. Similarly, in the Waarre Sandstone, Class E waters may be found together with Class D.

The sulphate concentration and the sulphate-chloride ratio varies widely in waters from the Lower Tertiary-Upper Cretaceous aquifers. In some Class D waters there are only a few parts per million of sulphate and the sulphate-chloride ratio is only about one, whereas in sea water and in many groundwaters this ratio is approximately 10. The low sulphate content is due to the action of anaerobic sulphate-reducing bacteria in the sediments during and possibly after their deposition, in the presence of carbonaceous matter (Johns, 1968). The sulphate-chloride ratio of the groundwater in these sediments therefore largely reflects the composition of their connate water.

#### Classes E and F

These two classes of water are similar in that they have appreciable concentrations of calcium chloride which does not occur in most other groundwaters. In both classes the magnesium-chloride ratio is less than 20. However, in Class E the sodium-chloride ratio is between 80 and 95, while it is less than 80 in Class F (Table 19-2). These very hard waters have been found in the Otway Basin only in the Lower Cretaceous Otway Group of non-marine mudstones and arkoses, and in a few cases from the overlying Upper Cretaceous Waarre Sandstone in the Otway Basin. Similar waters have been described in several overseas oilfields (Hudson and Taliaferro, 1925).

The hypothetical salts in water from the Waarre Sandstone in Port Campbell No. 3 well (Class E) and from the Otway Group in Eumeralla No. 1 well (Class F) are as follows:—

	Port Campbell No. 3	Eumeralla No. 1
Calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$ , . . . . .	10.6 e.p.m.	5.9 e.p.m.
Calcium sulphate, $\text{CaSO}_4$ , . . . . .	0.5 e.p.m.	10.1 e.p.m.
Calcium chloride, $\text{CaCl}_2$ , . . . . .	25.6 e.p.m.	139.4 e.p.m.
Magnesium chloride, $\text{MgCl}_2$ , . . . . .	12.8 e.p.m.	1.1 e.p.m.
Sodium chloride, $\text{NaCl}$ , . . . . .	361.1 e.p.m.	174.1 e.p.m.

The chlorinity of most of these waters is high, some approaching that of sea water. In these formations, which may be sealed in the deeper parts of the basin, there is probably very little movement of fluids. The alkalinity does not rise above about 10 e.p.m. (mostly sub-classes l and m).

The Otway Group sediments are generally believed to be non-marine, (Bock and Glenie, 1965), so it is difficult to envisage depositional environment of concentrated sodium and calcium chloride waters.



The predominant exchangeable cation in fresh-water sediments is usually calcium. When such sediments are later contacted by oceanic water, three equivalents of calcium ions are released into the water in exchange for one equivalent of magnesium and two of sodium ions which are absorbed onto the sediments (Spencer and Murata, quoted by Piper and Garrett, 1953). Calcium chloride waters have been found in fresh-water sediments in California after the entry of contaminating sea water into the aquifers (Hudson and Taliaferro, 1925; Piper and Garratt, 1953). Such cation exchange hardening of groundwater can explain the origin Class F waters in the Otway Basin, in which the sodium and magnesium chloride cations are reduced with respect to the oceanic ratios, suggesting the removal of these cations from solution, while the calcium-chloride ratio is increased. However, the problem remains as to when the Otway Group sediments might have had contact with saline water containing oceanic salts. The sediments may have been deposited under fresh-water conditions with sea water infiltrating them during the Upper Cretaceous marine transgression which led to the deposition of the Waarre Sandstone. However, the relatively low permeability of most of the Otway Group sediments probably limited this infiltration.

On the other hand, the sediments may have been deposited under conditions involving rapid transport from a fresh-water environment to one in which there could be mixing with sea water, as in a delta. The products of the reaction between the sediments having a high proportion of exchangeable calcium ions and the diluted sea water of the delta may have been retained as the connate water of the relatively impermeable sediments. The connate water, which may initially have been of relatively low chlorinity may then have been gradually concentrated as a result of the semi-permeable membrane properties of deeply buried, fine-grained sediments. During compaction, fine-grained sediments under considerable hydrostatic pressure retain ions while permitting the gradual escape of water from the formation, thereby concentrating the interstitial solutions, which in this case would contain mostly sodium and calcium chlorides (De Sitter, 1947; Bredehoeft, *et al.*, 1963). Clay membranes may also modify the ionic composition of the trapped water by permitting the escape of certain ions such as sodium and bicarbonate, while retaining other ions selectively (Graf, *et al.*, 1966). The extent to which these semi-permeable membrane properties of the fine-grained but deeply buried sediments in the Otway Basin have brought about changes in the formation fluids is unknown.

In Class E waters there is no evidence from the water analyses that sodium ions have been removed from solution, although this may have occurred. The sodium-chloride ratio is approximately the same as in ocean water. In the Otway Basin these waters probably occur only in the upper parts of the Otway Group and the overlying Waarre Sandstone in which there are also some soft Class D waters with high sodium-chloride ratios. The sodium bicarbonate waters probably occur in those parts of the Waarre Sandstone which were deposited in sea water during the transgressive phase of the first depositional cycle recognized by Bock and Glenie (1965).

Class E waters might therefore result from the mixing of waters which originally belonged to classes D and F. The low sodium-chloride ratio of Class F would be increased by the high sodium-chloride ratio of Class D while the magnesium-chloride ratio in the mixture would remain low, as in Classes D and F.

## CONCLUSION

From this brief discussion of the six main classes of groundwater found in the Otway Basin, it may be seen that considerable information about the genesis of the groundwater, and about the environment of deposition and lithology of the enclosing rocks can be obtained from water analyses. The geochemical characteristics of any particular groundwater reflect the chemical and mineralogical composition of the aquifer, the composition of its connate water, the hydrological properties of the aquifer (especially its porosity and permeability) the amount and composition of other water moving into the aquifer, and various modifications due to chemical reactions, especially cation exchanges, which take place between the aquifer and its water.

(December, 1966)