

GEOCHEMISTRY OF GROUNDWATER FROM UPPER CRETACEOUS-LOWER TERTIARY SAND AQUIFERS IN SOUTH-WESTERN VICTORIA, AUSTRALIA

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Abstract: Several chemically different types of groundwater have been discovered in confined sand aquifers of the Upper Cretaceous-Lower Tertiary sediments in the Otway Basin, southern-western Victoria. The main geochemical variables involved in the genesis of these groundwaters are considered separately. They are:

- (a) cation exchanges which cause softening or hardening of the water;
- (b) availability of carbonic acid within the aquifer and the formation of sodium bicarbonate;
- (c) addition of different amounts of oceanic salts mainly from saline connate water in the sediments;
- (d) variations in the ratio of sulphate to chloride as a result of sulphate accumulation or bacterial sulphate reduction.

These variations can be followed more easily from water analyses when the ionic concentrations are expressed as chloride ratios (concentrations of particular ions as percentages of the chloride concentration in equivalents per million). Some of the variations are fairly regular in their distribution in the basin while others are more irregular.

Four main classes of water based on sodium and magnesium-chloride ratios are described, with subclasses based on chlorinity and alkalinity. Waters representative of three of these main classes have been described in similar aquifers in other sedimentary basins.

Introduction

During a deep drilling program being carried out by the Victorian Mines Department for groundwater in the Otway Basin of south-western Victoria, several chemically different types of groundwater have been discovered in confined sand aquifers of the Upper Cretaceous-Lower Tertiary Wangerrip Group of sediments. There are considerable variations in the ionic concentrations, the total salinity, the hardness and the pH of these groundwaters. An attempt is made here to explain the origin of these geochemical variations and to draw attention to the similarity between many of these waters and those from comparable aquifers elsewhere in the world.

Upper Cretaceous-Lower Tertiary aquifers of the Otway Basin

The Otway Basin in Victoria extends from Port Phillip Bay in the east, for about 200 miles to the west where it continues into South Australia. It extends beneath the waters of Bass Strait and the Indian Ocean in the south and has a poorly defined northern limit which is largely covered by extensive sheets of Newer Basalts. However, for the purposes of this discussion the term Otway Basin will be used to describe that part of the basin shown in Fig. 1. The Wangerrip Group of sediments increases in thickness from a few

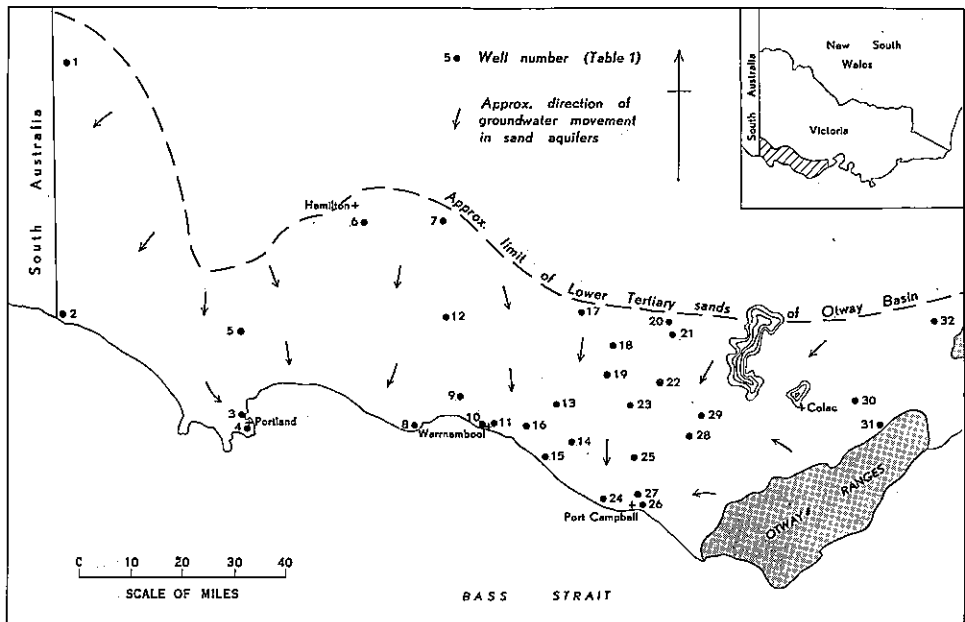


Fig. 1. Map of the Otway Basin in Victoria showing well locations and approximate directions of groundwater movement in Upper Cretaceous-Lower Tertiary sand aquifers.

feet along the northern edge of the basin to more than 5000 feet in the southeastern part of the basin around Port Campbell, and 6000 feet in the southwestern part near the South Australian border. These sediments represent the older two of four depositional cycles which have been recognized in the Basin¹). The quartz sands and carbonaceous silty sands of the aquifers in the Wangerrip Group were deposited during the regressive phases of the cycles under conditions which varied from shallow-water marine to paralic, estuarine and fresh-water at different times and in different areas. Some of these

sediments have carbonaceous or argillaceous cementing materials²⁾, but many are poorly cemented and highly permeable. They are overlain by later Tertiary and Quaternary sediments and Upper Pliocene-Pleistocene basalts to a depth which varies from a few hundred to 3000 feet.

The locations of the deep wells in the Otway Basin along with the approximate directions of ground-water movement in the Upper Cretaceous-Lower Tertiary aquifers, as determined from the isopiestic lines, are shown in Fig. 1. The intake areas are situated around the margins of the basin, especially at the foot of the Otway Ranges and along the water courses where Wangerrip Group sediments are exposed. Some groundwater may also infiltrate through the basalts into deep leads and thence into the basin.

The analyses of water samples collected during production or prolonged pumping tests in the Otway Basin are reported in Table 1, with the ionic concentrations expressed in parts per million. The sample depth usually represents that depth interval in the well which has the best quality water as indicated by electric-logging techniques, and from which water is produced through slotted casing with little possibility of serious contamination with waters from other levels.

These analyses illustrate the wide variations in the chemical composition of the groundwaters of the Otway Basin considered here. The total content of dissolved solids varies from a few hundred to many thousands of parts per million (ppm). The pH varies 5.2 to 8.9, as measured in the laboratory. Some of the waters are soft, containing very low concentrations of calcium and magnesium salts, and many contain relatively high concentrations of sodium bicarbonate. Others are hard, with relatively high concentrations of magnesium chloride, calcium and magnesium bicarbonates, and sodium chloride. Some waters contain appreciable amounts of sulphate while others contain virtually no sulphate at all.

Geochemistry of groundwater from similar aquifers in other sedimentary basins

Similar types of groundwater to those in the Otway Basin were described by Thresh³⁾ in the Tertiary Thanet sands of the London Basin. Thresh demonstrated that the soft, sodium bicarbonate-rich waters had undergone a process of natural softening by cation exchanges between the sediments and the water. The Thanet sand was shown experimentally to be capable of softening hard water containing calcium and magnesium ions by removing these ions from solution and replacing them by an equivalent concentration of sodium ions. These changes were found to take place as hard water near the intake area moved down dip towards the centre of the London Basin. Natural soft-

TABLE I
 Analyses of well waters from Upper Cretaceous-Lower Tertiary sand aquifers in the Otway Basin, Victoria, expressed in parts per million.
 (Analyses performed by the Mines Department section of the State Laboratories, Victoria.)

Well No.	Well Reference (Vic. Mines Dept.)	Sample Depth (ft)	Parts per million											Total Hardness (CaCO ₃)	pH		
			Total Solids (calc.)	Na+K	Ca	Mg	Cl	HCO ₃	CO ₃	SO ₄	NO ₃	SiO ₂					
1	Kanawinka, 6	147	439	87	36	12	146	152	Nil	Nil	Nil	Nil	Nil	-	6	142	7.2
2	Glenelg, 1	2323	1330	420	5	4	306	544	38	3	3	3	3	-	12	29	8.5
3	Portland, 2	3003-3390	1409	435	5	3	219	656	33	60	60	60	60	-	-	26	8.1
4	Portland, 3	3120-4661	992	300	10	6	213	395	24	30	30	30	30	-	14	52	7.8
5	Heywood, 10	1728-3015	766	140	52	32	203	296	Nil	36	0.02	7	262	7.4	7	262	7.4
6	Monivae, 4	590-904	2972	550	152	264	1636	214	30	120	-	6	1467	8.1	6	1467	8.1
7	Yalimba, 1	633	2416	570	120	130	1223	265	9	97	-	9	834	7.5	9	834	7.5
8	Belfast, 4	1747-2636	1085	285	24	27	305	399	Nil	30	-	14	172	7.6	14	172	7.6
9	Yangery, 1	1785-2247	4560	1470	34	38	1232	1120	116	551	Pres.	-	239	8.2	-	239	8.2
10	Wangoom, 6	1545-2784	4710	1240	142	89	1259	1812	Nil	170	-	-	722	8.0	-	722	8.0
11	Wangoom, 2	1931-3168	4445	1190	144	75	1243	1614	Nil	170	-	11	669	8.2	11	669	8.2
12	Kangertong, 5	936-1012	1330	430	10	6	330	427	72	51	-	-	49	8.9	-	49	8.9
13	Pannure, 2	1928-2129	7065	1970	128	187	2337	2108	Nil	326	5	10	1090	7.8	10	1090	7.8
14	Nirranda, 3	2566-2699	550	87	60	12	97	232	16	37	Nil	8	198	8.5	8	198	8.5
15	Mepunga, 10	3526-3560	822	177	46	24	236	298	14	16	Nil	11	212	8.0	11	212	8.0
16	Mepunga, 7	2207-2506	5180	1170	226	213	1791	1568	Nil	210	Nil	-	1443	7.5	-	1443	7.5
17	Mortlake, 1	670-707	1895	310	141	92	473	802	Nil	77	-	-	730	8.0	-	730	8.0
18	Glenormiston, 2	1356	1087	270	38	15	214	511	Nil	20	-	20	154	8.0	-	154	8.0
19	Terang, 1	1600-1650	2534	700	68	63	941	643	Nil	104	5	10	428	7.8	10	428	7.8

20	Koort-Koort-Nong, 3	530- 673	2115	460	104	52	431	915	Nil	121	Nil	32	472	8.3
21	Koort-Koort-Nong, 1	757- 852	996	220	53	33	291	329	15	46	Trace	9	267	8.3
22	Tandarook, 1	1779-1874	3662	1090	90	80	1457	582	45	318	-	-	555	8.2
23	Ecklin, 3	-	4610	1310	47	129	1518	1330	Nil	257	Nil	16	649	7.6
24	Narrawaturk, 2	2770-4402	610	130	31	20	160	216	Nil	Nil	7	9	162	8.3
25	Timboon, 5	2328-3023	315	80	11	8	102	96	Nil	16	Nil	-	63	6.2
26	Paaratte, 1	1625-2000	348	40	44	13	70	146	Nil	12	5	5	165	8.2
27	Paaratte, 2	2200-2800	450	115	10	3	61	232	Nil	14	-	9	36	7.9
28	Cooritejong, 1	1374-1600	565	160	17	15	252	94	Nil	21	-	4	103	7.5
29	Carpenteit, 1	1069-1148	7730	2390	269	122	3824	903	Nil	222	-	-	1171	7.9
30	Birregurra, 1	1056-1063	850	260	11	8	218	296	.15	42	Nil	-	61	-
31	Bambra, 49	600- 635	290	80	16	7	147	24	Nil	11	Nil	7	69	5.2
32	Waddallah, 2	350- 400	4310	1160	119	163	1887	716	Nil	250	-	11	961	7.1

ening of groundwater by cation exchange was also described by Renick⁴⁾ and Riffenburg⁵⁾ in the U.S.A. Such reactions are now known to occur in many parts of the world when water containing relatively high concentrations of calcium and magnesium ions enters an aquifer with a high proportion of sodium amongst its exchangeable cations. Under different circumstances natural hardening of groundwater by removal of sodium ions from solution and their replacement with calcium and, perhaps, magnesium ions has also been described⁶⁾. This requires calcium to be the predominant exchangeable cation in the sediment, as occurs in some fresh-water sediments, and sodium in a relatively high concentration in the groundwater.

Several more detailed investigations of the geochemistry of groundwater in sand aquifers similar to those in the Otway Basin have now been carried out in Cretaceous sands in Belgium⁷⁾, the London Basin⁸⁾, and Cretaceous-Lower Tertiary sands in the Atlantic and Gulf Coastal Plain of U.S.A.^{9,10)}. In each case a similar pattern of variations in the geochemical characteristics of the groundwaters has been described in zones with increasing distance from the intake area.

Nearest the intake area the water is soft and of low salinity. It contains free carbonic acid which begins to react with the aquifer sediments to form calcium and magnesium bicarbonates. The water becomes hard and of moderate salinity as it moves down dip from the intake area. Calcium and magnesium ions are then removed from solution and are replaced by sodium ions as a result of cation exchange reactions. The limited amount of carbonic acid available from the atmosphere and bacterial activity at the intake area is supplemented by the decomposition of carbonaceous matter within the sediments. Soft, sodium bicarbonate-rich groundwaters, with relatively low concentrations of chloride and sulphate, are found in this zone. Farthest from the intake area the waters become harder again and much more saline as a result of mixing with connate sea water which has been incompletely flushed from the sediments since the time of their deposition.

All of these types of groundwater are also found in the Upper Cretaceous-Lower Tertiary sand aquifers of the Otway Basin in Victoria. However, in only a few parts of the Otway Basin is there a regular succession of these characteristic water types on moving down-dip from the intake areas, as there is, for instance, in the Atlantic and Gulf Coastal Plain in U.S.A.⁹⁾. One reason for the greater irregularity in the Otway Basin may be that each well does not tap exactly the same aquifers. There are minor geochemical variations with depth in each system of aquifers which make comparisons between the analyses of composite samples of groundwater on a regional basis more difficult. In addition, the main geochemical reactions involved in the genesis of the Otway Basin waters seem to be more or less independent of each

other, and each may proceed to a different extent in different parts of the basin.

The geochemical history of any particular groundwater, as well as the overall regional variations, can be more accurately described if the main geochemical reactions involved are considered separately. These are as follows:

1. cation exchanges between the aquifer and groundwater, involving mainly sodium, calcium and magnesium ions;

2. variations in total carbonate and bicarbonate content (the alkalinity) through the addition of carbonic acid to the water, and the formation of sodium bicarbonate;

3. variations in the chlorinity of the water through the addition of chlorides (mainly sodium chloride) from connate water which is gradually flushed from the sediments;

4. variations in the sulphate content, and especially in the ratio of sulphate to chloride, as a result of the accumulation of sulphates in the sediments or the bacterial reduction of sulphates at the time of deposition and, possibly, for some time since then.

Use of chloride ratios in water analyses

These geochemical variations can more readily be followed from water analyses when the ionic concentrations are expressed as a proportion of the chloride concentration for the particular water. Mills and Wells¹¹⁾ used "reacting values" or chemical equivalents of various ions per thousand equivalents of chloride to demonstrate the relationship of oil-field brines to sea water. However, the ionic concentrations are probably best expressed as chloride ratios according to the system developed by Anderson¹²⁾. The chloride ratio of a particular ion in solution is,

$$\frac{\text{ionic concentration in equivalents per million}}{\text{chloride concentration in equivalents per million}} \times 100.$$

Anderson^{13,14)} was able to show, by using chloride ratios, that a large proportion of the dissolved solids in many surface waters and groundwaters in Victoria was of oceanic origin. He matched the composition of many groundwaters, particularly from Tertiary limestone aquifers, by diluting sea water and adding varying amounts of calcium and magnesium bicarbonates which could have been derived from the aquifer by the action of carbonic acid.

For practical purposes, the only sources of chloride ions in these aquifers are:

1. from rainwater containing oceanic salts of cyclic origin, which may be concentrated by evaporation and transpiration before entering the aquifer¹⁴⁾;

TABLE 2

Analyses of the well waters expressed in chloride ratios, with the class of water, its chlorinity and alkalinity.

Well no.	Chloride ratios (epm/100 epm Chloride)							Class of Water	Chlorinity (epm)	Alkalinity	
	Na+K	Ca	Mg	HCO ₃	CO ₃	SO ₄	NO ₃			epm	sub- class
1	95	40	23	56	0.0	1.0	-	B	4.0	2.5	k
2	210	2.9	3.8	110	15	0.7	-	D	8.6	10.2	m
3	260	3.4	3.2	150	15	17	-	D	7.4	11.8	m
4	220	8.3	8.2	110	13	10	-	D	6.0	7.3	m
5	110	46	46	86	0.0	13	-	C	5.7	4.9	l
6	52	16	47	7.6	2.2	5.4	-	A	46.1	4.5	l
7	71	17	31	13	0.9	5.9	-	A	34.5	4.7	l
8	140	14	25	67	0.0	7.9	-	C	9.6	6.5	l
9	180	4.9	8.9	53	11	33	-	D	34.7	22.2	n
10	150	20	21	84	0.0	9.9	-	C	35.5	29.7	n
11	150	21	18	76	0.0	10	-	D	35.1	26.5	n
12	200	5.4	5.4	75	26	12	-	D	9.3	9.4	m
13	130	9.7	23	53	0.0	10	-	C	65.8	34.6	n
14	140	110	37	140	19	28	-	C	2.7	4.3	l
15	115	34	30	73	7.0	4.9	-	C	6.7	5.4	l
16	100	22	35	49	0.0	8.7	-	C	50.5	24.7	n
17	100	53	57	99	0.0	12	-	C	13.4	13.1	n
18	195	32	20	140	0.0	6.7	-	C	6.0	8.4	m
19	120	13	19	40	0.0	8.3	0.3	D	26.5	10.5	m
20	165	43	36	125	0.0	21	-	C	12.1	15.0	n
21	120	32	33	66	6.1	12	-	C	8.2	5.9	l
22	115	11	16	23	3.7	16	-	D	41.0	11.0	m
23	135	5.5	25	51	0.0	13	-	C	42.7	21.8	n
24	125	34	36	79	0.0	15	2.4	C	4.5	3.5	k
25	125	19	23	55	0.0	11	-	C	2.9	1.6	k
26	92	112	54	121	20	17	0.0	B	2.0	2.8	k
27	295	29	15	200	0.0	17	4.6	D	1.7	3.8	k
28	99	12	17	22	0.0	6.2	-	D	7.1	1.5	k
29	96	12	9.3	14	0.0	4.3	-	D	107.8	14.8	n
30	180	9	11	79	8.1	14	-	D	6.1	5.4	l
31	82	19	14	9.4	0.0	5.6	-	B	4.2	0.4	k
32	95	11	25	22	0.0	9.8	-	B	53.2	11.7	m
Sea Water*	87	3.7	19.4	0.4	0.0	10.4	-	B			
Marine*											
Mudwater	87	3.4	19.5	4.7	0.0	5.4	-	B			

* Analysis of sea water calculated from mean of 77 analyses¹⁵).

** Analysis of marine mud-water calculated from Murray and Irvine¹⁶).

2. from saline water trapped in the sediments since the time of their deposition (connate water) or migrating into them later.

Because the chloride ion is so little affected by chemical reactions which may take place within the aquifer, the chloride ratios, especially of sodium, calcium, magnesium and sulphate, provide the best means of comparing the proportions of these ions in different groundwaters. In particular, this method allows the role of oceanic salts in the genesis of a particular groundwater to be demonstrated.

Chloride ratios in groundwater analyses from the Otway Basin

The chloride ion is an important constituent of all the groundwaters considered in the Otway Basin. The chloride ratios of the main ions in these waters are given in Table 2. The chloride ratios for sea water and for water in marine mud are given for comparison. For sea water the sodium-chloride ratio is 87, i.e., the concentration of sodium (epm) is 87 per cent of the chloride concentration, the remaining 13 per cent of the chloride being assumed to be magnesium chloride in the hypothetical combination of ions. In many aquifers, such as the mid-Tertiary limestones overlying the sand aquifers of the Otway and Murray Basins, this proportion of sodium to chloride ions is usually the same as that in sea water. This is because of the constancy of these ionic proportions in solutions containing salts of oceanic origin, whether from cyclic salts or connate sea water in the aquifer.

In Well 1 (Kanawinka), near the edge of the Otway Basin, the sodium-chloride ratio is approximately the same as in sea water, but the calcium-chloride and bicarbonate-chloride ratios are higher. This suggests that the groundwater has undergone little chemical change apart from the accumulation of oceanic salts in low concentrations and the solution of calcium carbonate from the aquifer. However, in Well 3 (Portland) the sodium-chloride ratio is three times that of sea water, while the calcium and magnesium-chloride ratios are much less than the oceanic ratios. Since much more magnesium and probably more calcium would originally have accompanied the chloride in the groundwater, some must have been removed to be replaced by sodium ions as a result of cation exchange. This explains the greatly increased sodium-chloride ratio, at least in part. Sodium bicarbonate may also be derived from the aquifer by the action of carbonic acid (see below). In Well 6 (Monivae) the sodium-chloride ratio is reduced while the calcium and magnesium-chloride ratios are increased relative to the oceanic ratios. Calcium and, particularly, magnesium have been added to this water as chlorides while sodium has probably been removed. That is, the water may have undergone natural hardening by cation exchange.

By comparing the cation-chloride ratios of one groundwater with another and with those of sea water various cation exchanges can be followed regardless of the hardness or salinity of the water. The cation-chloride ratios of the water in which some of the sediments, especially the non-marine sediments, were deposited may not have been the same as those of present-day sea water. Nevertheless, the close relationship between the groundwater composition in many aquifers to that of diluted sea water, with additional calcium and magnesium bicarbonate, suggests that the ion-chloride ratios of sea water have not markedly changed since Mesozoic times at least. The observed differences of ionic proportions in many groundwaters appear to be best explained in terms of reactions within the enclosing rocks either at the time of their deposition or later¹⁷). At worst, the use of ion-chloride ratios of sea water serves as a constant with which to compare the compositions of different waters, even if they occur in non-marine sediments.

Classes of water based on chloride ratios of cations

The chloride ratios of the main cations and their relationship to those of sea water are used here to divide the waters of the Otway Basin into four main

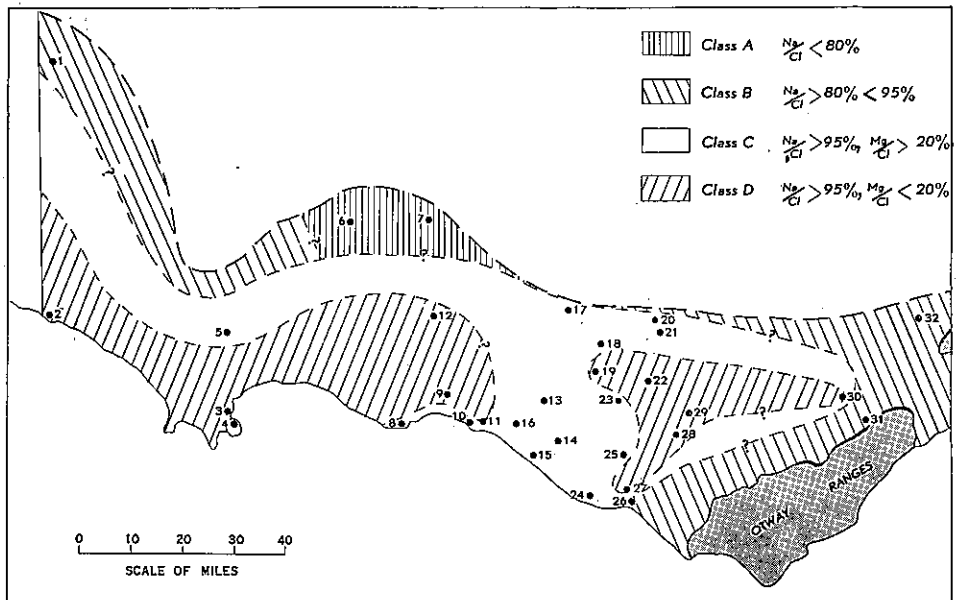


Fig. 2. Approximate distribution of the main geochemical classes of groundwater in the sand aquifers of the Otway Basin.

classes. Other variations in groundwater, which are more or less independent of those producing changes in the cation-chloride ratios, are here described in sub-categories of these main classes. The classes are defined as follows:

- A. sodium-chloride ratio < 80;
- B. sodium-chloride ratio > 80, but < 95;
- C. sodium-chloride ratio > 95, magnesium-chloride ratio > 20;
- D. sodium-chloride ratio > 95, magnesium-chloride ratio < 20.

These classes differ from the zones of earlier workers which were each based on different geochemical variables.

The classes do not necessarily represent stages in the progressive down-dip changes of any particular sample of groundwater, although in some cases they do (See Fig. 2). Nor do the classes refer to the usefulness of the water for any particular purpose, which is largely determined by the total salinity.

CLASS A

The sodium-chloride ratio is significantly less than the oceanic ratio, while the magnesium- and calcium-chloride ratios are higher than in sea water (Table 2). These waters are much harder than most waters of equal salinity, probably as a result of cation-exchange hardening, whereby sodium ions are removed from solution and replaced by magnesium and, perhaps, calcium ions. The main hypothetical salts in solution for groundwater from Well 7 are as follows:

Calcium bicarbonate,	$\text{Ca}(\text{HCO}_3)_2$,	4.34	epm
Calcium sulphate,	CaSO_4 ,	1.65	epm
Magnesium sulphate,	MgSO_4 ,	0.38	epm
Magnesium chloride,	MgCl_2 ,	10.3	epm
Sodium chloride,	NaCl ,	24.2	epm

In this class of water much of the dissolved matter consists of magnesium and calcium salts, especially magnesium chloride, which is in relatively high concentration when compared with that of sodium chloride.

The aquifers from which these waters were obtained were laid down predominantly under fresh-water conditions. Under these circumstances it is known that calcium ions usually predominate among the exchangeable cations of the sediments, as they do in many soils. When these sediments are later permeated by water containing cations in oceanic proportions they release calcium and adsorb sodium ions, and perhaps, some magnesium ions¹⁸). The resulting groundwaters contain relatively high concentrations of calcium chloride⁶).

However, the Class A waters which are found near the northern margin of the Otway Basin have higher concentrations of magnesium than calcium

salts in solution. These waters are derived from aquifers which are overlain by thick basalts in which much of the groundwater has a similar composition to that in the sands beneath them. It seems likely, therefore, that most of the cation exchange takes place in these basalts before the water enters the sand aquifers. The predominant source of chloride in these basalts is sodium chloride of cyclic origin which reacts with decomposing feldspars and ferromagnesium minerals. Some of the sodium ions associated with chloride are thereby removed from solution in exchange for magnesium and, to a lesser extent, calcium ions. More magnesium chloride and less sodium chloride therefore appear in solution. These waters also contain calcium bicarbonate derived from the aquifer by the action of carbonic acid, but their alkalinity is fairly low.

CLASS B

For this class of water the sodium-chloride ratio is approximately the same as in sea water, i.e. between 80 and 95, while the calcium and magnesium-chloride ratios are greater than in sea water (Table 2). There has been little or no cation exchange within the aquifer, nor has there been addition of much sodium other than as sodium chloride to the water. Calcium and magnesium bicarbonates have been added to diluted sea water which is otherwise unchanged apart, perhaps, from some accumulation of sulphates or their reduction by sulphate-reducing bacteria (See below). These waters are hard compared to those of Classes C and D with equal salinities. The oceanic salts were derived to some extent from cyclic salts at the intake areas, but mainly from connate water which is gradually flushed from the sediments as they become consolidated. Wells 1, 26, 31 and 32 produce water of this class, and all are situated not far from the margins of the basin (Fig. 2). The hypothetical salts in the water from Well 32 (Wabdallah) are:

Calcium bicarbonate,	$\text{Ca}(\text{HCO}_3)_2$,	5.94	epm
Magnesium bicarbonate,	$\text{Mg}(\text{HCO}_3)_2$,	5.81	epm
Magnesium sulphate,	MgSO_4 ,	5.20	epm
Magnesium chloride,	MgCl_2 ,	2.39	epm
Sodium chloride,	NaCl ,	50.8	epm

CLASS C

The sodium and magnesium-chloride ratios are both greater than in sea water, i.e., greater than 95 and 20, respectively (Table 2). Apart from the cations associated with the chloride of oceanic origin these waters contain sodium, calcium and magnesium bicarbonates, and sometimes sulphates, derived from the aquifer. The hypothetical salts contained in water from Well 8 (Belfast) are as follows:

Calcium bicarbonate,	$\text{Ca}(\text{HCO}_3)_2$,	1.20	epm
Magnesium bicarbonate,	$\text{Mg}(\text{HCO}_3)_2$,	2.22	epm
Sodium bicarbonate,	NaHCO_3 ,	3.14	epm
Sodium sulphate,	Na_2SO_4 ,	0.63	epm
Sodium chloride,	NaCl ,	8.59	epm

These waters are moderately hard relative to their salinities (hardness 60 when the salinity is 300 ppm, and 1400 when the salinity is 5000 ppm). They are found over a wide area of the Otway Basin especially to the north of Port Campbell (Fig. 2). The aquifers from which they are obtained include shallowwater marine and estuarine sediments. These waters may be derived from Class B waters, and some may later become Class D waters, but this relationship is uncertain.

The explanation offered by Foster¹⁰) for the presence of relatively large amounts of sodium bicarbonate in waters from the Atlantic and Gulf Coastal Plain, U.S.A., does not appear satisfactory for these waters in the Otway Basin. Foster showed experimentally that hard water containing calcium bicarbonate, with an alkalinity of 3.5epm, was converted to soft, sodium bicarbonate water with an alkalinity of 15epm after contact with lignite, calcium carbonate and a sodium-rich ion-exchange resin. The calcium and magnesium concentrations were greatly reduced, while the sodium concentration was increased as a result of cation exchange ratios. More sodium was found in solution than the equivalent amounts of calcium and magnesium originally present. Foster suggested that more calcium must have been made available by the solution of calcium carbonate in the presence of lignite, and that this was also removed by cation exchange to be replaced by more sodium in the form of sodium bicarbonate. At equilibrium this water contained very little calcium or magnesium. However, in Class C waters of the Otway Basin, the calcium and magnesium concentrations are relatively high. There is no evidence here that the added sodium has been derived from the aquifer in exchange for calcium or magnesium ions, although this may have occurred to some extent.

There is, however, an alternative source of sodium bicarbonate. With the gradual decomposition of carbonaceous matter at elevated temperatures within the sediments free acid may be liberated which can react with sodic feldspar minerals, which comprise about 5 per cent of many of the sediments in the Wangerrip Group of the Otway Basin²), or cause hydrolysis of clay minerals with appreciable concentrations of adsorbed sodium ions, i.e. replacement of the sodium by hydrogen ions. This would give sodium hydroxide which, after further reaction with carbonic acid, would produce sodium carbonate and bicarbonate, leaving hydrogen clays instead of sodium clays. These reactions take place in the absence of free acid when sediments which

were deposited under marine or saline conditions, having a predominance of sodium among the exchangeable cations and a high pH, are leached with fresh water¹⁹). Adsorbed sodium ions are relatively easily displaced by hydrogen ions whereas calcium and magnesium ions, which may also be present, are not. High concentrations of sodium bicarbonate may therefore occur together with calcium and bicarbonates in solution. The latter may be derived from the action of carbonic acid on feldspars or small amounts of calcareous matter in the aquifer. Because sodium bicarbonate is so readily soluble, alkalinities as high as 34.7epm (2108ppmHCO₃), which is much higher than occurs in Class A or B waters, are found in Class C.

CLASS D

The sodium-chloride ratio is considerably greater than in sea water, i.e. >95, but the magnesium-chloride ratio is less than in sea water i.e. <20 (Table 2). Sodium has been increased relative to chloride mainly through the addition of sodium bicarbonate to the water. Magnesium ions, which may originally have been present in a concentration equal to or greater than 20 per cent of the chloride (epm) have been removed from solution. Calcium ions have probably been removed from solution, too, but the original concentration present in the groundwater nearer the intake area cannot be accurately determined. Seldom is the calcium-chloride ratio reduced to less than that in sea water. These waters are often very soft with high alkalinities due mainly to the presence of sodium bicarbonate.

The hypothetical combinations of ions in groundwater from Well 3 (Portland) are as follows:

Calcium bicarbonate,	Ca(HCO ₃) ₂ ,	1.00	epm
Magnesium bicarbonate,	Mg(HCO ₃) ₂ ,	1.48	epm
Sodium bicarbonate,	NaHCO ₃ ,	10.25	epm
Sodium carbonate,	Na ₂ CO ₃ ,	1.09	epm
Sodium sulphate,	Na ₂ SO ₄ ,	1.25	epm
Sodium chloride,	NaCl,	6.17	epm

These waters have undergone natural softening by cation exchange in sediments which were deposited under shallow-water marine conditions and have a high proportion of sodium amongst their exchangeable cations. The relatively greater proportions of calcium and magnesium ions in the groundwater entering such a region of the aquifer, compared to those in the sediments, enables calcium and magnesium ions to be adsorbed and sodium ions to be released into solution. Hydrolysis of sodium minerals probably also plays a part in producing high concentrations of sodium bicarbonate in these waters, as in Class C, but the proportion of sodium bicarbonate derived from this

source is uncertain. It is not yet clear what conditions in the aquifer favour the formation of Class D waters rather than Class C, or whether the difference is only one of degree, involving the same geochemical processes. Class D waters occur mainly in the south-western and central-eastern areas of the Otway Basin in Victoria (Fig. 2). A general progression can therefore be seen with water of Classes A and B near the margins of the basin, Class C waters further down-dip, and Class D waters mainly in the deeper central parts of the basin.

In each of these broad Classes of groundwater in the Wangerrip Group aquifers of the Otway Basin the overall composition of the waters is somewhat variable as a result of other geochemical processes affecting the chlorinity, the alkalinity and the sulphate-chloride ratio.

Variations in chlorinity

The chlorinity of groundwaters in the Otway Basin, that is, the chloride concentration in equivalents per million, varies within wide limits (Table 2). Other geochemical variations due to cation exchanges, formation of carbonic acid within the aquifer, or bacterial reduction of sulphate, seem to be more or less independent of the chlorinity. Variations in the chlorinity of groundwater largely reflect the extent to which saline connate water has been flushed from different parts of the aquifer by less saline water moving down-dip from the intake area. However, in some areas the drainage efficiency at the intake area may be so poor that the water entering the aquifer is of relatively high salinity¹⁴). This is probably true of some of the intake areas along the northern edge of the Otway Basin where the chlorinity of river waters is often quite high. Clearly, the chlorinity of the water in which the sediments were deposited is of great importance. Marine and fresh-water sediments will have connate interstitial waters of different chlorinities. Within marine sediments, however, the ease with which the connate sea water can be flushed out depends on several factors including the porosity and permeability of the sediments, the structure of the sedimentary basin, and the distance from the intake area.

In the south-western area of the Otway Basin the chlorinity of the best quality water from Upper Cretaceous-Lower Tertiary sand aquifers is less than about 10 epm. Low chlorinity waters also occur in the south-eastern and northern parts of the basin, both areas being relatively close to intake areas. However, near Hamilton in the northern part of the basin, and to the east of Warrnambool the chlorinities are generally between 20 and 40 epm, with some as high as 108 epm (Fig. 3). In these areas the movement of low chlorinity water from the edges of the basin is less efficient in flushing the

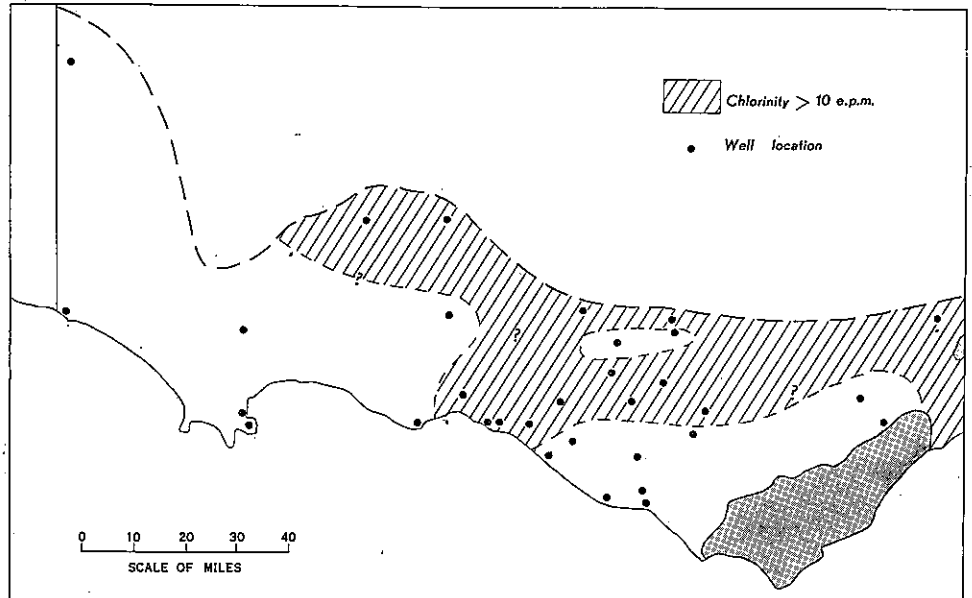


Fig. 3. Chlorinity of groundwater in the Otway Basin. In the hatched area the best quality water from the sand aquifers of each well has a chlorinity greater than 10 e.p.m.

saline connate water from the sediments either because of the structure of that part of the basin or the relatively lower permeability of the sediments there. Variations in the chlorinity of groundwater may therefore be useful in elucidating the structure of the Otway Basin and facies changes within its sediments, as is possible in the limestones and marls of the Murray Basin in northwestern Victoria²⁰).

In the Class B waters considered here the chlorinity varies from 2 to 53 e.p.m. These different waters may be distinguished as sub-categories of the same class by writing the chlorinity, to the nearest whole number, after the class symbol. Hence, water from Well 26 is represented by the symbol B2, and water from Well 32 as B53.

Variations in alkalinity

In each of the main classes of water in the Otway Basin there are variations in the alkalinity (the total content of bicarbonate and carbonate ions expressed in equivalents per million). However, the average alkalinity and *pH* increase progressively from Class A to Class D. These quantities are a measure of the total concentration of carbonic acid available for reaction within

a particular groundwater-aquifer system. The alkalinity is more or less independent of the chlorinity and so is more useful than the bicarbonate-chloride ratio.

The concentration of carbon dioxide provided at the intake area from the atmosphere and bacterial action seldom allows the alkalinity to be greater than about 7 epm (i.e. 427 ppm bicarbonate).

In fact, the alkalinity in many aquifers is less than about 4epm, depending on local conditions at the intake area. However, the alkalinities of many Class C and D waters in the Otway Basin exceeds 12epm. Sulphate-reducing and other bacteria living in the sediments at the time of their deposition, and possibly for some time since then, produce carbon dioxide which may later be incorporated into groundwater as the interstitial water is flushed from the sediments^{17, 21}). But the most important source of carbon dioxide in aquifers such as the Upper Cretaceous-Lower Tertiary sediments of the Otway Basin is provided by the gradual decomposition of carbonaceous matter which is present in nearly all of them^{10, 2}). In Class C and D the formation of sodium bicarbonate, which is much more soluble than calcium or magnesium bicarbonate, allows the alkalinity to rise to 30epm or more where the necessary carbon dioxide is available. Those areas of the Otway Basin where the

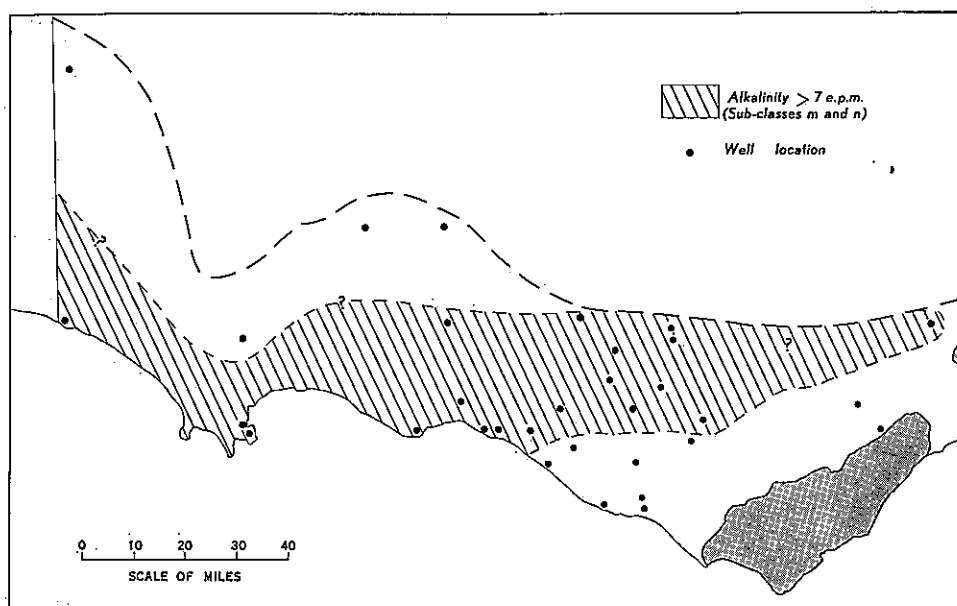


Fig. 4. Alkalinity of groundwater in the Otway Basin. In the hatched area the best quality water from the sand aquifers of each well has an alkalinity greater than 7 epm.

alkalinity of the present water samples exceeds 7epm are shown in Fig. 4. They extend from the coastal areas in the south-west, to the central and north-eastern parts of the basin.

The waters in each main class may be sub-classified according to their alkalinity as follows:

Sub-class	Alkalinity (epm)	Bicarbonate (ppm)
k	< 4	> 244
l	4-7	244-427
m	7-12	427-732
n	> 12	> 732

Water from Well 3 may then be distinguished from that in Well 28 by using the symbols D7m and D7k respectively (Table 2). These waters are related from the point of view of cation exchange softening and chlorinity, but they differ considerably in their alkalinities. Waters in sub-class k may come from an aquifer with very little carbonic acid available, or may have some free carbonic acid which has not yet been used up by the formation of bicarbonates. Waters of sub-class l are usually those whose limited carbonic acid has already been used in the formation of bicarbonates. Higher alkalinities in sub-classes m and n, require an additional source of carbonic acid and the formation of sodium bicarbonate within the aquifer.

Variations in sulphate-chloride ratio

The concentration of sulphate ions in waters of the Otway Basin varies from almost zero up to many hundreds of parts per million (Table 1). The sulphate-chloride ratio varies from 0.7 to 33, but in about half of the waters this ratio lies between 7 and 13 (Table 2). Since the main source of chloride and sulphate in these waters is saline water remaining in the sediments since their deposition, this variation primarily reflects variations in the composition of the interstitial water at that time. The sulphate-chloride ratio in sea water is about 10. However, in 1895 Murray and Irvine¹¹), showed that, in water in marine muds the sulphate-chloride ratio is reduced to about 5 and the bicarbonate concentration correspondingly increased (Table 2). It has since been demonstrated that the interstitial water of seafloor sediments may have its sulphate almost completely reduced by sulphate-reducing bacteria before the sediments are buried to a depth of more than a few feet^{17, 21}). This

involves the action of anaerobic bacteria in the presence of oxidizable organic matter²²). If this interstitial water were later made available as groundwater it would show an appreciable content of oceanic salts with the exception of sulphate which would be replaced by bicarbonate to a greater or lesser extent. That such a process has occurred in the Otway Basin sediments is evidenced by the many water analyses in which the sulphate-chloride ratio is less than 10 (Table 2). However, sulphate-reduction in the Otway Basin, as elsewhere, is often patchy in distribution, depending on the local development of suitable conditions¹⁷).

In some areas of the Otway Basin the groundwaters show an increased sulphate-chloride ratio relative to sea water. During the deposition of the sediments there were probably isolated coastal areas where concentration by evaporation or a local terrestrial source of sulphate allowed the proportion of sulphate to chloride to increase. The distribution of those waters with sulphate-chloride ratios reduced or increased relative to sea water does not appear to be closely related to any of the other chemical variations considered.

Conclusions

The geochemistry of groundwaters from sand aquifers such as those of the Upper Cretaceous and Lower Tertiary of the Otway Basin is best understood if the main geochemical processes which produce variations in water composition are considered separately. The geochemical processes considered here are cation exchanges and formation of sodium bicarbonate, release of carbonic acid within the aquifer with consequent variations in alkalinity, incorporation of different amounts of saline connate water giving variations in chlorinity, and variations in sulphate-chloride ratio produced by sulphate accumulation or bacterial sulphate-reduction in those residual waters.

The chloride ion is a major constituent of all the groundwaters of the Otway Basin. Most of the chloride is of oceanic origin, either from cyclic salts entering the aquifer at the intake area, or from saline connate water which has been gradually flushed from the sediments since the time of their deposition. When the ionic concentrations are expressed as chloride ratios the role of oceanic salts in the genesis of these groundwaters can be demonstrated. Natural softening or hardening by cation exchanges between the groundwater and the aquifer sediments, and the increase or decrease of sulphate relative to chloride concentrations can be followed in different parts of the basin.

Four main classes of groundwater based on sodium and magnesium-chloride ratios have been described for the Otway Basin, with sub-classes based on chlorinity and alkalinity. While some of the geochemical variations

can be followed progressively down-dip from the intake areas, others are more irregular in their distribution. However, knowing their approximate regional distribution, a prediction may be made about the likely composition of groundwater in many parts of the Otway Basin.

Groundwaters similar to those of Classes B, C and D in the Otway Basin have been described in one or more of the zones recognized in other comparable sedimentary basins where detailed geochemical studies have been carried out. However, waters belonging to Class A either do not exist or have not been recognized in these other basins before. These waters are usually found separately in fresh water sediments or basalts.

The use of symbols such as A4k or C6n enables a fairly accurate description of the main features in the geochemical history of a particular water to be given. Such a system of classification of water types, with or without modification to allow for variations in sulphate content, may be useful in other groundwater studies.

Acknowledgements

The author wishes to thank Dr. D. E. Thomas, Director of the Geological Survey, Victorian Mines Department, for permission to publish this paper. The assistance of Messrs. C. R. Lawrence, R. C. Glenie, P. E. Bock and P. R. Kenley, by way of information supplied and constructive criticism of the manuscript, is gratefully acknowledged.

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