The Occurrence of Monohydrocalcite in Two Small Lakes in the South-East of South Australia

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Abstract

Monohydrocalcite is the main constituent of beach rocks surrounding Lakes Fellmongery and Butler near Robe in the south-east of South Australia. It occurs as hard pelletal aggregates with a sponge-like texture which resembles calcareous tufa.

At Lake Fellmongery, it appears that the monohydrocalcite is formed in saline waters with a high Mg/Ca ratio, high pH, and in the presence of blue-green algae. Isotopic data suggest that the monohydrocalcite is not secreted by the algae but rather that it is precipitated from saline waters.

The composition of monohydrocalcite derived from the most comprehensive chemical analysis is $(Ca_{0.9053} Mg_{0.0788} Fe_{0.0022} Sr_{0.0047} Na_{20.0133} K_{20.0008})CO_3 \cdot 1.15H_2O$. All the water is firmly bound in the crystal structure, which appears to be stable when dry, but transforms in water to calcite.

X-ray powder diffraction data have been indexed on a hexagonal unit cell containing 9 (CaCO₃ · H₂O) and yield lattice parameters of a = 10.566 Å, c = 7.573 Å. The strongest reflections are: 4.333 100; 3.078 70; 1.9308 65; 2.829 50; 2.1665 45; 5.283 35.

Introduction

Monohydrocalcite (CaCO₃ · H₂O) was first reported by Krauss and Schriever in 1930 as a dehvdrated product of CaCO₃ · 6H₂O. Since then monohydrocalcite has been synthesized by many workers (Halla, 1937; Brooks, Clark, and Thurston, 1950; Baron and Pesneau, 1956; Monaghan and Lytle, 1956; Tassell, 1962; Kinsman and Holland, 1969; Malone and Towe, 1970; Towe and Malone, 1970; and Duedall and Buckley, 1971), usually as a byproduct during attempts to synthesize dolomite. Carlström (1963) was able to show that otoliths of the tiger shark (Calcocerdo cuvier) were composed of monohydrocalcite and aragonite, while Marschner (1969) found that carbonate scales formed in airscrubbers of air-conditioning plants and at the mouths of cold water pipes consisted mainly of CaCO₃ · H₂O.

The first reported occurrence of monohydrocalcite in a geological environment was by Sapozhnikov and Tsvetkov (1959) who found that calcareous encrustations in Lake Issyk-Kul, Kirgistan, consisted entirely of monohydrocalcite. More recently Fischbeck and Müller (1971) found it to be the major constituent of knob-, mushroom-, and cauliflower-shaped speleothems in a small cave of the Fränkische Schweiz, Western Germany. In 1929, Mawson reported to the Geological Society of London on an algal-reef formation at Karatta Lake near Robe in the south-east of South Australia. An analysis of this "foliaceous cavernous limestone of Lake Karatta recently formed from *Lithothamnion*-like algal growths" indicated approximately 10 percent water. There was no reason, however, to suspect that this was a new mineral and no further investigations were made to determine how the water was incorporated.

The Lacustrine Environment

During a visit to the south-east of South Australia as part of a continuing study of the geochemistry of recent carbonate sediments of the region, the author's attention was drawn to the beach rock surrounding what is now called Lake Fellmongery. Not only was this the first lake of the region to be found surrounded by beach rock, but X-ray diffraction of the tuffaceous-like material showed it to be composed entirely of monohydrocalcite. Similar beach rock was also found 'around Lake Butler.

Lakes Fellmongery and Butler are two small lakes near Robe in the south-east of South Australia (Figs. 1 and 2). Both lakes occur in shallow depressions in the Robe Dune, one of a number of back-shore, beach-ridged, calcareous and siliceous sand dunes described by Sprigg (1952). These dunes rise to a maximum of 50 m above the surrounding flat countryside; the successive lines of dunes extending some 50 km to the east represent old shore lines of the prograding coast. The Robe Dune corresponds to the lowest sea-level during Quaternary times, and has been subject to partial submergence since.

There are a number of small lakes nearby, one of which, Chara Swamp, is isolated while the others are connected by Drain L which enters Guichen Bay near Lake Fellmongery. No evidence could be found for development of monohydrocalcite beach rock in these lakes.

Lake Fellmongery is approximately 1 km east of the town of Robe (Fig. 2) and is isolated from the sea by sand-dunes. It is roughly kidney shaped with approximate dimensions 600×500 m. Unlike other lakes of the region, which dry up during the summer, the water of Lake Fellmongery is permanent. Maximum depth of water is 6 m but over most of the lake is 3-4 m.



FIG. 1. Map of south-east of South Australia showing positions of stranded beach ridges.



FIG. 2. Locality of Lake Fellmongery and Lake Butler in relation to township of Robe and Guichen Bay.

Calcareous beach rock surrounds Lake Fellmongery and is best developed on the northern and eastern shores. Typical beach development is shown in Figure 3(a), and an idealized cross-section in Figure 4. The gently sloping beach, 2–10 m wide, is surrounded by vegetation-covered dunes of aragonite and magnesian calcite.

When Lake Fellmongery was first visited, beach rocks on the northern and eastern shores were covered by white spume. These shores are most exposed to the prevailing winds and the open lake becomes quite choppy during windy conditions. As previously mentioned, the beach rock is best developed on these shores. No spume was collected so it is not possible to comment on its chemistry.

At the edge of the gently sloping beach platform (Fig. 4), wave action has eroded the compacted beach rock to form a mass of broken and jagged material. Further attrition of the friable rock gives rise to a gravel of individual pellets which accumulates at the base of the beach platform in 2-3 m of water. Towards the center of the lake, the pellet grain size diminishes through coarse to fine sand to extremely fine-grained muds (ooze) which cover most of the lake bottom to a depth of 2-3 m. A number of cores of these sediments were taken using a piston corer similar to that described by Ginsburg and Lloyd (1956).

The gravel and sand near the base of the beach platform are composed of individual pellets derived from the beach rock, together with fine-grained calcareous and carbonaceous material. The mineralogy of this material determined by X-ray diffraction was found to be high-magnesian calcite (approximately 33 mole percent $MgCO_3$). Except near the sheltered southern and western shores, the





(b)

FIG. 3.(a) Typical beach development at Lake Fellmongery; (b) beach of Lake Butler which is now used as a boat haven.

upper 25-30 cm of the sediment pile contain some abraded pellets of monohydrocalcite. The muds consist of high- and low-magnesian calcites together with variable amounts of aragonite, quartz, and carbonaceous material.

The much smaller $(350 \times 200 \text{ m})$ Lake Butler, previously isolated, is now opened to the sea at Guichen Bay by an artificial canal, for use as a harbor by the local fishing fleet. Beach rock at Lake Butler is



FIG. 4. Idealized cross-section of beach at Lake Fellmongery.

more extensive (Fig. 3b) and there is evidence of a narrow stranded beach platform up to 1 m above the more extensive platform.

No streams enter either lake. Water in Lake Fellmongery must therefore be derived from rainfall. from run-off from the surrounding dunes, and by sub-surface water flow. Normally much of the beach is exposed, but in November 1971 after heavy winter rainfall (annual average = 62.81 cm) it was completely submerged. This represented a rise of 70 cm from February 1971. Similar fluctuations were reported by Johnson (1956) for Lake Butler before it was opened to the sea. He found a thin layer of fresh water overlying a wedge-shaped body of salt water which extends inland from the sea through the permeable aeolinite dunes. Fluctuations of the water level in the lake corresponded with considerable seasonal fluctuations (up to 2.5 m) of the water table. It has also been reported that in times of extremely low lake level, fresh water springs broke out on the southern shore of the lake. Because of its similarity and proximity, Lake Fellmongery is probably subject to the same fluctuations of the water table.

Water chemistry of Lake Fellmongery, nearby groundwaters, and the Southern Ocean are given in Table 1. The data for Lake Fellmongery (February) represent dilution of seawater by groundwater together with some evaporation and precipitation of calcium carbonates. Following heavy winter and spring rainfall in 1971, the water was further diluted by groundwaters in November. Water temperature was 17°C during this period.

Beach Rock Morphology

Beach rocks of both lakes are hard pelletal aggregates with a sponge-like texture which resembles

TABLE 1. Water Chemistry of Lake Fellmongery, Nearby Groundwaters, and Southern Ocean (in ppm)

	Lake Fellmongery (February)	Lake Fellmongery (November)	Drain L.	Groundwater	Southern Ocean
ъΗ	8.83	8.60	7.90	7.95	8.2
HCO	680	564	253	435	140
so2-	2140	1630	190	240	2650
C1	13700	10000	1000	400	18980
Br ⁻	50		1221		65
Ca Mg Na K	80 1660 5380 410	94 940 5650 238	64 90 570 20	162 50 250 20	400 1270 10560 380
Sr Ba	17 0.2	1.4	15		
P Mg/Ca	<0.01 20.8	<0.01 10	1.55	0.31	3.17



FIG. 5. Small beach rock of aggregated pellets of monohydrocalcite covered with a mucilaginous layer of blue-green and green algae (dark color).

calcareous tufa (Fig. 5). Much of the beach consists of level compacted material, but there are also irregular shaped masses seldom more than 0.5 m in diameter which have the appearance of cauliflowers. These masses are extremely cavernous with small shells of molluscs, sand grains, and weed fragments trapped within the voids. Much of this rock appears to have formed as a crust on underlying dune rocks. There is no regular texture in the rocks.

From data presented by Sapozhnikov and Tsvetkov (1959) and Sapozhnikov and Viselkina (1960), it would appear that the beach rocks of Lake Issyk-Kul and those of the South Australian lakes are very similar in size and morphology. Photographs of speleothems from the West German caves also bear a remarkable resemblance.

Each mass of beach rock is made up of individual pellets, 0.5 - 2.0 mm in diameter, consisting of cryptocrystalline carbonate together with organic carbon



FIG. 6. Photomicrograph of monohydrocalcite from Lake Fellmongery. Note nucleus of organic matter in both pellets.

(Fig. 6). In those few places where any texture is obvious within the pellets, organic matter appears to have been the nucleus for carbonate growth.

An examination of the literature on monohydrocalcite shows that spheroids are the most favored morphology. Only monohydrocalcite found by Carlström (1963) in otoliths of the tiger shark and single crystals synthesized by Lippmann (1959, 1973) and Kohatsu and McCauley (1973) have trigonal bipyramidal morphology. No such crystals were found in the beach rocks from either lake.

Sapozhnikov and Tsvetkov (1959) reported that the monohydrocalcite from Lake Issyk-Kul was covered with a thin slimy layer but did not characterize it. The beach rocks at or near the shore of Lake Fellmongery are covered by a layer of mucilaginous matter (Fig. 5). Examination has shown this to be composed mainly of blue-green algae, *e.g.*, *Oscillatoria*, *Schizothrix calcicola*, *Spirulina* sp., *Trichodesmium* sp. and *Rivularia* sp. Green algae (*Chlorella*) are also present. Beach rocks away from the water's edge are covered by a grayish layer of algal remains.

Analyses

Chemical analyses of two different samples of monohydrocalcite from Lake Fellmongery from which all visible shell and organic matter had been removed are compared with published chemical analyses of natural monohydrocalcites in Table 2. Since no impurity phases could be detected on the X-ray diffraction patterns, the monohydrocalcite is assumed to be a solid solution (Ca_{0.9053} Mg_{0.0738} Fe_{0.0022} Sr_{0.0047} Na_{20.0138} K_{20.0008}) CO₃ · 1.15 H₂O which is based on the more comprehensive analysis (1) of Table 2.

TABLE 2. Chemical Analyses (in percent) of Selected Monohydrocalcites

	Sapozhnikov and Tsvetkov	Hull and Turnbull	This (1)	study (2)
CaO	46.58	42.86	42.5	43.4
MgO	0.21	1.05	2.49	0.90
Fe0	0.22	0.03	0.13	0.06
Sr0	**	0.04	0.40	
Na ₂ O		0,42	0.69	
K20		0.07	0.07	
CO2	36.43	35.05	33.6	34.0
H ₂ 0 ⁻	5.30	1.65	2.1	2.1
H20 ⁺	10.95	13.36	15.9	15 96
Insoluble	2.11	5.25	5.0	2.5
Total	101.83	99.78	102.88	98.93

Both analyses indicate 1.15 moles of water, which is a slight extension of the known compositional range.

Crystallographic data for monohydrocalcite was first given by Lippmann (1959) from Weissenberg photographs of artificially-prepared single crystals. Systematic extinctions correspond to the space groups $P3_{(1,2)}21$ and $P3_{(1,2)}12$. The lattice constants were given as a = 10.62 Å and c = 7.54 Å with a cell content-derived from a density of 2.38 g/cm³-of $9(CaCO_3 \cdot H_2O)$. There exists a well-defined pseudocell with $a' = 6.13 \text{ Å} = a/\sqrt{3}$ and c = 7.54 Å. Recently Kohatsu and McCauley (1973) have determined the space groups P3₁21 or P3₂21 from precession and Weissenberg photographs and have obtained sub-cell lattice parameters of a = 6.092 Å and c = 7.529 Å from back-reflection Weissenberg data, but have indicated that the real structure has a tripled unit cell.

It was on the pseudo-cell which contains 3 $(CaCO_3 \cdot H_2O)$ that Brooks *et al* (1950) indexed their powder diffraction pattern except for one line. All other published powder diffraction data of synthetic and natural monohydrocalcite have been indexed as-

TABLE 3. X-Ray Powder Diffraction Data for Various Monohydrocalcites

-							
-	hk1	Brooks et al.	Sapozhnikov and	Marschner	hkl	Hull and Turnbull	This study
a '	= a//3	(1950)	Tsvetkov	(1969)	l	(19/3)	
	100	6.06	F F/	5 261	110	5 271	5.283
	100	5.26	5.54	5.201	110	6 227	6 333
	101	4.30	4.49	4.313	111	4.327	3 916
	102	3.05	3.15	3.064	210	3.900	3.910
	111	2.804	2.90	2.820	102	3.491	3.499
	003			2.510	211	3.142	3.140
	201	2.478	2,514	2.487	112	3.072	3.078
	112	2.356		2.366	300	3.042	3.050
	103	2.259	2.28	2.268	202	2.912	2.917
	202	2.152	2.17	2.159	301	2.825	2.829
	210	1.982	1.989	1.993	220	2.634	2.642
	113		1.940	1.937	212	2.548	2.554
	211	1,918	1.926	1.928	003	2.520	2.524
	004	1.866			221	2.490	2.494
	203	1.812	1,811	1.8185	103	2.430	2.434
	104		1.770	1.7730	302	2.372	2.375
	212		1.746	1.7624	113	2.274	2.278
	300	1.758	1.746	1.7596	203	2.2065	2.2103
	301	1.710		1.7125	401	2.1845	2.1899
	114	11710		1.6024	222	2.1625	2.1665
	114	1 589					
	302	1.302		1.5935	312	2.103	2.0543
	212	1 6 5 2	1 553	1 5620	213	2.0315	2.0390
	213	1.520	1.223	1 5233	410	1,993	1,9968
	220	1.520	1 / 90	1 / 927	303	1 942	1.9447
	105	1.403	1 4 3	1 4495	411	1 9275	1,9308
	105	1.444	1.4 3	1 4367	223	1 8225	1.8250
	311	1.430	1.423	1,4307	114	110225	1.7823
	222	1.400		1.9120	142 3	20	1 7663
	214	1 262		1.0090	142,5	30	1.1001
		1.362		1 26/2	221		1 715
	312		1.358	1.3042	142		1 566
	400			1.3192	145		1 5221
	223	1000	1.303	1.3089	224		1.05
	401	1.312		1.3002	061		1.475
					115,0	144	1.455
					333		1.4444.
					251		1.438
					144		1.3/3
					252		1.366.
					440		1.320
					225		1.313
	<u>.</u>	6.15	6.13	6.092		10.544	10.566
	<u>c</u>	7.61	7.54	7.534		7.559	7.573

suming Lippmann's pseudo-cell as the unit cell (Table 3). Most recently Hull and Turnbull (1973) have used monohydrocalcite from Lake Fellmongery to determine its stability in relation to aragonite and calcite. They obtained a more complete diffraction pattern with all reflections being indexed on Lippmann's hexagonal unit cell with parameters a = 10.544 Å and c = 7.559 Å.

Using a Philips wide range goniometer with graphite-crystal-monochromated copper radiation and pure calcite (a = 4.989 Å, c = 17.062 Å) as an internal standard, the author has been able to obtain a more extensive powder pattern which is given in Table 3. Hexagonal unit cell parameters are a = 10.566 Å, c = 7.573 Å. Differences in unit cell parameters are probably due to variations in water content and the incorporation of impurities during crystal-lization. Monohydrocalcite samples from the shores of both lakes are well crystallized as indicated by the absence of X-ray line broadening.

A Rigaku "Thermoflex" DTA-DTG was used to follow the dehydration of monohydrocalcite from Lake Fellmongery. The DTA curve (Fig. 7) shows dehydration commencing at 154°C, indicating that the water is strongly bound, although not as strongly as the water in samples from Issyk-Kul where dehydration first occurs at 250°C. This is followed at 340°C by the gradual combustion of organic carbon which, according to Swaine (1969), is indicative of brown coal or peat-like carbonaceous matter. In this region there is no indication of an aragonite \rightarrow calcite transformation. The final exotherm at 800°C is typical of calcite decomposition, and it must therefore be assumed that calcite is formed by the dehydration of monohydrocalcite. These results have been confirmed by the use of a high-temperature X-ray diffractometer. Figure 8 shows that dehydration commences at 150°C to give calcite rather than aragonite.

Weight losses calculated from the TGA curve correspond closely to the chemical data when account is taken of adsorbed water, organic carbon, and the insoluble fraction.

Isotopic data for monohydrocalcite from Lakes Fellmongery and Butler are compared in Table 4 with the PDB standard (a marine calcite), reef corals from Heron Island, Queensland (Weber and Woodhead, 1970), average values for freshwater carbonates and biogenic carbonates, and the organic carbon derived from the algae. Monohydrocalcite from both lakes is heavier than the PDB standard whereas the corals are lighter. The high δ^{13} C values indicate that the water is derived from an evaporative basin, whereas the δ^{18} O values can be explained by the thermodynamic requirement for ¹⁸O to concentrate in water of crystallization. Monohydrocalcite from Lake Butler is lighter than that from Lake Fellmongery reflecting isotopic exchange with seawater. The isotopic data suggest that the beach rock has not been secreted by algae but rather that it is precipitated from saline waters.

The stability of monohydrocalcite has long been in question. Brooks *et al* (1950) reported that their synthetic material was unstable and readily dehydrated to aragonite. On the other hand Sapozhnikov and Tsvetkov (1959) found that the material from Lake Issyk-Kul had not altered over a period of 10 years. Marschner (1969) found that the air-dried monohydrocalcite did not change in 3 months, but readily transformed to calcite on heating. Hull and Turnbull (1973) have carried out a detailed thermodynamic study of monohydrocalcite both natural and synthetic, and have determined that it is metastable with respect to calcite, the only product of dehydration.

Air-dried monohydrocalcite from Lake Fellmongery has not dehydrated over a period of 3 years, but was found to transform slowly in the presence of water to yield calcite. This transformation is retarded if magnesium is present. Thus it would be expected that monohydrocalcite constantly submerged in lake water would gradually transform while that above the high-water mark would be stable. This is the case in both Lake Fellmongery and Lake Butler. Because of this instability with respect to calcite, it is unlikely that monohydrocalcite will be found in other than Recent sediments. Careful examination of Recent carbonate sediments from ephemeral lakes associated with the Coorong lagoon north of Lake Fellmongery has revealed trace quantities of monohydrocalcite. The characteristic pelletal morphology, if retained, may be indicative of its existence in older sediments.

Formation of Monohydrocalcite

Previous syntheses of monohydrocalcite have in most cases been from seawater, with the addition of various ions and biological agents. Monaghan and Lytle (1956), Kinsman and Holland (1969), Chave and Suess (1970), Malone and Towe (1970), and Duedall and Buckley (1971) have all suggested that the presence of various cations or organic matter inhibits the nucleation of calcite. One common factor in all syntheses and natural occurrences of monohydrocalcite is the presence of magnesium,



FIG. 7. DTA/DTG curves for monohydrocalcite.

which Pytkowicz (1965, 1973) has shown to inhibit the growth of the more stable calcite. Monaghan and Lytle and Malone and Towe have also suggested that these additives may alter the pH. Although few indications of pH conditions are given in the literature, it would appear that a value greater than 8.0 is necessary for the formation of monohydrocalcite.

Recent papers by Fischbeck and Müller (1971) and Broughton (1972) indicate two possible modes of formation of monohydrocalcite:

- (i) chemical precipitation from either airborne water droplets or at the solution/atmosphere interface, and
- (ii) biological activity.

Following the discovery of monohydrocalcite on scrubbers of air-conditioning plants and at the mouths of cold-water pipes, Marschner (1969) proposed that it formed from cold water in its contact zone with air. Possible places where it could be expected to be found are the spray zones of waterfalls, nearshore parts of lakes, and in caves. Subsequently Fischbeck and Müller discovered it in speleothems from a German cave and reasoned that it precipitated



FIG. 8. High temperature X-ray diffractometer traces of the dehydration of monohydrocalcite (using nickel filtered copper radiation), showing the appearance of $104_{calcite}$ and the disappearance of 112_{mono} peaks.

TABLE 4. Carbon and Oxygen Isotopic Data for Monohydrocalcite and Algae Compared with Average Values for Other Carbonates

Sample	δ ¹³ C	δ ¹⁸ 0
Monohydrocalcite		
Lake Fellmongery	+4.5	+4.4
Lake Butler	+1.2	+1.8
PDB standard (marine calcite)	0	0
Reef corals (Heron Island)	-1	- 4
Freshwater carbonate (average)	-10	-16
Biogenic carbonate (average)	-10	dependent
Algae from Lake Fellmongery	-20	-

from solutions which are transported in the cave as aerosols.

Broughton has suggested an alternative. Various European and American workers have described the important role of micro-organisms in forming "moonmilk." He suggested that bacteria and algae are responsible for its formation. The work of Malone and Towe (1970) also suggests that microorganisms may be responsible for its precipitation.

The water chemistry of Lake Fellmongery (Table 1) is not unlike that of seawater and is subject to only small variations throughout the year. Of particular interest is the high Mg/Ca ratio (> 10) and pH (> 8.60) both of which are thought to favor formation of monohydrocalcite. Water temperature does not seem to be an important factor as monohydrocalcite has been synthesized in the temperature of Lake Issyk-Kul at a depth of 5 m is $18.3 \pm 1.3^{\circ}$ C (reported in Lippmann, 1973). The temperature of Lake Fellmongery was 17°C during November.

The presence of organic carbon with $\delta^{13}C = -20\%$ in individual spherules of monohydrocalcite is evidence for the close association of algae with its formation. They probably act as favorable sites for nucleation of monohydrocalcite by increasing the pH and producing carbon dioxide in a microenvironment. Experiments are at present being carried out at the Baas Becking Geobiological Laboratory, Canberra, using algae from Lake Fellmongery to precipitate monohydrocalcite.

Recently Davies, Bubela, and Ferguson (in preparation) have formed spheroids of monohydrocalcite at the interface between nesquehonite and an aqueous phase containing calcium, magnesium, chloride, sulfate and carbonate. This phase is also rich in algae and other micro-organisms.

There is therefore evidence for both chemical precipitation and biological activity. However, the most essential requirement for the formation of monohydrocalcite is probably a micro-environment in which algae and other micro-organisms are essential components.

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