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DAWSONITE AND NORDSTRANDITE IN THE PERMIAN BERRY FORMATION OF THE SYDNEY BASIN, NEW SOUTH WALES

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ABSTRACT

Dawsonite [$NaAlCO_3(OH)_2$] and nordstrandite [$Al(OH)_3$] are associated in Permian marine strata of the Sydney Basin. The dawsonite, which appears to have developed in a highly alkaline tidal or supratidal flat environment, occurs as fibrous aggregates in siltstones, as carbonate replacements in pseudomorphs after glauberite and in nodules contained within dolomite. The dawsonite probably formed by the reaction between sodium aluminate and carbonate-rich solutions whereas the nordstrandite appears to have developed from dawsonite through the loss of soda.

INTRODUCTION

Dawsonite [$NaAlCO_3(OH)_2$] and nordstrandite [$Al(OH)_3$] are rare authigenic minerals which previously have not been found in association within a single rock mass. Palache *et al.* (1960) have described several occurrences of dawsonite of low-temperature hydrothermal origin but the more recent work of Hay (1963) on the saline soils at Olduvai Gorge in Tanzania, Smith and Milton (1966) on the Green River Formation in Colorado and Loughnan and See (1967) on the Greta Coal Measures of the Sydney Basin, New South Wales, has shown that the mineral may develop in a diagenetic environment.

Nordstrandite on the other hand, has only been recorded from two localities. The mineral was first synthesised by van Nordstrand *et al.* (1956) and subsequently was found in natural occurrences within cavities in limestones from Guam (Hathaway and Schlanger, 1962 and 1965) and Sarawak (Wall *et al.* 1962). In both cases the origin of the nordstrandite is uncertain.

Recently, dawsonite and nordstrandite were discovered by one of us (R.G.) in the Permian marine Berry Formation, which forms part of the Shoalhaven Group, along the western margin of the Sydney Basin. The host rocks are siltstones and dolomites and in places the two minerals are in intimate association. A wide array of hydrated sulphate minerals, mostly of recent origin, accompany the dawsonite and nordstrandite.

GEOLOGY OF THE SHOALHAVEN GROUP

The Sydney Basin of central eastern New South Wales is a broad structure that covers an area in excess of ten thousand square miles. It contains both Permian and Triassic

TABLE 1. STRATIGRAPHIC SECTION OF THE SOUTHERN AND WESTERN PARTS OF THE SYDNEY BASIN

		Western Sector	Southern Sector	
TRIASSIC	Non-marine	*Wianamatta Group* *Hawkesbury Sandstone* *Narrabeen Group*		Non-marine
PERMIAN		*Illawarra Coal Measures*	*Illawarra Coal Measures*	
		Charbon Sub Group Nile Sub Group	Sydney Sub Group Cumberland Sub Group	
	Marine	*Shoalhaven Group*	*Shoalhaven Group* Gerrigong Volcanics	Marine
		Berry Formation Megalong Conglomerate	Berry Formation Nowra Sandstone Wandrawandrian Siltstone Conjola Formation	

Basement of older Palaeozoic and granite.

strata which attain a total thickness of more than 12,000 feet. The Permian rests unconformably on a basement of granites and older Palaeozoic sediments principally Devonian in age. In the southern and western parts of the basin, the Shoalhaven Group generally forms the lowermost unit of the Permian strata. The presence of sporadic marine fossils, mainly brachiopods, pelecypods and bryozoa, indicates the sediments are primarily of marine origin. However, it is possible that some of the strata developed under nonmarine conditions. In the west, the Shoalhaven Group is subdivided into the Megalong Conglomerate and the Berry Formation (Table 1). The Megalong Conglomerate for the most part rests directly on the eroded surfaces of older Palaeozoic rocks and granite but in several places it is underlain by arkose that infills depressions in the basement.

The Megalong Conglomerate. The Megalong Conglomerate is variable in thickness but attains a probable maximum of 500 feet. It is composed of a basal conglomerate 10 to 100 feet thick in which angular fragments of quartzite, granite, porphyry and slate are set in a matrix of coarse lithic sandstone. Virtually all the conglomeratic fragments are of local origin having been derived from the rocks comprising the basement. As Carne (1903) noted, the conglomerate is particularly coarse at the base but the fragments decrease in size upwards. Large isolated boulders composed principally of quartzite, occur sporadically through the Megalong Conglomerate. Carne (1908) considered these boulders may have been transported by ice but failed to find "direct evidence of glaciation." Many subsequent workers however, have accepted the presence of these erratics as indicative of widespread glaciation during the Permian.

Medium-grained, lithic sandstones with minor amounts of conglomerates and silts comprise much of the upper part of the Megalong while in places, flaggy sandstones and lenticular carbonate beds immediately underlie the Berry Formation in the more marginal areas. The presence of ripple marks, shallow-trough cross stratification and fine silty beds throughout the Megalong attest to the existence of protracted periods of low-energy deposition of the strata.

The Berry Formation. In the southern part of the basin the Berry Formation attains a maximum thickness of 2,260 feet but the unit thins along the western margin and in the vicinity of Glen Davis it approximates 200 feet. Correlation between the Berry and the Mulbring Formation, the uppermost unit of marine strata in the Hunter Valley, has not been established with certainty but similarities in texture, structure and composition between the two formations leaves little doubt that the Mulbring is the northerly extension of the Berry.

The Berry Formation is composed of a predominance of blue-grey siltstones which are remarkably homogeneous throughout the western part of the basin. Abundant silt to fine sand-sized angular grains of quartz and well-ordered illite characterise the siltstones and generally kaolinite is present additionally but in subordinate amounts. Rounded pebbles of quartzite, porphyry and granite, although not very abundant, are disseminated throughout the siltstones and form a conspicuous feature of the sediments. A number of interbedded sandstone units can be traced for great distances along the strike and, near the top of the formation, lenticular and rounded carbonate masses are prevalent. The carbonates contain an abundance of evenly distributed, angular, silt-sized quartz grains and minor amounts of clay minerals. Although many of these masses are spheroidal to subspheroidal in forms, there is no evidence of either concentric or radial structures.

The nordstrandite and much of the dawsonite found to date occur either within or associated with the dolomite but possibly extension of this work may reveal a more widespread distribution of both minerals.

Pseudomorphs of calcite after single and twinned crystals of glauberite ($Na_2SO_4 \cdot CaSO_4$) occur sporadically at a number of horizons within the Berry Formation and are particularly prevalent near the top of the unit. These pseudomorphs, known as *glendonites* (Palache *et al.*, 1960), may exceed 12 inches in length. However, in parts of the Glen Davis area somewhat smaller glendonites containing abundant dawsonite generally with dolomite, occur and elsewhere gypsum-bearing glendonites have been recorded. According to David *et al.* (1905) the lack of specific orientation of the glendonites within the enclosing siltstones indicates "that the original crystals must have grown at some distance below the surface of the mud." Apparently the only solutions of hypersalinity sufficient to cause salt precipitation, were restricted to pores within the unconsolidated muds. This would suggest a broad tidal or possibly a supratidal, flat environment for the formation of the glendonites.

Drilling and seismic data have permitted the construction of isopachs on the Berry Formation and these indicate the presence of broad shallow shelf areas. Extending basinwards from the western and southern depositional margins, the sediments thicken very gradually for distances of 40 to 50 miles in the west and as much as 80 miles in the south and north-

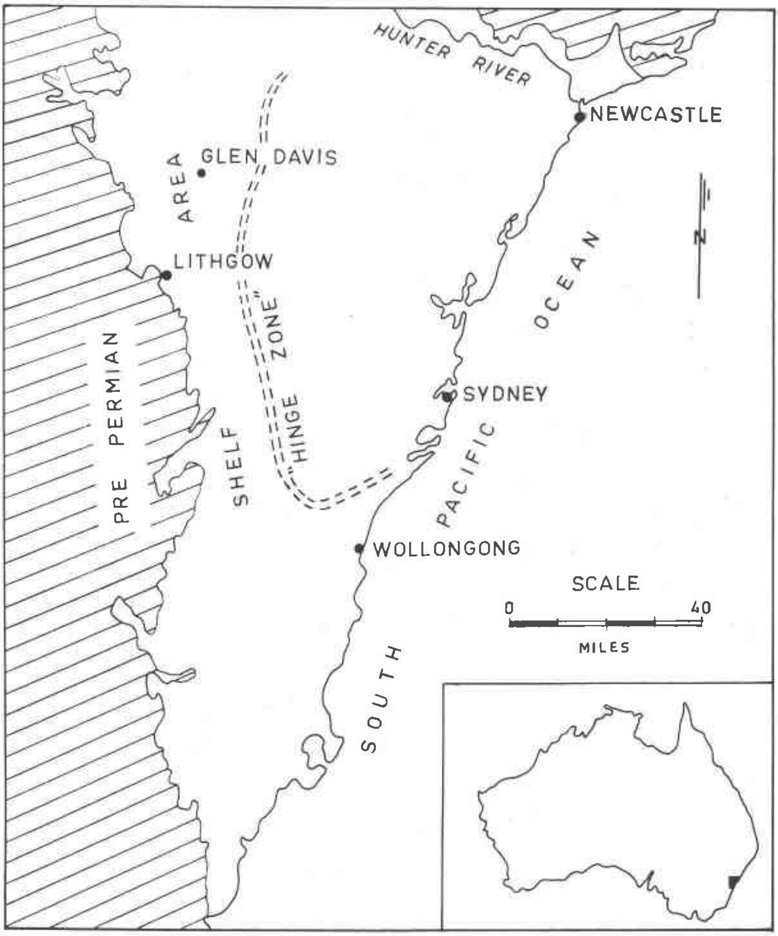

FIG. 1. Sketch map of the Sydney Basin during the Permian, showing the extent of the Shoalhaven Group and the approximate locations of the shelf area and the "hinge line."

west. The approximate position of the outer margin of the shelf is shown as the "hinge zone" on the accompanying map (Fig. 1) and beyond this zone, the isopachs are closely spaced and reflect the rapid thickening of the sediments. Detailed mapping by one of us (R.G.) in the vicinity of Glen Davis has shown the presence of a subsidiary depression on the shelf and extension of this work may reveal further depressions. The shallow gradient of the shelf was such that minor changes in sea level produced marked transgressions and regressions and possibly led to the development of shallow lakes or lagoons in the depressions. Sporadic worm burrows and the churned nature of many of the beds, undoubtedly due to animal activity, afford further evidence of the shallow-water conditions that prevailed during deposition of the Berry Formation. The sand bodies are believed to represent strand line deposits formed during periods of relative stability in the basin. The absence of channels and contemporaneous scours in the Berry sediments suggests there was little drainage from the land and presumably the climate was too arid to produce a drainage pattern.

The environmental model that emerges for the Berry therefore, is an extensive shallow shelf area extending landwards into broad tidal and probably supratidal flats over which an arid climate apparently prevailed. The salts appear to have developed from supersaline pore waters within the exposed muds. The difficulty with this model is to account for the dissemination of conglomeratic fragments in the siltstones for although these fragments are of local origin, having been derived either from the basement or more probably the underlying Megalong Conglomerate, the arid climate would preclude transport by stream activity. Raggatt (1938), in describing the Mulbring Formation, the lateral equivalent of the Berry Formation in the Hunter Valley, recorded the presence of similar conglomeratic fragments which he attributed to the action of ice-rafting during periods of glaciation. However, examination by one of us (R.G.) of several hundred rock fragments from the Berry revealed that although many are facetted possibly as a result of insufficient abrasion of cleavage and joint blocks, none contained striations. Moreover, the absence of rock flour and pulverised primary minerals such as feldspar, the existence of shallow shelf areas devoid of contemporaneous erosion channels and the remarkably even distribution of the pebbles are features which are difficult to reconcile with glacial activity. If glaciation were widespread surely some concentration of rock fragments would be expected within the sedimentary succession. Nevertheless, no other entirely satisfactory explanation has been advanced to account for the mechanism of emplacement of the conglomeratic fragments and for the present glacial activity must remain a possibility.

A number of sulphate salts occur as superficial exudation products on recent exposures of the siltstones. The salts are listed in Table 2 and of these all appear to be of recent origin with the possible exceptions of jarosite and natrojarosite, which occur as powdery films along bedding planes in the siltstones. Presumably the remaining sulphates have been derived from the reaction of the breakdown products of the jarosites with dolomite and dawsonite. The general paucity of secondary potassium salts is probably due to the early fixation of this cation in the illite, which is the dominant clay mineral present. The well-ordered nature of the illite supports this concept.

TABLE 2. SECONDARY SULPHATE MINERALS IN THE BERRY FORMATION

Alunogenite	$Al_2(SO_4)_3 \cdot 18H_2O$
Basaluminite	$Al_4SO_4(OH)_{10} \cdot 5H_2O$
Bloedite	$MgSO_4 \cdot Na_2SO_4 \cdot 4H_2O$
Epsomite	$MgSO_4 \cdot 7H_2O$
Gypsum	$CaSO_4 \cdot 2H_2O$
Hexahydrite	$MgSO_4 \cdot 6H_2O$
Hydrobasaluminite	$Al_4SO_4(OH)_{10} \cdot 36H_2O$
Jarosite	$KFe_3(SO_4)_2(OH)_6$
Natrojarosite	$NaFE_3(SO_4)_2(OH)_6$
Pickeringite	$MgAl_2(SO_4)_4 \cdot 22H_2O$
Thenardite	$NaSO_4$

The Nile Sub-Group. The final vestiges of marine transgression in the western part of the Sydney Basin are apparent in the Nile Sub-Group which forms part of the Illawarra Coal Measures. The basal units of the sub-group cover the entire western shelf and consist of carbonates containing chert fragments together with claystones and minor amounts of shales. These are succeeded by a calcarenite which represents partial reworking of the underlying carbonate rocks. The marine units pass upwards into a terrestrial facies of carbonaceous shales with plant impressions and coal seams.

OCCURRENCE OF DAWSONITE AND NORDSTRANDITE

Dawsonite occurs as aggregates of very fine needles arranged as sheaves, tufts and more commonly, spherulitic masses measuring a millimeter or more in a diameter, within the siltstone and dolomite. The aggregates in the siltstones are disseminated and generally form only a minor constituent of the rock. However, in places particularly where outcrops of the siltstone are protected by overhanging strata, glendonites containing dawsonite and measuring up to 100 mm in length can be observed (Fig. 2). Dawsonite may constitute as much as 70 percent of these glendonites with dolomite and/or siltstone comprising the remainder.

In the dolomite, dawsonite occurs associated with calcite, kaolinite and/or nordstrandite as nodular masses (Fig. 3), which are aligned in the general direction of the bedding, suggesting an early syngenetic origin. The nodules may exceed 20 mm in diameter and contain spherulitic dawsonite as the most abundant mineral, commonly in association with calcite. The calcite may be present either as discrete grains up to 1 mm in length or as spherulitic masses that appear to be pseudomorphs after dawsonite. In places, grains of calcite form a rim around the nodules. In some of the nodules kaolinite is the dominant mineral to the complete

FIG. 2. A glendonite pseudomorphed by dawsonite in the Berry Formation, near Glen Davis, N.S.W.

or almost complete exclusion of dawsonite. Much of the kaolinite is massive and textureless but in places it is present as polycrystalline aggregates, which have a border of coarser-grained and well-cleaved outgrowths of the same mineral.

Nordstrandite occurs as anhedral to euhedral crystals that range up to 1 mm or more in length (Fig. 4). The euhedral crystals appear rhombic in outline whereas the anhedral grains resemble quartz in being angular, clear and colourless and in showing first order birefringence colours. However, the relief of the nordstrandite is much greater than that of quartz and distinction between the two minerals is easily facilitated on the basis of this property. Dawsonite is invariably associated with the

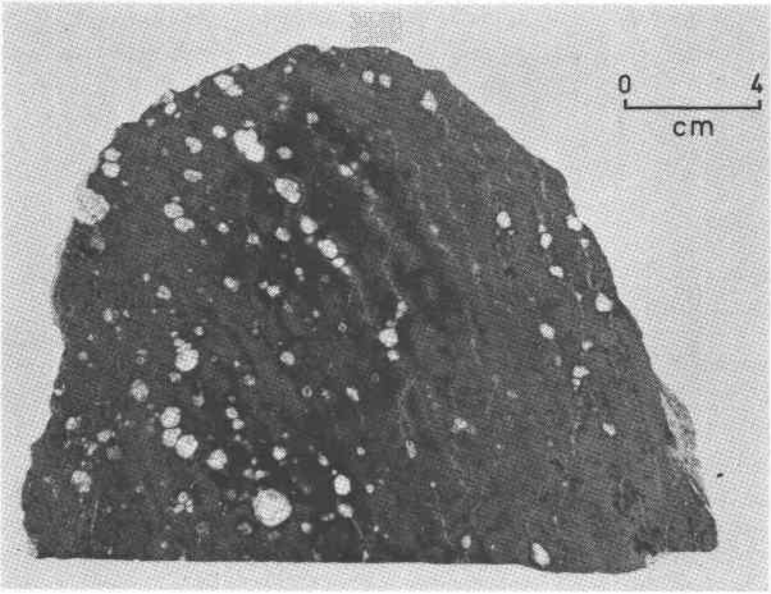

FIG. 3. Nodular masses of dawsonite (white) in dolomite from the Berry Formation, Glen Davis, N.S.W. Note the veins of calcite believed to be infilled syneresis cracks.

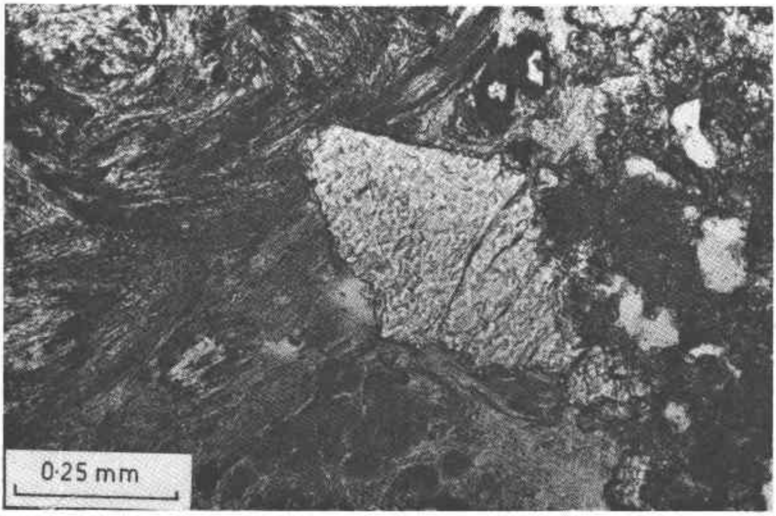

FIG. 4. A subhedral crystal of nordstrandite in a dawsonite nodule, Glen Davis, N.S.W.

nordstrandite and in many of the dawsonite-rich nodules, crystals and grains of nordstrandite form a continuous rim around the nodule. Elsewhere however, nordstrandite occurs within the spherulitic masses of dawsonite. Calcite and kaolinite may be present additionally but nordstrandite has not been observed in physical contact with kaolinite.

Thin veins of calcite, generally of the order of 0.1 mm in width but ranging up to 0.5 mm traverse the dolomite in various directions and abut but do not extend into the nodules. Unlike the nodules the veins have diffuse boundaries with the enclosing dolomite and in places quartz grains protrude from the dolomite into the calcite veins. These veins are believed to represent infilled syneresis cracks formed during crystallisation of the dolomite although the diffuseness of the boundaries suggests some replacement of the dolomite by calcite. The fact that the veins do not continue into the nodules does not necessarily imply that their development preceded that of the nodules. On the contrary, the abundance of quartz in the dolomite and its absence from the nodules rather suggests that the origin of the nodules was penecontemporanceous with that of the dolomite and this is supported by the alignment and attenuation of the nodules in the general direction of bedding.

CHEMICAL AND X-RAY DATA

Relatively pure samples of dawsonite suitable for X-ray, chemical and thermal studies were readily obtainable by handpicking the glendonites and nodules. On the other hand, the samples of nordstrandite recovered from the nodules by this method contained appreciable quantities of carbonates and concentration of the mineral proved necessary. This was achieved by treatment with warm 10 percent acetic acid. The acid dissolved calcite and dawsonite and left a residue containing approximately 90 percent nordstrandite with quartz the principal contaminant. This strength of acid is generally sufficient to remove appreciable quantities of gibbsite from bauxite but appeared to have little effect on the nordstrandite and apparently the stability of the nordstrandite in this respect is due to its relatively coarse grainsize.

Chemical analyses were made of the dawsonite and nordstrandite concentrates by Messrs. Pyle and Rice of the N.S.W. Department of Mines Chemical Laboratory and the results are given in Table 3 together with the theoretical values for the two minerals. X-ray diffraction, thermogravimetric and differential thermal analyses were also made on the prepared samples. In Table 4, the X-ray diffraction results for the two minerals are compared with data taken from the literature and it will be observed that the values are in very close agreement. An X-ray diffraction pattern was also obtained for a prepared mixture of nordstrandite

TABLE 3. CHEMICAL DATA

	Nordstrandite		Dawsonite	
	(1)	(2)	(3)	(4)
SiO_2	7.9	—	0.29	—
Al_2O_3	58.7	65.4	35.60	35.4
Fe_2O_3	0.17	—	0.10	—
TiO_2	0.01	—	0.01	—
MgO	0.30	—	—	—
CaO	0.30	—	—	—
SrO	0.06	—	—	—
Na_2O	0.02	—	21.10	21.5
K_2O	0.22	—	0.02	—
MnO	0.01	—	—	—
CO_2	0.2	—	31.41	30.6
H_2O+	31.0	34.6	11.85	12.5
H_2O-	1.05	—	—	—
Total	99.9	100.0	100.25	100.0

1. Glen Davis, N.S.W.—Analyst T. D. Rice, N.S.W. Dept. of Mines Chemical Laboratory.
2. Theoretical composition of nordstrandite.
3. Glen Davis, N.S.W.—Analyst J. H. Pyle and T. D. Rice, N.S.W. Dept. of Mines Chemical Laboratory.
4. Theoretical composition of dawsonite.

and gibbsite and the two sets of lines were clearly resolved. Samples of dawsonite heated to a temperature of 700°C yielded weak lines attributable to sodium aluminate.

Several of the X-ray patterns obtained for the nodules contained weak reflections that could not be related to a specific mineral. The strongest of these reflections occurred at *d* values of 6.42, 6.24 and 6.16 Å and generally only one or two were evident in a single pattern. Similar reflections were also found in some of the patterns of secondary salts and presumably they represent alteration products as yet unidentified.

DISCUSSION

Dawsonite of authigenic origin has been described previously from only three localities in the world: Olduvai Gorge in Tanzania, the Green River Formation in Colorado and the Greta Coal Measures at Muswellbrook in the northern part of the Sydney Basin, New South Wales.

According to Hay (1963) the dawsonite at Olduvai Gorge has resulted from the reaction of sodium carbonate and bicarbonate solutions with nepheline, trachytic glass and clay minerals in an arid and highly alka-

TABLE 4. X-RAY DATA FOR NORDSTRANDITE AND DAWSONITE

Nordstrandite						Dawsonite					
(1)		(2)		(3)		(4)		(5)		(6)	
d	I/I_1	*d*	I/I_1	*d*	I/I_1	*d*	I/I_1	*d*	I/I_1	*d*	I/I_1
						6.16	2			6.59	VVW
4.78	100	4.785	100	4.789	100	5.68	100	5.70	VS	5.69	VVS
4.32	16	4.33	20	4.322	12			5.16	VVW		
4.20	10	4.20	15	4.207	10			4.91	VVW		
4.15	10	4.15	13	4.156	7			4.49	VVW		
3.89	2	3.89	7	3.887	4			4.31	VVW		
3.60	2	3.60	7	3.60	4	3.36	16	3.36	S	3.37	VS
3.17	4	3.18	11	3.022	2					3.10	VVW
2.83	6			2.85	2						
				2.704	1	2.77	17	2.78	MS	2.79	VS
				2.663	<1	2.60	15	2.61	MW	2.60	S
				2.497	<1	2.49	1			2.51	VW
				2.480	3						
2.45	3			2.450	1						
2.39	8	2.39	15	2.392	9						
				2.349	<1						
2.26	12	2.26	15	2.263	15					2.22	VVW
				2.148	1	2.15	2			2.15	VW
				2.074	1					2.06	VVW
				2.033	1						
2.02	5	2.01	11	2.016	8	1.99	10	2.00	W	1.99	MS
				1.943	<1						
1.90	7	1.898	11	1.901	8						

1. Glen Davis, N.S.W.—Quartz lines omitted.
2. Synthetic nordstrandite-van Nordstrand et al. (1956).
3. Guam—Hathaway & Schlanger (1965).
4. Glen Davis, N.S.W.
5. Muswellbrook, N.S.W.—Loughnan & See (1967).
6. Green River Fm., Colorado—Smith & Milton (1966).

line environment. Natrolite, other zeolites and carbonates are associated with the dawsonite and the pH of the surface rocks and soils ranges from 9.5 to 10.6. The dawsonite in the oil shales and dolomites of the Green River Formation in the Piceance Basin, Colorado is also accompanied by zeolites, particularly analcite, together with nahcolite, trona and a wide array of other authigenic silicates and carbonates and again there is every indication that the sediments were laid down under strongly alkaline conditions. The fact that dawsonite can be synthesised from solutions of sodium aluminate in the presence of excess sodium hydroxide and carbon dioxide (Bader, 1938) affords further evidence of the high pH values required for the genesis of the minerals. However, it should be noted that the dawsonite found in Permian coal measure sandstones at Muswellbrook in the Sydney Basin (Loughnan and See, 1967) is not associated with zeolites and there is little evidence beyond the presence of dawsonite to suggest unusually high pH conditions.

Despite the lack of supporting evidence at Muswellbrook, a strongly alkaline environment relatively rich in soda and alumina and deficient in the strong acidic radicals such as Cl^- and SO_4^{2-}, presents the optimum conditions for the formation of dawsonite. Apparently the alumina is mobilised as sodium aluminate and precipitation of dawsonite occurs where these solutions encounter increased concentrations of the carbonate ion. The problem is to account for the high concentration of soda in the sediments.

Concentration through evaporation is an obvious possibility. However, in the case of the Berry Formation, the widespread distribution of marine fossils attests to the essentially marine origin of the strata and the normal evaporation of marine brines should have yielded sulphate minerals such as anhydrite and gypsum and chlorides such as halite. Anhydrite and halite have not been encountered in the Berry sediments but gypsum, apparently of recent origin, has been found. The association of glendonites, which are believed to represent pseudomorphs after glauberite, with the dawsonite could offer a possible mechanism for the selective removal of sulphate ions from the brines. In accounting for the origin of these glendonites in the Sydney Basin, Gibbons and Gordon (1969) pointed out that whereas gypsum is the early product of sea water evaporation under warm conditions, concentration of the brines by freezing tends to precipitate mirabilite ($Na_2SO_4 \cdot 10H_2O$) as the earliest mineral phase. They believe that alternate freezing and thawing could result in the formation of glauberite at the expense of gypsum and mirabilite.

A further complication is that dawsonite occurs in the glendonites and presumably has pseudomorphed glauberite. It is difficult to envisage a chemical environment that on the one hand would promote solution of calcium and sulphate ions and on the other, cause precipitation of sodium and aluminium. Moreover, since the glendonites have been replaced in part by dawsonite and dolomite, formation of these minerals presumably occurred at a period subsequent to deposition of the enclosing siltstones. Yet, in the beds of massive dolomite which also contain dawsonite, the distribution of detrital quartz is similar to that in the surrounding siltstones suggesting that the dolomites and siltstones formed contemporaneously. Possibly there was more than one period of dawsonite and dolomite development.

The absence of analcite in the Berry Formation is a further puzzling aspect for surely solutions sufficiently alkaline to mobilise alumina would also dissolve considerable quantities of silica. The silicate rather than the carbonate of sodium and aluminium therefore, would be the anticipated mineral phase resulting from partial neutralisation of these solutions.

It is apparent that the mechanism of formation of the dawsonite in the Berry Formation is far from understood and much experimental work is needed to determine the environment that gave rise to the mineral. When this is achieved our knowledge of many aspects of the Sydney Basin will be enhanced.

Interpretation of the mode of formation of the nordstrandite does not appear to be fraught with the same difficulties as that of the dawsonite. The fact that nordstrandite commonly occurs as rims around the margins of dawsonite nodules suggests that it is a secondary product formed through the loss of soda from the latter mineral and probably the development of nordstrandite instead of the normal polymorph gibbsite, is due to its origin in this manner.

$$\underset{\text{Dawsonite}}{NaAlCO_3(OH)_2} + H_2O \rightleftharpoons \underset{\text{Nordstrandite}}{Al(OH)_3} + NaHCO_3$$

It should be noted, however, that in the two natural occurrences of nordstrandite recorded previously from Guam (Hathaway and Schlanger, 1962, 1965) and Sarawak (Wall *et al.*, 1962) dawsonite was not found in association with the mineral. Perhaps further investigations of these deposits will reveal the presence of dawsonite.

Although illite is the dominant clay mineral in the Berry Formation it is not associated with the kaolinite in the nodules contained within the dolomite. This would suggest that the kaolinite is not detrital but rather that it has crystallised within the nodules and certainly the vermicular outgrowths on the polycrystalline aggregates indicate that at least some of the mineral present is of authigenic origin. Kaolinite may form either as a residue from the weathering of an aluminosilicate mineral or through silicification of an aluminous mineral. In the absence of any evidence of a pre-existing aluminosilicate mineral it would appear that the second alternative is more likely and that the kaolinite developed through the silicification of nordstrandite.

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