

Buddingtonite (NH_4 -feldspar) in the Condor Oilshale Deposit, Queensland, Australia

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ABSTRACT. Buddingtonite of similar composition and properties to that described from the type area, is uniformly distributed throughout the upper 600 m of strata in the Condor Oilshale Deposit near Proserpine, Queensland. The mineral, which constitutes up to 16% and averages nearly 10% of the strata, is associated with abundant montmorillonite, siderite, and quartz as well as minor amounts of disordered kaolinite, illite, calcite, pyrite, cristobalite, and an unnamed species of the jahnite group. The buddingtonite is concluded to be of diagenetic origin. It developed in an ammonium-rich environment, most probably at significant depth within the mud beneath a stratified lake. Its progenitor, however, remains unknown. The occurrence of this mineral is also of interest in that ammonia could prove an important by-product in the commercial exploitation of the oilshales.

THE existence of an ammonium analogue of K-feldspar had long been foreshadowed on theoretical grounds (see Barker, 1964) but the mineral was not found in natural environments until comparatively recent times. The initial discovery was at the Sulphur Bank mercury mine, California, by Erd *et al.* (1964), who established the composition as $\text{NH}_4\text{AlSi}_3\text{O}_8 \cdot \frac{1}{2}\text{H}_2\text{O}$ with about 5% substitution of potassium for ammonium, and named it buddingtonite in honour of the late Professor A. F. Buddington. Although buddingtonite contains 0.5 mole of water per unit cell, the mineral is closely related in crystal structure and most physical and optical properties to sanidine and orthoclase. Subsequently, Gulbrandsen (1974) described the widespread distribution of the mineral in the Meade Peak Member of the Phosphoria Formation in southeastern Idaho where it constitutes up to 50% of the host rock. In the Idaho occurrences the mineral contains variable amounts of K-feldspar in solid solution and is associated with albite, illite and, less frequently, montmorillonite, dolomite, chert, and phosphorite. The budding-

tonite at Sulphur Bank occurs within altered andesites and was considered by Erd *et al.* (1964) to have resulted from reaction of ammonium-rich, hot spring waters with plagioclase. Gulbrandsen (1974) on the other hand, attributed the presence of the mineral in the Phosphoria Formation to diagenesis.

Recently, buddingtonite of similar composition to that at Sulphur Bank was encountered in several samples from the Early Tertiary Condor Oilshale Deposit near Proserpine in central coastal Queensland (fig. 1) and an ensuing systematic study of the

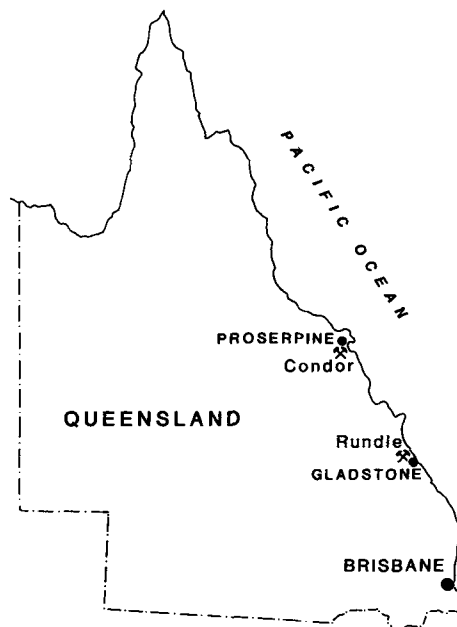


FIG. 1. Map of Queensland with locations of the Condor and Rundle Oilshale Deposits.

core from Borehole CDD34, which penetrated a complete section of this deposit, has revealed that the mineral is uniformly distributed throughout the upper 600 m of strata. Indeed, of the 450 samples obtained at regular intervals from this section of the deposit, 409 contained buddingtonite in amounts ranging up to 16% with the average being nearly 10%.

The discovery is of interest in that similar mineralogical studies undertaken of cores from other oilshale occurrences of comparable age in coastal Queensland, including the Rundle deposit near Gladstone (fig. 1), have revealed that although the strata possess many features in common with those at Condor, buddingtonite is either absent or particularly sparse. Moreover, since buddingtonite decomposes at about the temperature that oil is released from the kerogen, ammonia could prove an important by-product in the commercial exploitation of the Condor deposit.

Geological setting. The Condor deposit is located at the northwestern, onshore end of the Hillsborough Basin (fig. 2), a graben that developed toward the close of the Cretaceous in volcanic and intrusive rocks of Late Palaeozoic and Mesozoic age and, in which an estimated 3000 m of fine-grained clastic and volcanoclastic sediments were deposited during the Tertiary (Paine, 1972). The area has little relief and, as a result, outcrops are

exceedingly poor, and knowledge of the structure, stratigraphic succession and composition of the strata is restricted to the upper 1200 m of the sequence preserved on shore. Such information has been gleaned entirely from the subsurface exploration for petroleum and oilshale (Gary, 1975; Green and Bateman, 1981).

According to Green and Bateman (1981), the sandstone at the base of the Condor Oilshale Deposit (fig. 3) is of fluvial origin and was laid down at a time when the rate of sedimentary influx more than compensated the rate of subsidence. The basal sandstone passes upward into a carbonaceous unit, which comprises coal and sandstone in addition to dark-coloured shales, and evidently marks a change from fluvial to swampy-deltaic conditions. A clearly defined surface separates the *carbonaceous* unit from the overlying thick sequence of oilshales, which toward the base are brown-black but higher in the succession have a uniformly dull, yellow-brown colour. The oilshales consist mostly of dense, massive to partly laminated, silty, kerogenous claystones and were considered by Green and Bateman (1981) to have formed in a shallow, saline, euxinic lake or bay. The succeeding *transitional* unit is composed of laminated oilshales with intercalated, thin, graded beds of siltstone and sandstone whereas in the *upper* unit siltstone and sandstone predominate and kerogenous claystone

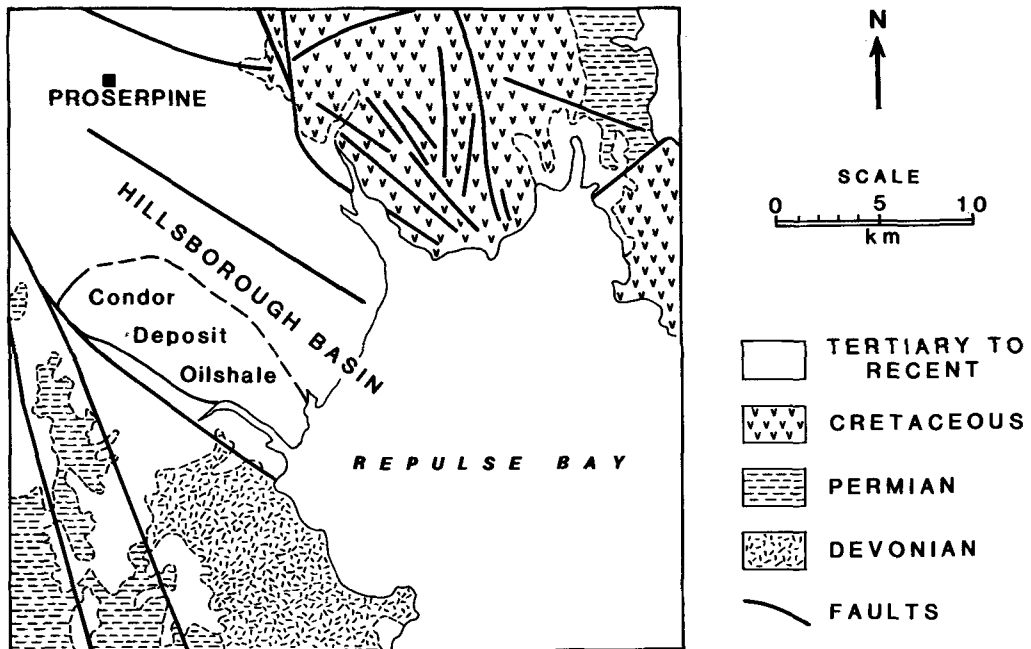


FIG. 2. Geological sketch map of the onshore portion of the Hillsborough Basin. After Paine (1972).

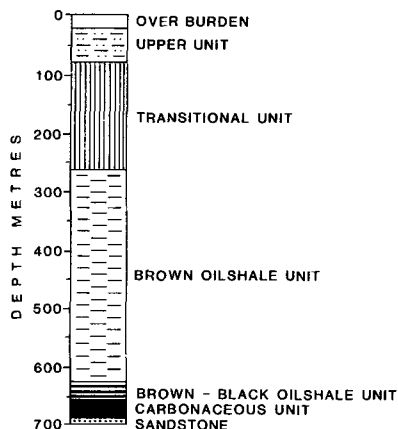


FIG. 3. Stratigraphical succession exposed in Borehole CDD34 of the Condor deposit.

and shale are relatively sparse. The siltstone and sandstone beds in these units were believed indicative of regressive phases in the deposition of the strata. All units have a uniform dip toward the northeast at 14–16° and in places are intersected by strike faults.

From X-ray diffraction examination of the core samples from Borehole CDD34, montmorillonite, quartz, and siderite are the dominant mineral constituents of both the kerogenous and non-kerogenous strata. Nevertheless, kaolinite is generally present and in some samples, particularly from the base of the brown-black oilshale unit and the underlying strata, it is quite abundant. Throughout most of the succession kaolinite has a disordered structure but below about the middle of the brown-black oilshale it is essentially well-ordered. Buddingtonite is restricted in occurrence to the strata above the middle of the brown-black oilshale unit.

Of the minor components pyrite is common while apatite, calcite, illite, cristobalite, and an unnamed aluminophosphate of the jahnsite group have sporadic development only and dolomite and feldspar other than buddingtonite are rare. Since montmorillonite is the dominant constituent of the strata and in places is associated with cristobalite, volcanic ash was probably the source for much of the sediments. Nevertheless, the presence of sand-size quartz grains give credence to at least some contamination by terrigenous detritus.

The precise age of the Condor Oilshale Deposit is not known but, from the limited evidence available, Green and Bateman (1981) considered it developed during the Early Tertiary.

Although the Rundle sedimentary succession is comparable in many aspects including age, thick-

ness, kerogen content and clay mineral composition to that at Condor, there are nevertheless, significant contrasts that undoubtedly reflect differences in the depositional environment of the two deposits. Thus, in the Rundle deposit cyclic sedimentation is characteristic (Coshell, 1982) and ostracod, gastropod, fish, crocodile, and turtle remains are relatively common (Lindner and Dixon, 1976) whereas at Condor cyclicity is not so apparent and the strata are essentially devoid of fossil fauna. Moreover, at Rundle, K-feldspar and plagioclase are almost invariably present and buddingtonite is extremely rare while in the Condor strata the relative abundance of the feldspars is reversed.

The source of the kerogen has not been established with certainty but the consensus of opinion (Hutton *et al.*, 1980) favours derivation mainly from planktonic algae. However, the sporadic occurrence of wood fragments and coal macerals attests to some contribution from vascular plants and it is possible that at least part of the organic matter in the brown-black oilshale unit at Condor resulted from erosion of the underlying carbonaceous unit.

Characteristics of the Condor buddingtonite. The characteristics of the Condor buddingtonite were determined after concentration of the mineral by a procedure involving initial dissolution of carbonate minerals with dilute hydrochloric acid and, following redispersion, removal of the clay minerals by wet sieving through a 325 mesh screen. Since the density of buddingtonite is much lower than that of other feldspars and also of quartz (2.38 g cm⁻³ for buddingtonite compared with 2.55–2.65 g cm⁻³ for other feldspars and quartz), the light fraction was recovered from the sample retained on the 325 mesh screen by means of a centrifuge and a bromoform-alcohol liquid of specific gravity 2.45–2.50 g cm⁻³. The technique in general, proved satisfactory for core samples devoid of kerogen in that quartz in minor amounts was the only contaminant. But, because of the agglutinating effect of the kerogen, concentrates obtained from oilshales frequently contained clay minerals additionally.

An X-ray diffraction trace of a buddingtonite concentrate containing a small amount of quartz, is shown in fig. 4 and, in Table I, these data with quartz lines omitted are compared with those given by Erd *et al.* (1964) and Gulbrandsen (1974) for the mineral from the Sulphur Bank mine and the Phosphoria Formation respectively. From this table it is evident that on the basis of the X-ray diffraction data, there is little to differentiate the Condor buddingtonite from that described from the Sulphur Bank mine.

A close similarity also exists in the chemical composition of the mineral from the two localities

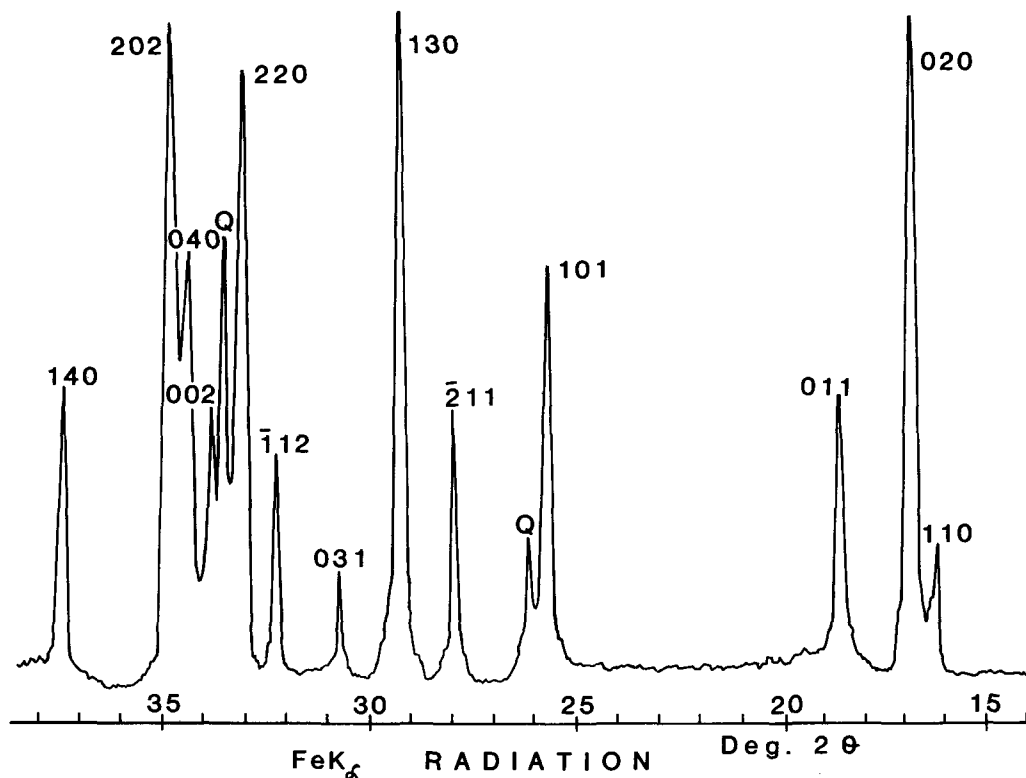


FIG. 4. X-ray diffraction trace of a buddingtonite concentrate from the Condor deposit. Q = quartz.

(Table II), particularly when the values for SiO_2 , Al_2O_3 , K_2O , $(\text{NH}_4)_2\text{O}$, and H_2O are recalculated to total 100% after allowance is made for 7% quartz in the Condor concentrate. The results however, do reveal greater substitution of potassium for ammonium in the Condor buddingtonite, corresponding to 8% sanidine in solid solution compared with about 5% in the mineral from the Sulphur Bank mine.

The infra-red absorption spectra in the ranges 200–1500 and 2700–3800 wave number for buddingtonite from the Condor deposit are compared with those for two monoclinic K-feldspars in fig. 5 and it will be observed that the essential differences lie in absorption bands at 1430, 2860, 3070, and 3295 cm^{-1} for the buddingtonite trace. Erd *et al.* (1964) attributed similar bands in the spectra for the Sulphur Bank mineral to the presence of the ammonium ion with that at 1430 cm^{-1} corresponding to NH_4 bending and those at 2860, 3070 and 3295 cm^{-1} to NH stretching (Table III).

Fig. 6, which represents the thermogravimetric curve for a relatively pure sample of the Condor buddingtonite, was constructed by joining points

determined after holding the sample for 1 h successively at each of the indicated temperatures. According to Erd *et al.* (1964), the buddingtonite from Sulphur Bank 'is completely anhydrous by 370°C ' and hence, the weight loss recorded in fig. 6 for the interval 200°C to 370°C is evidently due to depletion of water. Moreover, since no change to the X-ray diffraction trace was registered in this temperature range, the water is apparently zeolitic in character; a conclusion that is in accord with the findings of Erd *et al.* (1964) for the Sulphur Bank buddingtonite. Between 370°C and 625°C ammonium is slowly expelled as NH_3 and H_2O but the X-ray diffraction pattern remains virtually unaffected below 500°C . Above this temperature, however, there is a progressive decline in the intensities of the buddingtonite reflections accompanied by line broadening but although all ammonium is lost at 625°C , remnants of the feldspar pattern persist at least to 750°C . Possibly this is attributable to a small amount of potassium in the structure. An attempt was made to regenerate the buddingtonite structure from the sample heated to 750°C by holding it in contact with excess of a

TABLE I. X-ray diffraction data for buddingtonite from the Condor oilshale deposit, the Sulphur Bank mine and the Phosphoria Formation

hkl	Condor deposit		Sulphur Bank*		Phosphoria Fm†	
	d Å	I	d Å	I	d Å	I
110	6.75	13	6.75	16	6.77	12
020	6.52	87	6.52	96	6.52	68
011	5.92	35	5.91	33	5.92	28
101	4.33	53	4.33	65	4.32	71
211	3.98	32	3.98	33	3.99	36
130	3.82	100	3.81	100	3.82	76
031	3.63	14	3.63	12	3.64	11
131,121	—	—	3.60	5	3.60	4B
112	3.466	28	3.462	23	3.474	25
220	3.386	77	3.381	72	3.379	58
002	3.320	33	3.314	34	3.320	34
040	3.260	55	3.258	62	3.243	100
202	3.226	84	3.226	69	—	—
140,231	3.013	37	3.014	39	3.016	33
022	2.953	13	2.954	13	2.959	10B
141	2.902	18	2.910	20	2.904	25B
222	2.895	14	2.894	15	—	—
211	2.863	11	2.862	9	2.856	5B
132	2.769	6	2.767	9	2.772	8B
112	2.652	9	2.650	12	2.647	8B
141	2.605	17	2.604	23	2.606	14B

* From Erd *et al.* (1964). † From Gulbrandsen (1974) B = broad.

TABLE II. Chemical analyses

	1	2	3	4
SiO ₂	63.80	67.28	67.97	66.83
Al ₂ O ₃	19.16	20.21	18.02	19.75
Fe ₂ O ₃	1.88	—	0.42	—
TiO ₂	0.99	—	—	—
MgO	0.21	—	0.14	—
CaO	0.04	—	0.31	—
BaO	0.26	—	—	—
Na ₂ O	0.06	—	0.04	—
K ₂ O	0.62	0.65	1.03	1.13
(NH ₄) ₂ O	7.95	8.39	7.92	8.67
S	1.59	—	—	—
H ₂ O ⁺	3.28	3.47	3.31	3.62
H ₂ O ⁻	0.88	—	0.83	—
Total	100.69	100.00	99.99	100.00

1. From Sulphur Bank mine—Erd *et al.* (1964).
2. Ditto SiO₂ + Al₂O₃ + K₂O + (NH₄)₂O + H₂O = 100%.
3. From Condor deposit—analyst I. E. Wainwright.
4. Ditto SiO₂ + Al₂O₃ + K₂O + (NH₄)₂O + H₂O = 100% after allowance for 7% quartz present.

TABLE III. Infra-red data for buddingtonite

Source	Sulphur Bank*	Condor
NH stretching	3296	3295
NH stretching	3068	3070
NH stretching	2848	2860
NH ₄ bending	1419	1430

* from Erd *et al.* (1964).

5% solution of NH₄OH in an autoclave at 180 °C but after 17 days no change to the X-ray diffraction trace was detected.

Erd *et al.* (1964) found that based on optical examination, the Sulphur Bank buddingtonite 'is anhedral and cryptocrystalline but some tiny euhedral crystals up to 0.05 mm line cavities and cracks' and, from the scanning electron micrograph taken at relatively low magnification of a buddingtonite concentrate (fig. 7), the mineral in the Condor deposit is also anhedral. But, at higher magnification (fig. 8) it is evident that these

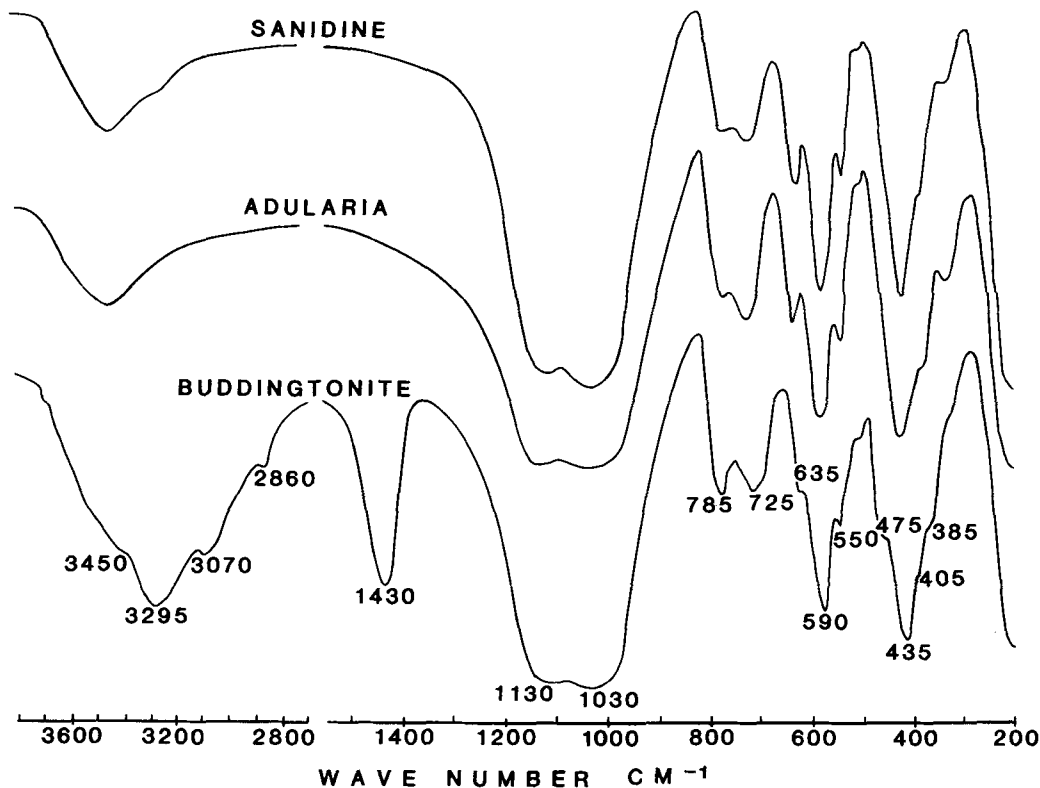


FIG. 5. Infra-red absorption spectra for sanidine, adularia, and the Condor buddingtonite.

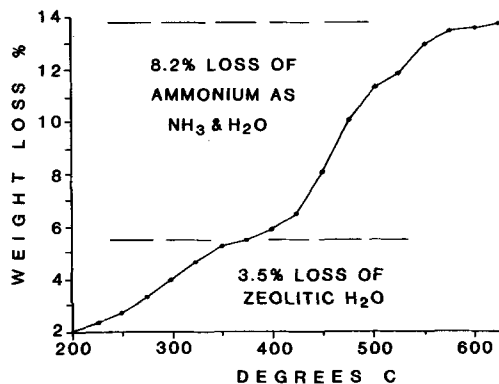


FIG. 6. Weight-loss curve for the Condor buddingtonite.

anhedral grains are in effect aggregates of prismatic crystals. The edges and corners of some of these crystals are slightly rounded but this may be attributable to abrasion in concentrating the mineral. Scanning electron micrographs were also obtained of freshly exposed surfaces of the oilshale from the Condor deposit and, as shown in fig. 7,

growth of relatively coarse buddingtonite crystals can be observed at the margin of a void within the rock.

Origin. The origin of buddingtonite in the oilshales and associated strata of the Condor deposit is at the present time, incompletely understood. That the mineral has not been recorded in the basement rocks of the Hillsborough Basin seems to preclude detrital derivation whereas the concept of hydrothermal development, similar to that invoked by Erd *et al.* (1964) to account for the occurrence at Sulphur Bank, is difficult to substantiate in the absence of thermal spring activity in the area. Gulbrandsen (1974) believed the buddingtonite in the Phosphoria Formation resulted from diagenesis and in all probability, the mineral at Condor arose by similar means. Nevertheless, there are a number of enigmatic aspects associated with its development at the latter locality.

In accounting for the apparent paucity of buddingtonite in the geological record, Barker (1964) concluded that it 'is rare simply because a suitable ammonium-rich environment is rare in the Earth's crust'. That is, the critical factor in the diagenetic

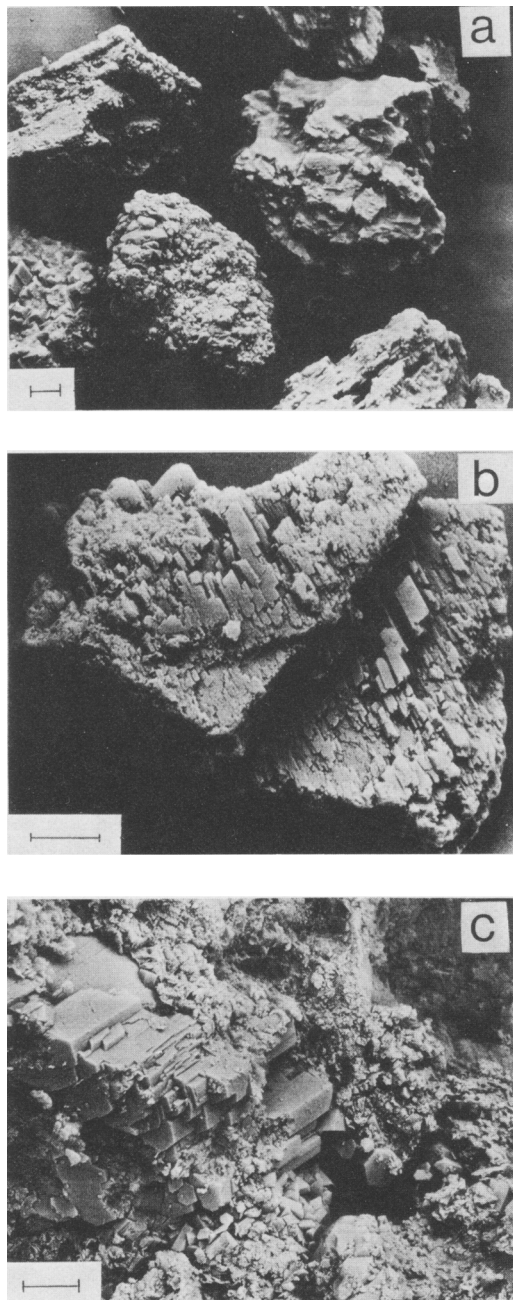


FIG. 7. Scanning electron micrographs (a) Grains in a concentrate of the Condor buddingtonite. (b) A single grain in a concentrate of the Condor buddingtonite. Note the polycrystalline form and the development of prismatic crystals. (c) A broken surface of oilshale from the Condor deposit. Note the development of relatively coarse crystals of buddingtonite near the margin of a void. The lengths of the bars are 0.01 mm.

development of buddingtonite is not so much the generation but rather, the retention of high concentrations of ammonium within the sediment and an environment that can give rise to such is rare indeed. It follows therefore, since buddingtonite is uniformly distributed throughout the upper 600 m at Condor, exceptional conditions persisted for a very long period in the Hillsborough Basin during the Early Tertiary. But, at Rundle, despite the fact that the strata have many aspects in common with those at Condor, buddingtonite is a rarity and these exceptional conditions, in general, did not prevail.

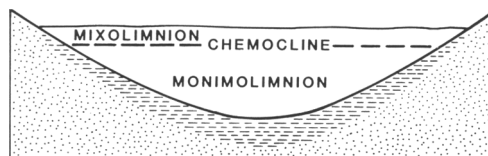


FIG. 8. Diagrammatic representation of a stratified lake. After Smith and Lee (1982).

In the absence of inorganic forms of nitrogen other than buddingtonite at Condor, bacterial degradation of proteins and amino acids in algal and possibly other organic remains appears the only conceivable means by which copious quantities of ammonium could be generated. In most sedimentary environments ammonium is readily lost through either oxidation or upward migration in gaseous form to the atmosphere. However, under certain circumstances the rate of loss may be greatly retarded. Thus, Rittenberg *et al.* (1955), in a geochemical study of bore cores from the upper 2 m of sediments in silled basins off the Californian coast, demonstrated that the ammonium content of the interstitial waters increases appreciably with depth and that this trend is accompanied by a corresponding decrease in the organic nitrogen content of the sediment. These authors also found that where bioturbating organisms are absent or rare, the ammonium concentration in the interstitial waters is considerably increased.

In brief, the most favourable site for deamination of proteins and the concentration of ammonium is apparently deep within organic-rich sediments that underlie a permanent body of anoxic water and in which benthonic organisms are virtually absent. Pertinent in this respect, Smith and Lee (1982) have proposed such an environment for the origin of the Green River oilshales of the Piceance Creek Basin, Colorado. According to these authors, deposition of the oilshales occurred in a stratified lake in which low density oxic water (mixolimnion) was separated from dense, anoxic water (monimolimnion) below by a chemocline that represented an effective

barrier to mixing and hence, the two bodies of water circulated independently (fig. 8). Bacterial activity was greatly restricted, although not entirely inhibited in the monimolimnion and the bulk of the organic debris settling through this zone accumulated in the bottom mud. However, in shallower parts of the basin, notably around the margins, the mud was in contact with oxic water resulting in increased bacterial degradation of the organic matter.

As observed above, a contrasting feature of the Rundle and Condor sedimentary successions is the virtual absence of faunal remains from the latter. Consequently, assuming these deposits developed in a stratified lake system similar to that proposed by Smith and Lee (1982) for the oilshales of the Piceance Creek Basin, much of the strata at Condor apparently accumulated in the mud below the monimolimnion where life was all but inhibited and ammonium concentrated, whereas at Rundle the water depth was somewhat shallower and frequent contact of the bottom mud with oxic water of the mixolimnion permitted survival of some benthonic life forms and facilitated loss of much of the ammonium. Nevertheless, it should be noted that to date buddingtonite has not been recognized in the Green River oilshales although according to Prien (1976), oil recovered from these rocks does have an unusually high nitrogen content.

The diagenetic development of buddingtonite also necessitates an aluminosilicate parent material that readily reacts with ammonium and in which all aluminium is in fourfold co-ordination. Erd *et al.* (1964) believed the buddingtonite at Sulphur Bank formed from plagioclase and, significantly, Marshall (1962) has shown that ammonium is strongly fixed at feldspar surfaces and may penetrate some distance into the structure of these minerals. Moreover, buddingtonite in the Condor deposit is in the form of anhedral aggregates and this, together with the fact that the strata, in contrast to those at Rundle, are virtually devoid of other feldspar minerals, gives credence to the concept of detrital feldspar as the progenitor. Nevertheless, the alteration at Sulphur Bank was by means of hydrothermal solution whereas at Condor the temperature apparently did not exceed ambient conditions and it is doubtful that in the latter environment, the rate of diffusion of ammonium into the framework structure of plagioclase and K-feldspar was such as to effect complete

pseudomorphs of buddingtonite after these minerals.

The suggestion by Gulbrandsen (1974) that buddingtonite in the Phosphoria Formation 'may have developed from volcanic glass . . . or from other products of volcanic glass alteration such as montmorillonite or zeolite' could pertain to the origin of the mineral at Condor since the strata in the latter deposit were probably derived, at least in part, from a volcanic source. However, neither zeolites nor glass fragments have been encountered at Condor and furthermore, the montmorillonite forming the bulk of the succession has most of the aluminium present in octahedral co-ordination.

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