THE PETROLOGY AND MINERALOGY OF SOME LOWER DEVONIAN BENTONITES FROM GASPE, P.Q.

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ABSTRACT

Six bentonites occurring in the Shiphead Member of the Forillon Series of the Gaspé peninsula are found to be composed dominantly of mixed layer illite-montmorillonite clays with or without small amounts of discrete illite, montmorillonite* and chlorite. Attention is drawn to the diversity of habit of the zircon in the grit fractions which in general contain sanidine, albite, quartz, biotite, zircon, and apatite, etc., and thus indicate acid to intermediate compositions for the parent ash falls. SiO_2 and alkalis have been removed and MgO and CaO added during diagenesis. Trace element data are presented and it is suggested that these and the heavy mineral suites should offer the best means of correlating bentonites over the area of deposition.

The Lower Devonian sequence of Gaspé (Logan, 1863; Cumming, 1959) comprises three major units. The second, the Gaspé Limestone series, is made up of eight members. In one of these, the Shiphead Member, a number of bentonites were noted by Russel (1947) and were later collected by Dr. R. E. Folinsbee of the University of Alberta and the present writer. Bentonites, formed by the partial decomposition of volcanic ash, frequently contain unaltered K-bearing minerals such as sanidine and biotite. The result of K/Ar age work on these minerals has appeared elsewhere (Smith *et al.*, 1961). The present paper is concerned with the chemistry and mineralogy of these beds and with inferences that can be drawn regarding their origin and diagenesis. Figure 1 shows the stratigraphic succession at Shiphead.

SECTION 1: FIELD DESCRIPTIONS

Bentonite 1 Light grey-green in colour, about 2′6″ thick, with a regular upper surface showing no signs of erosion. The uppermost layers however are thin and shaly, a characteristic of all the Gaspé bentonites (Fig. 2).

Bentonite 2 Of variable colour, grey at the top, khaki in the centre, to yellow-brown (in places) at the base. It is 14″ thick and very recessive.

Bentonite 3 Rather darker grey-green in colour than Nos. 1 and 2. It is 12″ thick and again the upper surface shows no sign of erosion.

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*Throughout this paper the term *illite* is used to mean a non swelling mica-like clay mineral with a basal spacing of approximately 10Å. *Montmorillonite* is used as a group name and is thus equivalent to the *smectites* of some writers.

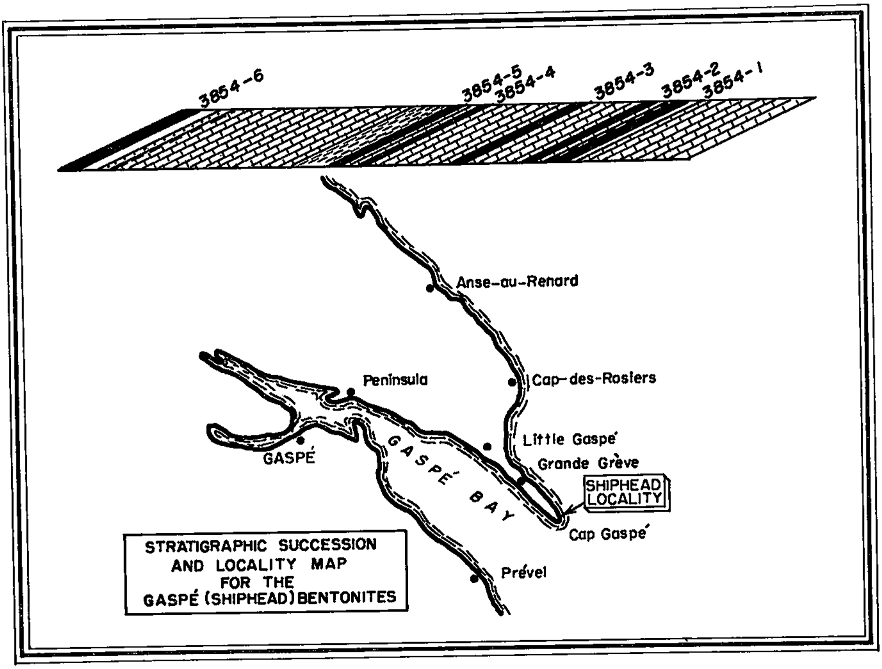

FIG. 1. Locality map, and stratigraphic sequence at Shiphead.

Bentonite 4 Thinner than the other beds, it pinches and swells, but averages about 6″. Much of the bed is either yellow or duck-egg blue, and plastic. At the centre is a layer of concretionary nodules. It also is very recessive.

Bentonite 5 14½″ thick with regular upper and lower surfaces. It is dark olive-green except for a few pods of yellow material. The surface of the underlying limestone is covered with grains of quartz (?) and flakes of biotite.

Bentonite 6 Scree obscures part of the bed but it is at least 1′6″ (and possibly 2′6″) thick. Again, it is dark olive-green, and shows better than any other bed the conchoidal fracture and waxy appearance common in older bentonites (e.g. Byström, 1956; Weaver, 1953). The upper surface is regular.

SECTION 2: MINERALOGY

The bentonites are made up largely of clay minerals but contain minor amounts of sand-size material.

The clay minerals: All the bentonites were found to consist dominantly of randomly interstratified, mixed layer illite-montmorillonite clays. The

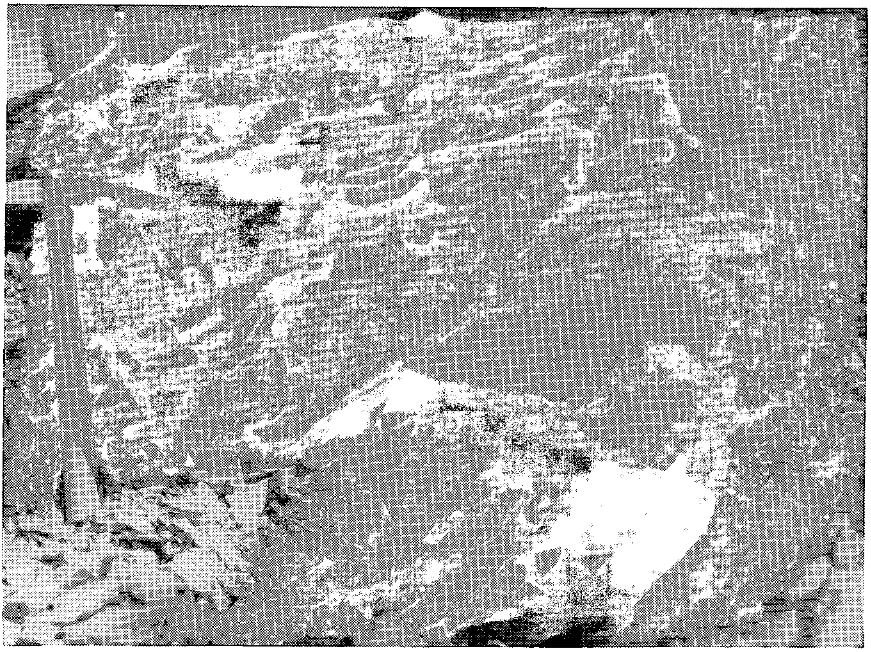

FIG. 2. A view of the outcrop of the bentonite 3854-1. The lack of fissility in the main part of the bentonite, and the slightly shaly top are well seen.

theory and techniques used to investigate such clays have been described by Hendricks & Teller (1942); Bradley (1945, 1950, 1953); Brown & MacEwan (1950); Weaver (1956, 1958), and others. The experimental procedure followed for the Gaspé clays was to sediment them from suspension onto a glass slide and then examine them with an x-ray diffractometer untreated, glycolated and heat treated (for further details see Table 1). Theoretical curves showing the migration of various composite peaks with changing amounts of illite and montmorillonite have been published by Brown & MacEwan (1950) and Weaver (1956). These were used to interpret the diffractometer traces; the results are summarized in Fig. 3 and Tables 1 and 2. All of the clays are basically similar being mechanical mixtures of randomly interstratified illite-montmorillonite with lesser amounts of chlorite, illite and in one case at least, montmorillonite. Although the mixed layer clay undoubtedly dominates all the other clays, no attempt has been made to determine quantitatively the relative proportions of the three or four components of the mechanical mixture. Some workers (e.g. Maiklem & Campbell, 1965) have tried to determine the proportions in complex clay mineral mixtures, but such attempts are fraught with difficulty and uncertainty; variations in the

TABLE 1. *d*-SPACINGS OF DIFFRACTOMETER PEAKS FOR THE GASPÉ BENTONITE CLAYS

		Sample Numbers					
Treatment	Reflection	3854-1	3854-2	3854-3	3854-4	3854-5	3854-6
Untreated	001/001	11.21	10.48	11.01	10.99	11.31	11.78
	Chlorite 002	7.17	—	7.15	7.17	7.17	—
	002/002	—	—	5.41	5.27	5.35	—
	Illite 002	4.95	4.95	4.98	—	5.02	4.95
	Chlorite 003	—	—	—	—	4.78	—
	002/003	—	—	—	—	4.69	—
	110, 020	—	4.49	4.48	4.50	4.52	4.49
	Chlorite 004	—	—	3.57	3.58	3.58	—
	003/004	3.23	3.24	3.24	3.23	3.23	3.23
Heat treated	001/001	9.93	9.99	9.93	9.98	9.99	9.80
	002/002	4.92	4.97	4.97	4.96	4.94	4.89
	110,020	—	4.50	4.45	4.50	4.50	4.49
	003/003	3.28	3.30	3.29	3.29	3.29	3.26
Glycolated	001/001	?	12.65	13.01	12.99	14.15	16.50
	Illite 001	9.97	9.95	9.99	—	9.99	10.04
	001/002	9.17	—	9.27	9.35	9.40	8.98
	Chlorite 002	7.19	—	7.15	7.17	7.17	—
	002/003	5.15	5.19	5.26	5.26	5.34	5.49
	Illite 002	—	4.98	5.01	—	—	—
	Chlorite 003	—	—	4.76	—	—	—
	110,020	—	4.50	4.50	4.49	4.52	4.48
	Chlorite 004	—	—	3.57	—	3.58	—
	003/005	—	3.32	3.35	3.34	3.35	3.34

The instruments used were a Philips "NORELCO" *x*-ray diffraction unit and Honeywell recorder unit. CuKα radiation and voltage and current settings of 35KV and 20 M.A. were used throughout. The combination 8-1-4 for scale factor-multiplier-time constant were generally found to give the most satisfactory results. The patterns of Fig. 3 were obtained using a recorder speed of 1/2" per min., diffractometer unit speed of 2°2θ per min. 1° slits were employed throughout. All *d*-spacings given in Å. Heat treatment 1 hr. at 550 °C. Glycolation period: 24 hrs.

degree of crystallinity, the randomness of interstratification and in the chemical composition of components such as illite, montmorillonite and chlorite, contribute largely to this uncertainty. The proportions of the mixed layer clay species calculated by the positions of the various reflections are not always in perfect agreement. Weaver (1956, p. 206) remarks, "In some cases the ratios of layers determined from the 10/12.4 Å curve and the 10/17 Å curve do not show exact agreement. In most cases this discrepancy may be caused by the presence of a few intergrown chlorite layers as the measured 10/12.4 Å value is usually too high and the 10/17 Å value too low. Heat treatment indicates that the chlorite layers are relatively scarce". Discrete chlorite occurs in four out of the six Gaspé bentonites and it seems very reasonable that some may be intergrown with the illite-montmorillonite mineral, particularly so in view of the pattern of high 10/12.4 Å and low 10/17 Å values. Where such discrepancies arise, average values have been taken.

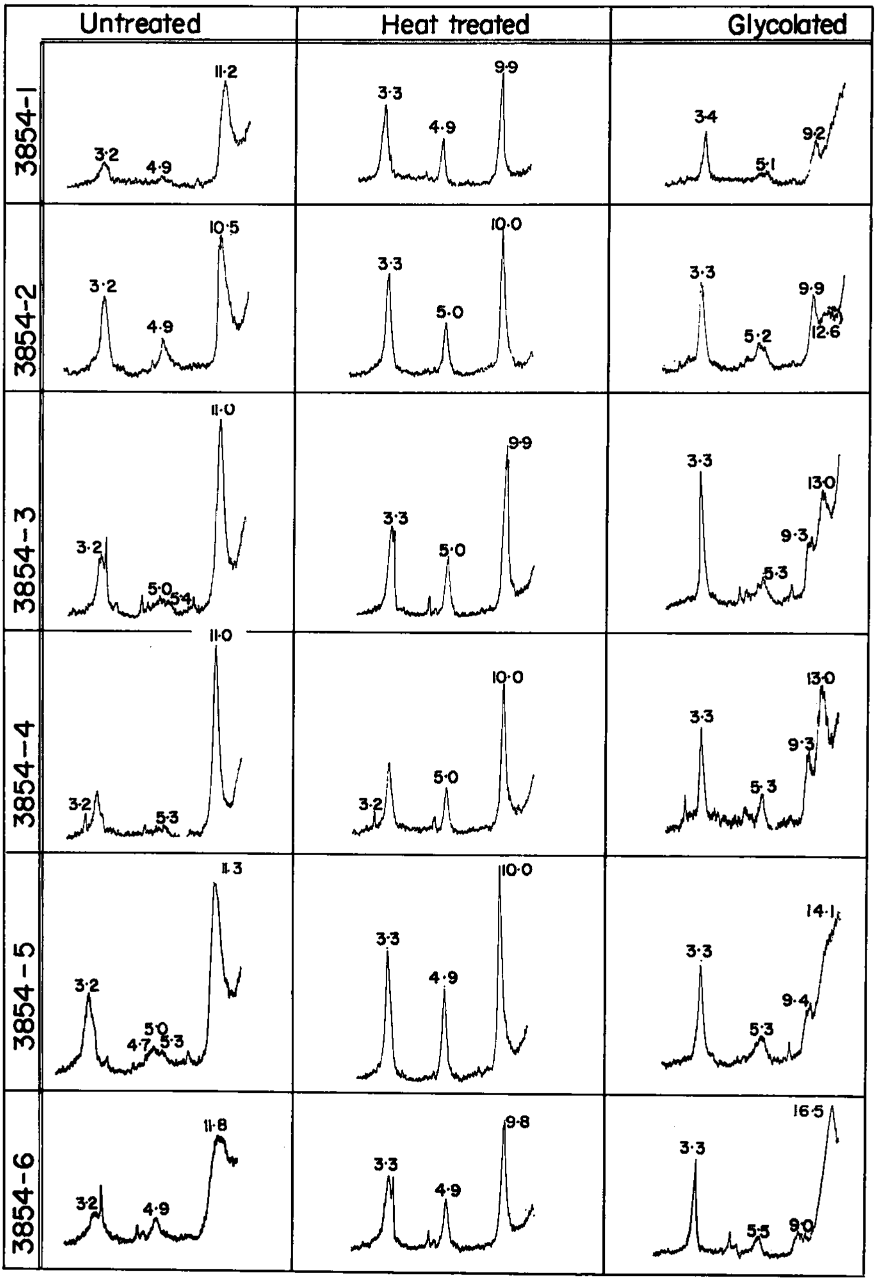

FIG. 3. Diffractometer traces obtained from the clay fractions of the Gaspé bentonites, untreated, heat treated and glycolated. (d-spacings in Å).

TABLE 2. CLAY MINERAL COMPOSITION OF THE GASPÉ BENTONITES

Sample No.	Illite	Chlorite	Montmorillonite	Randomly interstratified illite and montmorillonite
3854-1	×	×	—	× (Illite:Montmorillonite = 60:40)
3854-2	×	—	—	× (Illite:Montmorillonite = 75:25)
3854-3	×	×	—	× (Illite:Montmorillonite = 65:35)
3854-4	—	×	—	× (Illite:Montmorillonite = 65:35)
3854-5	×	×	—	× (Illite:Montmorillonite = 60:40)
3854-6	—	—	×	× (Illite:Montmorillonite = 35:65)

× denotes occurrence of mineral
— denotes absence of mineral

It is uncertain to what extent the discrete illite and montmorillonite results from breakdown during preparatory treatment of composite grains. Where such grains are made up of relatively large packets of illite and montmorillonite, as is perhaps indicated for the Gaspé clays by the broadness of the peaks (Méring, 1949), this effect may be considerable.

The sand fractions: The sand-size fraction of each bentonite was obtained by passing the whole rock through a jaw crusher followed by further disaggregation in water in a Waring blender, the clay suspension being repeatedly decanted. The material which at this stage was made up largely of aggregate grains, mainly quartz (chert) with pockets of clay material incorporated, was then treated with heavy liquids and a magnetic separator, and a number of mineral concentrates obtained. Table 3 summarizes the mineral content of the sand fractions of the bentonites.

Aggregate grains: Aggregate grains are completely dominant in all the sand fractions and are of two kinds. The first, and most common, is simply very fine-grained quartz in a matrix of clay minerals. These grains are believed to have originated when chert was formed as a result of the release of silica on the partial conversion of montmorillonite to illite. Such grains can usually be further disaggregated by prolonged treatment in a Waring blender, more clay being liberated in the process. Even when only very fine-grained material is examined, the clay fractions nearly always give quartz peaks on the diffractometer traces (Fig. 3), and these are thought to be due to the presence of this very fine-grained cherty material.

TABLE 3. MINERAL CONTENTS OF THE GASPÉ BENTONITE SAND FRACTIONS

	3854-1	3854-2	3854-3	3854-4	3854-5	3854-6
Aggregate grains	×	×	×	×	×	×
Quartz	×	×		×	×	×
"β" Quartz		×		×	×	
Sanidine	×	×			×	×
Albite	×	×				
Plagioclase					×	×
Biotite	×				×	×
Chlorite (after biotite)	×					×
Chlorite (after ?amphibole)	×					
Carbonate	×	×	×	×	×	×
Apatite	×	×	×	×	×	×
Zircon	×	×	×	×	×	×
Barite	×	×	×	×	×	×
Pyrite	×	×	×	×	×	×
Chromite	×					
Spinel			×			×
Rutile	×					
Garnet	×				×	
Brookite	×					
Sponge spicules	×	×	×		×	×
Spheroidal chert			×			
Acritarchs			×		×	

(× denotes presence of mineral etc.).

The second kind of aggregate grain is made up of quartz and alkali feldspar of varying sizes and degrees of crystallinity; pockets of clay minerals occur less commonly in these. Some individual grains were large enough to be identified by the very low −ve $2V$ as sanidine (Fig. 4–26).

Byström (1956) noted the abundance of aggregate grains during a study of the Kinnekulle bentonites and believed that the quartz in them was formed either when the volcanic glass was devitrified and altered to clay minerals, or else at a later stage when early formed montmorillonite was subsequently replaced by illite. The latter explanation is favoured for the Gaspé clays; it is thought that the silica that was released in the devitrification process in now located in the adjacent limestones as chert bands. Siever (1962) showed that amorphous silica is much more soluble in water, than crystalline silica. Since chalcedonic sponge spicules are well preserved in the Gaspé bentonites and show no signs of solution, this suggests that the silica in the chert was derived from glassy ash during devitrification.

Quartz: Quartz, as distinct from chert, is common in all but one of the bentonites, and varies from anhedral and angular grains to those showing perfectly the high temperature ("β") quartz habit (Fig. 4–27, 28). Many of the "β" quartz grains are rounded and embayed suggesting magmatic corrosion.

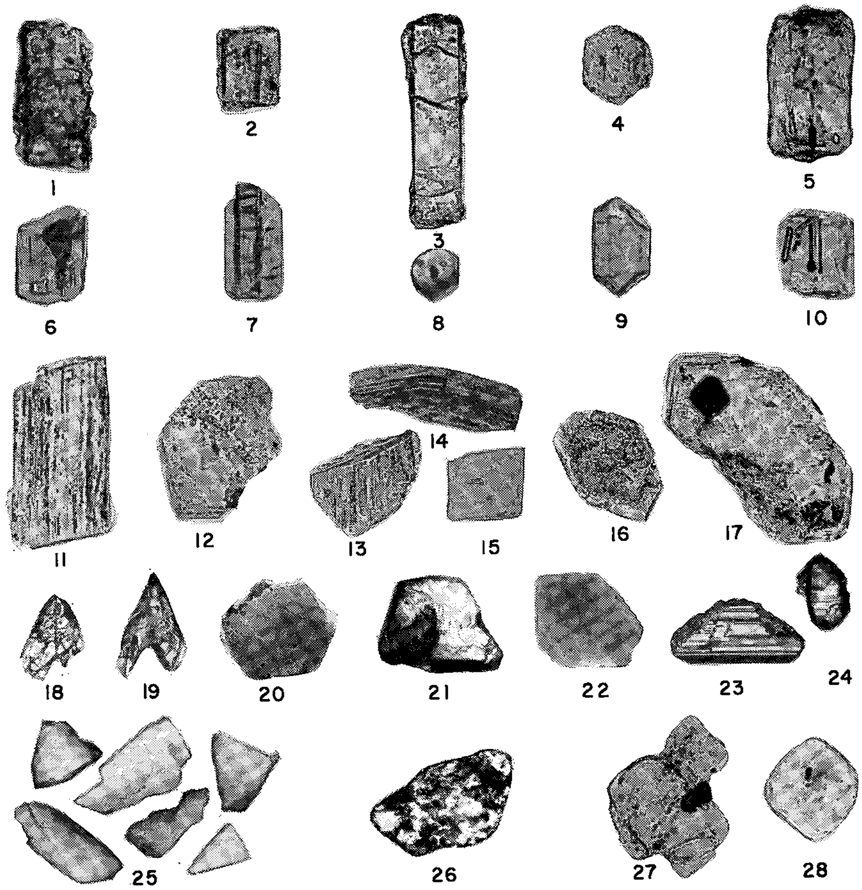

FIG. 4. Minerals from the Gaspé bentonites.

1. A euhedral prismatic apatite with {001} termination. The crystal is full of inclusions and has a ragged authigenic overgrowth in optical continuity. (3854-2).
2. A stumpy prismatic apatite with termination by {001}. Authigenic overgrowth is less well developed.
3. A long prismatic apatite with termination by {001}. Inclusions are few, but the authigenic overgrowth is well developed (3854-2).
4. A basal cleavage fragment of apatite showing euhedral outline.
5. A large stumpy apatite with a thin overgrowth and numerous inclusions. (3854-2).
6. An apatite with no overgrowth and large bubble and rod inclusions (3854-2).
7. An overgrowth of magmatic origin around an earlier apatite of the type illustrated in (3) above. (3854-3).
8. A basal cleavage fragment of an apatite showing rod inclusions in cross-section. (3854-3).
9. Apatite doubly terminated by pyramidal faces, overgrowing a small crystal of the type illustrated in (3) above. (3854-3).
10. A stumpy prismatic crystal with several rod-like inclusions.

11–17. Authigenic barite crystals showing development of euhedra (with {210}, {010}, *Feldspar:* Sanidine was identified in four bentonites—and in one was sufficiently abundant for K/Ar dating purposes. It is always fresh and unaltered, sometimes quite clear, sometimes containing bubbles and/or rod-like inclusions. Most grains are angular and anhedral (Fig. 4–25).

Albite was identified in two bentonites and plagioclase in two others. The plagioclase was tentatively put in the oligoclase-andesine composition range on the basis of simple optical tests on the few suitable grains available. In 3854-1, albite, full of bubble, rod and mineral inclusions, completely dominated sanidine.

Biotite: This occurs in three of the bentonites and from one (3854-6) sufficient was obtained for K/Ar dating. In some bentonites, the biotite, still retaining its euhedral or subhedral form, is partially or completely chloritised while in others it is completely fresh.

Chlorite: This appears as a replacement of biotite and either pyroxene or amphibole. The habits of the two types of material are quite distinct, one occurring as hexagonal flakes probably after biotite (d_{001} = 14.22 Å) and the other as irregular shreddy grains (d_{001} = 14.8Å). *X*-rays showed that the second material has a basal spacing appreciably different from the chlorite in the clay fraction of this bentonite (d_{001} = 14.35Å), indicating different compositions and thus different origins—i.e. the clay-grade chlorite did not result from the comminution of the coarser material.

Carbonates: This material appears as discrete grains, replacing plagioclase feldspar, and as organic remains. In the latter case it appears to be iron-rich in most instances.

Apatite: Euhedral, stumpy, hexagonal prisms are common, often being terminated by pyramid faces—usually poorly developed (Fig. 4–6 to 9). In other grains termination is by basal pinacoid. Occasionally a crystal of the first has overgrown a crystal of the second kind. Wyllie *et al.* (1962)

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and {001} etc.), bent crystals (14) and arrangement of inclusions parallel to the perfect basal cleavage (3854-1, 3854-2).

18–19. Broken geniculate twins of rutile.

20. Slightly rounded six-sided flake of biotite.

21. Anhedral grain of spinellide (?pleonaste) with stepped surfaces (3854-3).

22. Six-sided flake of biotite, showing virtual absence of inclusions.

23–24. Broken crystals of brookite showing characteristic striation of surfaces.

25. Several anhedral grains of sanidine showing clear, unaltered character (3854-5) (crossed polars).

26. A typical quartzo-feldspathic aggregate (crossed polars).

27. A cluster of three quartz crystals showing the high temperature ("β") habit. There are more inclusions in these grains than in most (3954-2).

28. A quartz crystal with the high temperature ("β") habit and rounding of corners by magmatic corrosion.

The magnification of all specimens ×360. They were photographed in plane polarised light; all are from 3854-1 unless otherwise stated.

suggested that the habit of apatite can indicate whether or not the parent rock is of igneous origin. During experimental work on the system $CaO—CaF_2—P_2O_5—CO_2—H_2O$ they found different habits to be characteristic of different crystallization histories: elongated, acicular crystals were formed as a melt was quenched, whereas more stumpy crystals formed in equilibrium with the melt; when primary apatite coexisted with a vapour phase during quenching, the crystals although still acicular were somewhat stouter than when a vapour phase was absent; cavities were frequently present, often running the length of a crystal. Many apatites from the Gaspé bentonites show a relatively stout prismatic habit compared with those figured by Wyllie *et al.*; also comparatively elongated prisms sometimes occur included within later stouter apatites, (Fig. 4–7). The reverse situation was not observed. Thus the Shiphead apatites show the reverse of the features observed by Wyllie *et al.*, in that the earlier primary crystals are distinctly more acicular than the later ones. This could perhaps be explained on their hypothesis by an increase in the vapour pressure, prior to the subsequent eruption of pyroclastic material, causing stouter prismatic development. Rod-like inclusions and cavities are common (Fig. 4–2, 6, 8 and 10) and the more elongated grains show quite well the fractures noted by Wyllie *et al.* in their primary apatite crystallites (Fig. 4–3).

Some apatites have ragged overgrowths, with a sharp junction between the two parts of a crystal, perhaps reflecting compositional differences. This overgrowth, which was only observed on the more elongated apatites is thought to be authigenic, possibly resulting from liberation of P on the devitrification of the volcanic glass.

Zircon: The zircons are particularly interesting and many have been illustrated in Fig. 5–1 to 29. The habit varies enormously, particularly within one bentonite (3854-1), from stumpy prismatic crystals bounded by pinacoid faces and with only the smallest pyramid faces (4), to crystals made up almost entirely of the pyramid faces (6); from slender, delicate needles (10) through 'waisted' prisms (11) to rounded prisms that might well be expected in the products of the third or fourth cycle of weathering (27). Many of the zircons have inclusions and these range from 'bubbles' to rods and minute mineral grains (1 to 17). Some grains have overgrowths (19) and yet others fine oscillatory zoning (21).

Poldervaart (1955, 1956) summarized much of the knowledge of zircons from igneous and sedimentary rocks, and his descriptions and those of other workers clearly show the affinities of the Gaspé bentonites with intermediate or acid rather than basic rocks. However, the habits found among the Gaspé zircons are typical of a range of such rocks from peralkaline to calc-alkaline.

It is thought unlikely that a single bentonite bed actually represents a series of ash-falls from successive eruptions that followed one another very closely, in view of the relative simplicity of the mineralogy of the sand fractions from any one bed—diversity of character of zircons does not extend to the other minerals. However, Slaughter & Earley (1965) have found that many of the Cretaceous bentonites of Wyoming are composite, being made up of several graded units—presumably from successive ash falls. In some cases, perhaps, these units represent explosions from the same vent; in others, isopachytes suggest eruptions from separate vents. Slaughter & Earley do, however, note (p. 30) that bentonite beds (as distinct from individual units) each have a characteristic mineralogy. These conclusions suggest that bentonites, even when they are composite, are usually derived from the same batch of magma although this may be tapped at slightly different times and places.

No field evidence of graded units in the Gaspé bentonites was noted, and the view that all the zircons in a particular bentonite are cogenetic is favoured although there are then several features that are remarkable and require explanation. These include the extreme range of habit, the great elongation of some of the prisms relative to others, the perfect unrounded euhedral habit of many crystals and the complete rounding of others, the presence of waisted zircons undoubtedly resulting from magmatic corrosion, zoning, and the abundance of inclusions. All these features are displayed by the zircons from the 3854-1 bentonite.

Larsen & Poldervaart (1961) found a wide variation in habit of zircon from the Bald Rock batholith, California. They believed that during palingenesis, prismatic euhedra grew in an interstitial melt whilst non-prismatic euhedra grew by recrystallization in the solid. Anhedral, rounded or resorbed grains (presumably) resulted from incomplete melting and/or failure of earlier zircon to recrystallize. While this could explain the general pattern of Gaspé zircon habits it does not account for the wide range within one group, e.g. among the prismatic zircons. Larsen & Poldervaart (1957) noted the predominance of certain habits of zircon in the Bald Mountain batholith of Oregon (although the sizes vary appreciably). They considered that factors affecting size and habit of zircon include (1) the physico-chemical environment in which it crystallizes; (2) the early and short range of crystallization (thus no appreciable change in environment is to be expected during crystallization); and (3) that although (initial) growth results in a wide range of habits and sizes, competition between crystals growing in the same environment will produce a relatively narrow range of favoured sizes and habits, which will be of high frequency and thus characterize the sample. They note, however, that the environment of crystallization in volcanic centres (as distinct

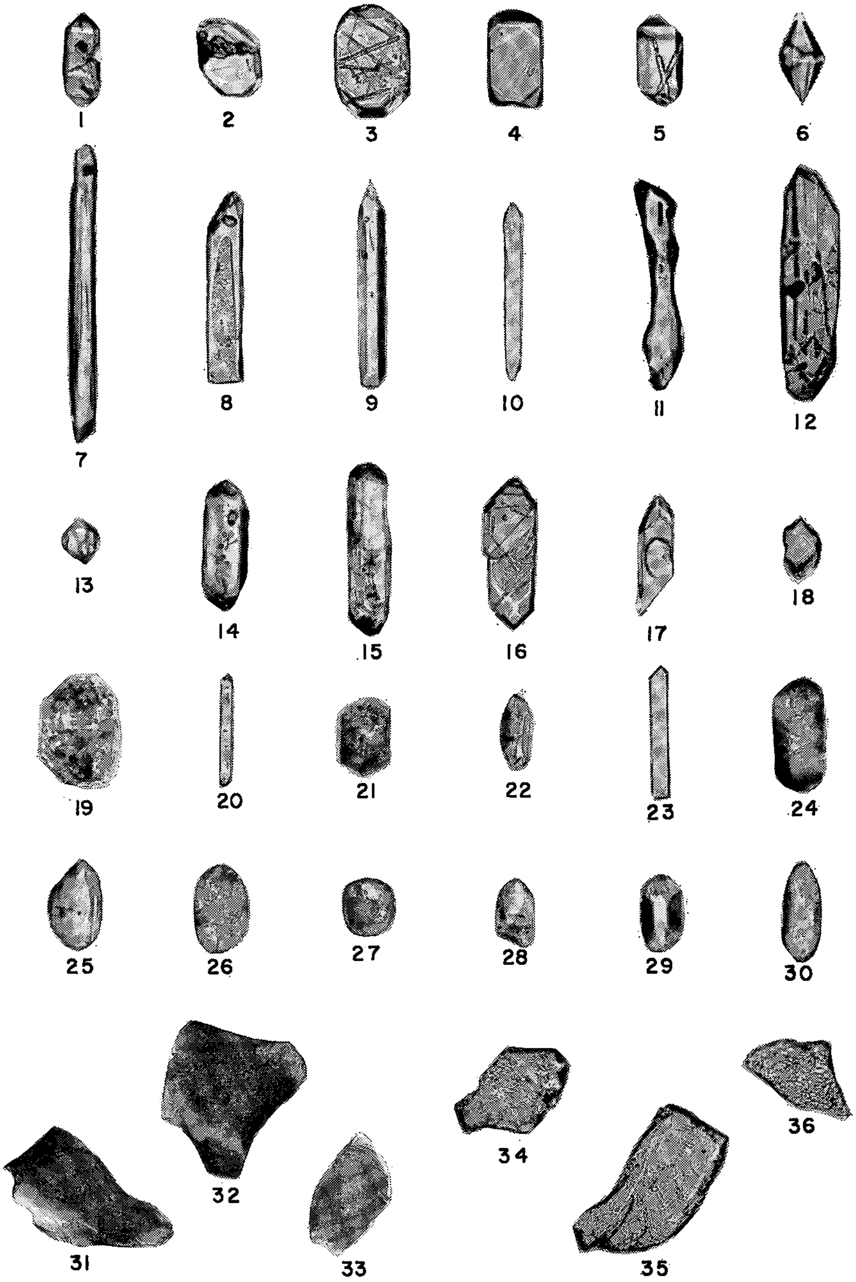

FIG. 5. Heavy minerals from the Gaspé bentonites.

1. Zircon euhedron showing pitting (3854-3).

from that in a batholith) may change rapidly and thus factors 2 and 3 above would not apply. A wide range of habits is surely an unusual mineralogical feature. Two or three habits (e.g. of feldspar) are not too uncommon in an igneous rock when a mineral is crystallizing over a large part of the cooling history, but six or more as are found in the Gaspé zircons is, as far as the writer is aware, unheard of. The explanation may lie in the particular sensitivity of zircon to its physico-chemical environment, so that numerous different habits are adopted during the crystallization of magma and passage to its position of final consolidation. Experimental work by Wyllie *et al.* (1962) on the habit of apatite has already been noted, and similar research on zirconium-bearing melts might well throw light on the habit of zircon in igneous rocks, thereby providing a more precise tool for tracing the crystallization histories of particular rocks.

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2. Zircon euhedron showing the rarely developed {001} form.
3. Zircon euhedron showing the rarely developed {001} form and numerous rod-shaped inclusions.
4. Zircon euhedron showing the rarely developed {001} form, stumpy prismatic habit and comparative absence of inclusions.
5. Zircon euhedron with two rod-like inclusions.
6. Pyramidal zircon euhedron showing almost complete supression of the prism faces.
7. Slightly corroded, long, needle-like prism of zircon.
8. Broken zircon euhedron with a very large cavity.
9. Zircon needle showing pitting.
10. 'Gem-quality' needle-like zircon with no inclusions.
11. 'Waisted' zircon crystal, believed to result from magmatic corrosion.
12. Large zircon euhedron showing pitting and many inclusions.
13. Small zircon with poorly developed prism faces.
14. Stumpy, slightly rounded zircon with mineral and bubble inclusions.
15. A rounded, slightly corroded zircon.
16. A zircon euhedron with numerous inclusions.
17. A broken zircon euhedron with a large bubble inclusion.
18. A small zircon euhedron showing prism, dome and pyramid faces.
19. A rather rounded zoned zircon with a euhedral overgrowth.
20. A small pitted needle-like zircon.
21. A zircon euhedron showing zoning.
22. A slightly rounded and pitted zircon.
23. A broken 'gem-quality', needle-like zircon.
24. A rather rounded rutile crystal.
25. A well rounded zircon showing pitting.
26. A well rounded zircon, which has grown around another mineral.
27. Very rounded zircon.
28. Well rounded broken zircon.
29. A slightly rounded stumpy zircon.
30. A rounded rutile crystal.

31–33. Anhedral grains of chromite showing absence of rounding and well developed conchoidal fracture surfaces.

34–36. Anhedral grains of garnet showing delicately etched surfaces.

(All minerals are from 3854-1 except No. 1).

(Magnification ×360, plane polarised light).

Another feature frequently recorded but awaiting satisfactory explanation is the coexistence of magmatically corroded and sharply euhedral crystals (see Poldervaart, 1956, and Bibliography). The hypothesis that zircons, originally formed in equilibrium with a magma, were subsequently put out of equilibrium by change of physical conditions on eruption, and corroded, is untenable when such delicate needles as those in Fig. 5 suffered no corrosion at all. The opposite situation would be more likely: zircons, either formed at an earlier stage in the crystallization history—or else incorporated with xenolithic material—were subsequently corroded in the new environment, sharply euhedral elongated prisms precipitating on later cooling. Karakida (1964) studied zircon concentrates from granitic xenoliths in volcanic rocks of southwest Japan, and compared them with concentrates obtained from the parent rock of the xenoliths. He was able to show that the percentage of rounded zircons increased with the degree of alteration of the xenoliths, thus indicating that the rounded zircons were due to corrosion. He also observed that the smallest zircons were the most rounded, a feature qualitatively true of the Gaspé bentonite zircons, and in contrast to sedimentary zircon concentrates where the opposite holds. Thus it seems probable that magmatically corroded crystals (including rounded pellet-like grains) were incorporated as such during the formation of the magma by the refusion of crustal rocks (this view appears to be favoured also by Larsen & Poldervaart, 1961; and Poldervaart, 1956). If this is the case, however, it is surprising that overgrowths on rounded, corroded zircon crystals are not much more common, particularly in plutonic rocks where relatively rapid cooling cannot be called upon to produce many new zircon nuclei.

The presence of oscillatory zoning in some of the zircon crystals (e.g. Fig. 5–21) and absence in others, is probably best explained by the incorporation at some stage of zoned zircon xenocrysts. Finally it is thought most unlikely that the very rounded zircons are of direct detrital origin in view of the absence of a suite of detrital heavy minerals.

Garnet: Anhedral colourless garnet is fairly common in 3854–1 (Fig. 5–34 to 36) and also occurs rarely in 3854–5. An interesting aspect is the presence of delicate etch markings. McMullen (1959) believed that since apatite, which is unstable in acid media, persisted alongside such garnets, basic solutions must be responsible for the etching. He found a 1*N* (NaOH) solution produced similar effects in a few days. Bramlette (1929) however obtained the same results with HF. Zaporozhtseva (1960) also came to the conclusion that low pH conditions (from 4–6) were most likely to be responsible. In the present instance, the environment was one in which apatite not only persisted but grew authigenically, and it seems unlikely that, in this case at least, the solutions etching the garnet could have been acid.

Pyrite: This occurs in all the bentonites, sometimes as pellets filling in megaspores, and sometimes as perfect cubes, pyritohedra, etc. Many grains have a brown, oxidized surface.

Chromite, spinel, etc.: A chrome-spinellide is abundant in bentonite 3854-1 (Fig. 5–31 to 33). All the grains are angular, show no trace of rounding, and have perfectly preserved conchoidal fracture surfaces. They are thus most unlikely to be of detrital origin, and since it is also most improbable that they are cogenetic with the other minerals in this bentonite (quartz, alkali feldspar, etc.) they are probably accidental xenocrysts derived from the rocks adjacent to the vent through which the ash was erupted. A green spinellide (hercynite?) occurs much less prolifically in 3854-3 and a yellow-brown spinellide sparsely in 3854-6. Similar origins are envisaged for these spinellids, as for that in 3854-1.

Organic constituents: These are of three types—acritarchs, sponge spicules and ostracods. One particular thin section showed a complete acritarch with spines protruding from the case (Fig. 6–9), but most of those in the sand fractions had lost their spines, presumably during preparation, and only the case remained.

Two ostracods were common (Fig. 6) and one was identified as Walsachia (1).

Sponge spicules were the most abundant organic constituent in all the bentonites, and included monaxons, tetraxons and hexaxons.

Since no attempt was made to collect the bentonite layer by layer, it is

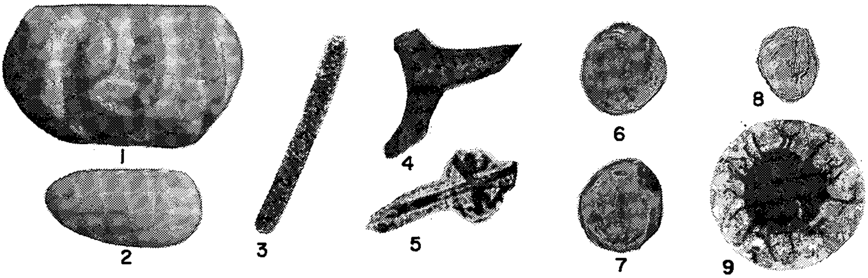

FIG. 6. Organic remains from the Gaspé bentonites.

1. Ostracod *Walsachia* abundant in 3854-1. Magnification: ×50.
2. Another ostracod from 3854-1. Magnification: ×50.
3. A monaxon sponge spicule from 3854-5 replaced by iron-rich carbonate. Magnification: ×360.
4. A broken tetraxon sponge spicule from 3854-5, seen looking down the fourth axis. This spicule is also replaced by iron-rich carbonate. Magnification: ×360.
5. A broken hexaxon sponge spicule from 3854-4 with chalcedonic walls and pyrite filling the axial canals. Magnification: ×360.

6–8. Poorly preserved Sphaeromorphid acritarchs, probably Leiosphaeridia sp. from 3854-1. Magnification: ×360.

9. Acanthomorphid acritarch, probably Baltisphaeridium sp. from 3854-6 seen in thin-section. Magnification: ×360.

not known to what extent any or all of the organic constituents were confined to the upper, possibly slightly reworked layers. It seems quite possible that much of the organic material could have been incorporated during settling of the ash through the water into which it fell.

The presence of discrete quartz in five and alkali feldspar in four out of the six bentonites, together with the occurrence of biotite and certain habits of zircon is taken to indicate that the source material was acid or intermediate in character. A survey of the literature on bentonites suggests it is probable that nearly all bentonites have been derived from acid or intermediate pyroclastic material. Thus Maddox (1930) observed pyrite, biotite, zircon, apatite and tourmaline in the sand fraction of Ordovician bentonite near Collingwood, Ontario and C. S. Ross commenting on this material likened its character to that of fine-grained pumice: Allen (1932) found montmorillonite with a relict pumiceous texture, sanidine, quartz, biotite, apatite and zircon in Ordovician bentonites in Minnesota; Kerr & Cameron (1936) recorded sanidine, acid plagioclase, hornblende and chlorite in the Tehachapi fullers earth (bentonite); Stephenson (1936) noted orthoclase, oligoclase, quartz and biotite in bentonites from the Upper Cretaceous of New Jersey; Hass (1948) reported up to 30% of an Upper Devonian bentonite in Tennessee to be biotite with lesser amounts of K-feldspar, Na-plagioclase and quartz; Weaver (1953) found biotite, albite, apatite and zircon in Ordovician K-bentonites; Byström (1956) described biotite, quartz and sanidine, from the Ordovician Kinnekulle bentonites of Sweden; Huff (1963) records abundant biotite and some zircon, apatite, magnetite and leucoxene, etc., in Ordovician K-bentonites of Kentucky; Slaughter & Earley (1965) found that feldspar, biotite, quartz and subordinate magnetite, hornblende and zircon are characteristic of the numerous Cretaceous bentonites of Wyoming. Many bentonites of Carboniferous to late Cretaceous age, used for K/Ar dating work in the Department of Geology at the University of Alberta, also have similar mineralogy, K-feldspar, biotite, quartz and zircon being particularly common.

Of course the bulk of violently erupted material is acid in character and it might, therefore, be expected that more bentonites will have acid and intermediate rather than basic affinities. However, the writer is not aware of any bentonites with 'basic' sand fractions containing, say, calcic plagioclase, olivine and pyroxene. The palagonite tuffs may be the basic equivalents of bentonites. Schultz (1963) has reviewed the occurrences of non-montmorillonite 'bentonites'. Possibly some of them (particularly those containing zeolites such as phillipsite) could have been derived from basic to intermediate parent ashes.

SECTION 3: CHEMISTRY

The chemical characteristics of bentonites are not yet very well documented, although chemical analyses have been given by a number of investigators including Kerr & Cameron (1936), Foshag & Woodford (1936), Fox & Grant (1944), Weaver (1953), Byström (1956), Gordon *et al.* (1956), and Maiklem & Campbell (1965). All of these bentonites have one feature in common—their compositions have no equivalents among common igneous rocks. They can be broadly grouped into those that have very low potash contents (simple montmorillonite bentonites) and those that contain appreciable amounts of potash (K-bentonites, sometimes called meta-bentonites) which when investigated by modern techniques are often found to be made up to a greater or lesser extent of a randomly interstratified illite-montmorillonite mixed layer clay (Weaver, 1953; Byström, 1956; Huff, 1963). Further subdivisions can be made on the basis of the exchangeable cations (Ca or Na) and on the extent of substitution of Mg for Al. A few bentonites cannot be fitted into either category, being made up of minerals such as kaolin, halloysite, phillipsite and clinoptilolite with or without montmorillonite, etc. (Schultz, 1963). The analysed Gaspé bed (3854-1) is clearly a K-bentonite, but is of mixed characteristics as far as the exchangeable cations are concerned. The MgO content is moderate. Some of the CaO is present as calcite and most of the Fe as pyrite.

If it is considered that the Al_2O_3 content is likely to have remained more or less constant, on the grounds of the low solubility of this oxide except in very strongly acid or alkaline environments, and that it is not observed reprecipitated elsewhere (i.e. in the limestone above and below the bentonites), then for a given composition of original ash the material added or subtracted after deposition can be calculated. As already noted, all the indications are that bentonites are derived from (pumiceous) acid to intermediate pyroclastics. In the case of this bentonite (3854-1) the presence of sanidine and quartz suggest that the original composition was rhyolitic. If it is assumed that the original volcanic ash had the composition of the standard granitic rock G-1 (Stevens *et al.*, 1960) then the percentages of material that must be added or subtracted to arrive at the composition of the bentonite are shown in Table 4. Obviously the original ash is only likely to have approximated G-1 in composition and the actual chemical changes will have been slightly different. It seems fairly clear, however, that the most significant changes have been an addition of CaO and MgO and a removal of SiO_2 and alkalis. The addition of the CaO and MgO is understandable in a sequence of limestones. The

Table 4. Composition of Gaspé Bentonite 3854-1

	I	II	III
SiO_2	60.01	66.30	−18.25
TiO_2	0.41	0.46	+0.13
Al_2O_3	15.67	17.31	—
Fe_2O_3	0.58	0.64	−0.32
FeO	2.01	2.22	+0.85
MnO	trace	trace	−0.03
MgO	2.78	3.07	+2.14
CaO	2.77	3.06	+1.16
Na_2O	0.48	0.53	−2.89
K_2O	3.84	4.24	−1.95
H_2O Total	9.66	—	—
P_2O_5	0.28	0.31	+0.16
CO_2	1.45	1.60	+1.24
S	0.45	0.50	+0.40
	100.17*	100.00*	+6.08 −23.44

Analyst: Ann Herring
*Totals corrected for Fe present as pyrite on basis of S content
I Composition of Gaspé bentonite
II Composition of Gaspé bentonite water free to 100%
III Composition of material added to or subtracted from the standard rock G-1 to give the composition of the Gaspé bentonite (Al_2O_3 assumed to remain constant).

removal of silica is equally reasonable in view of the common occurrence of chert in the adjacent limestones—both at Gaspé and elsewhere (see Fox & Grant, (1944); Bramlette (1946); Weaver (1953); Byström (1956); Siever (1962); and Huff (1963)). The removal of alkalies is less easily accounted for and will be discussed briefly later. Their ultimate destination is not obvious. They may be removed completely from the strata in solution, or perhaps in some instances captured by beds of glauconitic sandstone such as the prominent green calcarenites outcropping on the shore about 200 feet southwest of the bentonite exposures in the Shiphead section. It may also be significant that Cretaceous bentonites of Mississippi frequently grade up into glauconitic sands (Grim, 1953).

Various researchers have disagreed about the time of addition to, and removal of material from, the bentonites. Weaver (1953) and Byström (1956) favour alteration of volcanic ash on the sea floor and believe that chert only occurs below the bentonites and thus results from the more or less immediate reprecipitation from solution of silica dissolved during the early devitrification of the volcanic glass. Others, notably Bramlette (1946), have argued that diagenetic changes are more important, the ashes being altered to bentonites by water in the confining strata. Whilst post-consolidational percolation of solutions could deposit chert directly below a bentonite bed *only*, it is difficult to see how a chert can form in limestones *above* and *below* a bentonite (e.g. Huff, 1963), except during authigenic processes, and can certainly not have formed on the sea floor. What experimental evidence there is appears to favour alteration of the ash after burial. Marshall (1961) investigated the devitrification of natural glasses from a theoretical and an experimental standpoint. His results suggest that glass on the sea floor is unlikely to devitrify in over 100 m.y.—but that alteration could take place much more rapidly after burial to considerable depth (10 m.y. at 100 °C or 1,000 y. at 200 °C). It seems probable, however, that the ashes from which the bentonites were formed were not entirely glassy, but cryptocrystalline in part (as many natural pumices are) and the behaviour of such material would not be simply related to that of glass. Zen (1959) noted only partial devitrification of volcanic ashes obtained from gravity sediment cores from the Chile-Peru trench. The reason for the devitrification of some glass while the rest remains quite fresh is not clear. It could of course be very difficult to distinguish between material that had devitrified and that which was cryptocrystalline on deposition. Even more puzzling in this respect is Weaver's (1953) identification of volcanic glass in Ordovician K-bentonites. It is curious that the small amount of glass he reports was not devitrified along with the bulk of material when it was converted into bentonite. Zkhus & Yurevich (1961) have described the alteration of Tertiary volcanic ashes (glasses) with crystals of oligoclase-andesine, quartz and biotite as they pass through three stages finally being converted to a bentonite. They found that the glass alters to montmorillonite and also that the degree of alteration changes with the content of organic carbon as well as the age of the rock; they consider that transformation processes, initiated immediately after sedimentation, continue through diagenesis and into epigenesis.

As far as the writer is aware the only trace element data available for bentonites are those given for a few elements by Zkhus & Yurevich (1961) in their paper on the alteration of volcanic glass. It is thought, however, that such data may be useful in helping to confirm the nature of the source material of the Gaspé bentonites, as well as suggesting the character and extent of any enrichment that takes place during the formation and diagenesis of a bentonite. The six beds have been investigated in this way and the results are summarized in Table 5.

In a general way the trace element data are rather similar for all the bentonites and are consistent with acid to intermediate compositions for the source ashes. Most of the values lie between those of G-1 and W-1 (Stevens *et al.* (1960)) and appreciably nearer those of G-1. They are, however, in strong contrast to the average values for trace elements in shales and clays (Rankama & Sahama, 1950), and thus reflect the

TABLE 5. TRACE ELEMENT CONTENTS OF GASPÉ BENTONITES

	3854-1	3854-2	3854-3	3854-4	3854-5	3854-6	G-1	W-1
Li	39, 34 (36)	59, 36 (48)	32, 34 (31)	7, 8 (8)	41, 30 (35)	41, 46 (44)	24	12
Sc	17, 17 (17)	40, 44 (42)	31, 38 (35)	27, 23 (25)	25, 21 (23)	30, 31 (30)	4	43
Ti	4160, 4230 (4195)	7130, 8200 (7665)	3690, 5300 (4495)	1350–1640 (1495)	3270, 3330 (3300)	3290, 3290 (3290)	1950	8020
V	37, 38 (38)	28, 37 (33)	37, 45 (41)	5, 7 (6)	28, 25 (27)	19, 21 (20)	21	240
Cr	81, 76 (79)	18, 21 (19)	64, 77 (70)	14, 11 (13)	40, 41 (40)	29, 31 (30)	22	120
Mn	68, 61 (65)	125, 128 (127)	121, 117 (119)	70, 49 (60)	33, 33 (33)	30, 32 (31)	234	1440
Co	2, 3 (2)	2, 2 (2)	3, 2 (2)	2, 2 (2)	2, 4 (3)	3, 3 (3)	2.2	51
Ni	21, 18 (20)	5, 4 (4)	15, 16 (16)	2, 4 (3)	5, 6 (6)	4, 5 (4)	1.2	80
Cu	38, 41 (40)	43, 42 (42)	23, 21 (22)	8, 10 (9)	16, 15 (16)	20, 19 (20)	13	110
Ga	21, 21 (21)	29, 24 (27)	25, 22 (24)	16, 17 (16)	19, 20 (20)	27, 25 (26)	18	16
Rb	145, 143 (144)	167, 207 (187)	85, 82 (84)	89, 86 (88)	93, 92 (92)	163, 205 (184)	220	22
Sr	136, 140 (138)	118, 139 (129)	195, 143 (169)	199, 229 (214)	168, 177 (173)	92, 114 (103)	250	175
Zr	340, 390 (365)	1330, 1150 (1240)	268, 172 (220)	263, 436 (350)	212, 292 (252)	325, 412 (368)	210	100
Ba	127, 144 (136)	880, 650 (765)	172, 201 (186)	42, 51 (46)	142, 127 (135)	106, 132 (119)	1220	225
La	69, 75 (72)	74, 92 (83)	105, 120 (113)	47, 41 (44)	94, 81 (87)	112, 60 (86)	120	20

All values in parts per million; average values bracketed.

Concentrations were determined by the DC Arc method using a Hilger quartz/glass spectrograph, with a Pd internal standard, and G-1 and W-1 as standard comparative rocks. The techniques used were those standard in the spectrographic laboratory at Oxford; these are based on methods described by Ahrens & Taylor (1960).

Analysts: Natalie Garton, Julia Tetherton, D. G. W. Smith.

abnormal mode of origin of these clay rocks amongst aluminous sediments. Notwithstanding this, the increase in the values compared to G-1 for elements such as V, Ga, Ni and Cr, while perhaps in part indicating somewhat trachytic affinities for the parent ashes, also reflects the tendency of these elements to be concentrated in aluminous sediments. Both relative enrichment by loss from the bed of appreciable amounts of major constituents (such as SiO_2), and absolute enrichment by adsorption of the elements onto clay minerals may have been involved. The adsorption might have been a result of the circulation during consolidational processes of water trapped in the associated limestone beds. Zr deserves specific mention as it is probably contained almost entirely in the mineral zircon which crystallized prior to or during the eruption and thus can be expected not to be involved in the diagenesis which affected the clay minerals. The element is present in much higher concentrations than in W-1 and somewhat higher than in G-1. 3854-2 is particularly rich in this element.

The only elements that, at first sight, appear to be discordant in this pattern of behaviour are Sc, Sr, Ba and Rb. While the reasons for the appreciably high contents of Sc in the bentonites are not clear, the Sr, Ba and Rb figures can be explained. The data available on the abundance of Sr in various geological environments (e.g. Turekian & Kulp (1956); Campbell & Williams (1965); Rankama & Sahama (1950)) indicate that there is no particularly strong tendency for Sr to be enriched in clays, shales, etc., whereas notably higher concentrations do occur in carbonate rocks—particularly those with a content of (organic) aragonite. Thus the Sr, apparently missing from the Gaspé bentonites, may have migrated into the adjacent limestones, along with major constituents such as SiO_2. It would be interesting to know whether the limestone beds directly *above and below* contain concentrations of Sr. This would afford evidence as to whether the alteration from original ash (and the migration of Sr) took place on the sea floor or subsequently, after burial by superincumbent limestone strata. The alkali elements and Ba are characteristically enriched in shales, clays, etc., but it seems from the major element analysis that K and Na migrate from the bentonites rather than being concentrated in them. Ba and Rb which follow K, appear to do likewise. As has already been observed, the reason why the alkali elements do migrate from bentonites is not obvious; perhaps their leaching from the volcanic ash takes place prior to the formation of the clay minerals; this of course may also be true for the Sr. Thus the eventual formation of montmorillonite in these beds (rather than illite) is mainly a reflection of the chemistry after the leaching of alkalis.

SECTION 4: DISCUSSION

Since it became generally accepted that bentonites represent decomposed volcanic ash falls (and thus time planes) many writers have drawn attention to their potentialities for correlating over wide areas the strata containing them. The problem, however, is to distinguish one bentonite from another in a sequence of rocks containing several.

Maiklem & Campbell (1965) investigated the clay mineral compositions in the hope of characterizing four bentonites in the Belly River Formation of Alberta. They found "no major differences in the clay minerals of the bentonites". Since the clay mineral composition of a bentonite must largely reflect (and be reflected in) the chemical composition of the bed, any attempt at correlation of bentonites on the basis of their clay mineralogy must be based on the assumption that the chemistry of a particular bed remains the same over the area of correlation. Such an assumption could only be justified under certain conditions: (a) the initial composition of the volcanic ash fall was constant over the area of deposition, (b) changes taking place immediately after deposition e.g. on the sea floor, affected the whole bed equally, (c) diagenetic changes were the same. The first condition is probably quite generally true—except perhaps in the immediate environment of the volcanic vent where the character of an ash fall can vary quite rapidly. The second depends on the ash falling into a uniform environment (e.g. an area of shallow shelf seas) and the third on there being no appreciable differences in the physical conditions to which the bentonite was subjected after burial over the area of correlation. These conditions may be closely approached only in a sequence of flat lying sediments that have had essentially identical geological histories over the area of occurrence—in which case correlation will probably present few difficulties anyway.

Maiklem & Campbell's quotation of Weaver (1958a, 1958b, and 1959) in support of their contention that the Belly River bentonites were modified only slightly in their environment of deposition is not justifiable. Weaver suggested that the character of clay minerals is essentially established in the source area i.e. at the time of their formation (or liberation) by the weathering process, and then that this established character is modified only slightly in the final environment of deposition—due to cation adsorption, etc. The situation with bentonites is obviously quite different in that the clays are actually formed in the environment of deposition and Weaver (1958a, p. 169) actually cites the formation of montmorillonite from volcanic material in a marine environment as an example of (marine) diagenesis. The persistence of differences in the clay mineralogy of the Belly River bentonites and associated shales does not in itself indicate that the environment of deposition only slightly modifies the mineralogy. Initially different materials could have been altered in different ways and to different extents. Burst (1959) found in a study of the Eocene Wilcox Formation which extends from outcrop in S. Illinois and Missouri to a depth in excess of 13,000′ in Louisiana, that montmorillonite, prominent in surface outcrop, becomes less common below 3,000′ and not usually present in the unmixed state below 9,000′ to 10,000′. Thus between 3,000′ and 14,000′ mixed-layer illite-montmorillonite is common, the proportion of illite increasing with depth. Burst's work suggests that the clay mineral composition of bentonites is unlikely to be a reliable means of correlation in areas of folded strata.

Trace element data for the Gaspé clays are reported here (Table 5) and it is suggested that such data could be of more use than the major and minor element compositions in correlating bentonites, both because of the greater relative differences in concentration of certain trace elements between two bentonites, and because some trace elements are probably held more or less completely in crystalline phases (e.g. Zr in zircon), and thus are not involved in the glass/clay-mineral diagenesis.

The heavy mineral suites of bentonites are likely to be of use in the identification and correlation of a particular bentonite, for the same reason —i.e. they do not appear to be involved to any great extent in any diagenetic or authigenic changes in the bed. Thus the heavy mineral crop of one of the Gaspé bentonites (3854-1) contains prominent amounts of chromite, which should serve to distinguish it from the others (from which chromite was absent) over wide areas—probably over the whole area of deposition. Other features such as the character and relative abundance of zircon, apatite, feldspar and biotite are likely to be equally useful. The conclusion of Huff (1963) that no characteristic physical properties of the heavy minerals (of Ordovician K-bentonites from Kentucky) are consistently useful for stratigraphic correlation is most surprising and difficult to explain. If it is accepted that bentonites are derived from one fall of ash or even one batch of magma (and this is strongly indicated by the usual simplicity of heavy and light mineral suites), it is hard to see how significant variations can occur except either very near the explosion vent or gradational ones over very wide area. If marked local variations in the initial composition of a bentonite (ash fall) were common, it seems unlikely that any chemical or mineralogical feature would be of use in correlation. Slaughter & Earley's (1965) comprehensive study of the Cretaceous bentonites of Wyoming has conclusively shown that, in those bentonites at least—even where a bentonite is made up of several graded units—there are slight but distinct differences in the heavy minerals of the various bentonites, and that these permit identification. It may be possible, however, that elsewhere bentonites correlated on loose stratigraphic grounds do not always really belong to the same volcanic event. We can expect that the lateral extent of many bentonites may be quite limited covering only a few tens or a hundred or so square miles, as is the case with many pumice falls observed in areas of recent volcanicity. Such bentonites of smaller areal extent may have been carried by surface winds rather than by the higher altitude jet-stream winds postulated by Slaughter & Earley as the carriers of the ashes forming the Wyoming bentonites.

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