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# Miocene bentonites in the White Limestone Group, Jamaica

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Miocene bentonites in the White Limestone Group of Jamaica formed from volcanic ash that settled to the sea floor between 25 and 8.5 Ma. Trace element data, especially the Nb/Y ratios less than 0.5, suggest a subalkaline volcanic source, and the low Nb and Zr values suggest eruption from a volcanic arc setting. Similarities between the bentonites of the White Limestone Group and altered ash beds in ODP cores (Leg 165) suggest a source region in Central America, but variations between different ash beds suggest derivation from more than one volcanic centre during the Miocene.

KEY WORDS: White Limestone Group, bentonite, Miocene, Jamaica, volcanism.

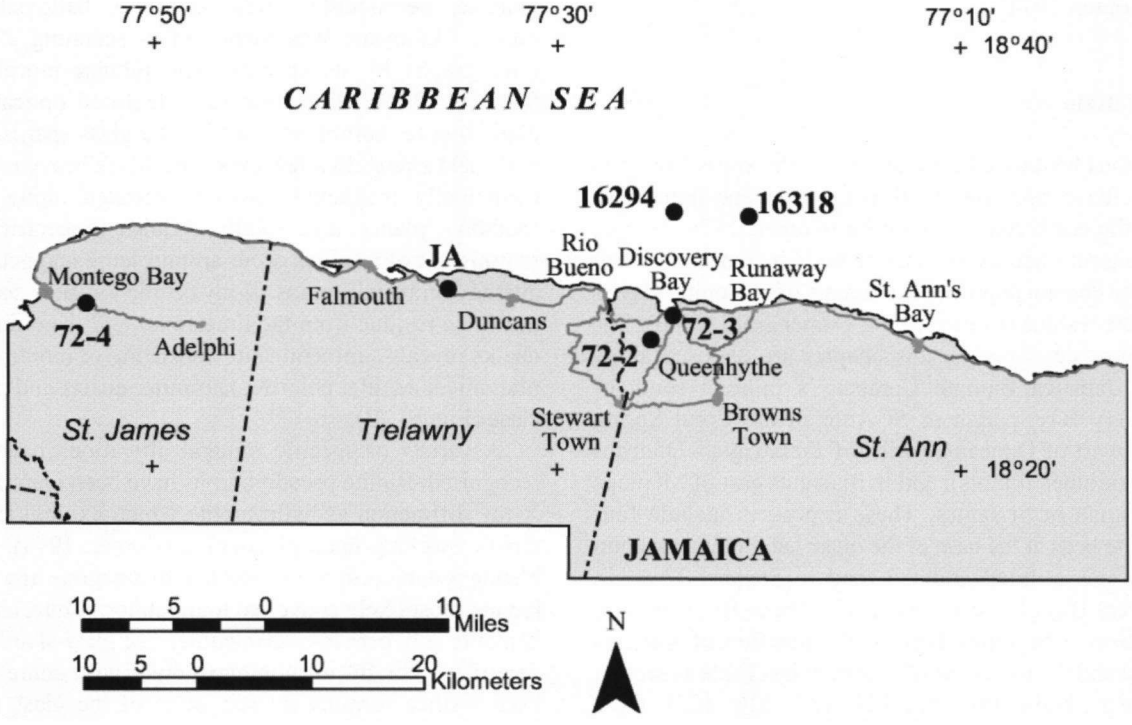


**Figure 1.** Map showing location of sections with Miocene bentonite.

## Introduction

The purpose of the present paper is to document the occurrence, composition, age and origin of Miocene bentonites in the Cainozoic White Limestone Group (Middle Eocene to Middle Miocene) of Jamaica. Much of the information summarised in this report has been presented in detail elsewhere (Comer, 1972, 1974, 1984; Comer *et al.*, 1980; Lyew-Ayee, 1986). However, the trace element data, and the discussion of their implications as to origin and source of the parent volcanic ash, are new.

The term bentonite is used in its 'classic' sense for

rocks composed predominantly of swelling clay (smectite) that formed by the alteration of volcanic ash. This clarification is necessary because bentonite has acquired a variety of different meanings over the years. The term bentonite was first introduced by Knight (1898) to describe a swelling, highly colloidal, plastic clay found in rocks of Cretaceous age in northern Wyoming, USA (Grim, 1968; Elzea & Murray, 1994). Hewett (1917) later showed that bentonite from the original site in Wyoming formed by the alteration of volcanic ash *in situ*. Many geologists continue to apply the term bentonite to rock composed mostly of a crystalline clay mineral formed by the chemical alteration of glassy volcanic material (Ross & Shannon, 1926). Other workers, particularly those who deal commercially in industrial mineral commodities, prefer a definition that is not based on genesis. Accordingly, Elzea & Murray (1994) defined bentonite as any clay consisting mostly of smectite minerals. This latter definition generalised the term bentonite to any rock composed predominantly of a clay mineral having an expandable 2:1 type silicate layer structure. In this paper we have adopted the definition of Ross & Shannon (1926) because the Miocene bentonites in Jamaica have been shown to originate by the chemical alteration of volcanic ash (Comer, 1974).

**Distribution**

Numerous bentonite beds, ranging in thickness from 5 to 15 cm, have been observed in the Miocene limestones along the north coast of Jamaica (Comer, 1974) (Figure 1). Bentonite occurs as discrete beds in limestones that typically contain appreciable amounts of bentonitic clay as insoluble residue (Comer, 1974; Comer *et al.*, 1980). The bentonites described in this chapter are exposed along Kaiser Jamaica Bauxite Company's railroad south of Discovery Bay, parish of St Ann; in the Coral Spring quarry west of Duncans, parish of Trelawny (= Duncans quarry of other authors); and in road cuts east of Montego Bay, parish of St James. These exposures include four bentonite beds at the base of the quarry at the first junction of Kaiser's railroad and the road to Stewart Town in Discovery Bay (Table 1: section 72-3; beds 107, 108, 119, 122), twelve bentonite beds at the junction of Kaiser's railroad and the road west of Queenhythe (Table 1: section 72-2; *e.g.*, beds 106, 105, 128, 127, 126, 125), three bentonite beds in the Coral Spring quarry (Table 1: section JA; beds JA605A, JA606, JA607), and two bentonite beds along the road to Adelphi east of Montego Bay (Table 1: section 72-4; beds 111, 112).

Bentonitic material similar to that found in exposed limestones also has been identified in unconsolidated Miocene chalk sampled by two piston cores (Table 1: sections 16318, 16294; beds 318, 294). The cores were retrieved from the axes of scoured submarine valleys that are entrenched into the steeply sloping Caribbean Sea floor on the south flank of the Cayman Trough (Comer, 1974). The white, unlithified chalk from these and three other piston cores was identified as Montpelier Formation (Miocene in age) by Edward Robinson (pers. comm. to L.S. Land, 1971) based on the analysis of microfossils. The five locations of unlithified Miocene chalk are in a 400 $km^2$ area extending from 5 km north of Discovery Bay to the east northeast approximately 50 km. In this area, the sea floor slopes northward from more than 1,500 m to 4,200 m below sea level (Land, 1979a, b).

**Mineralogy**

Mineralogy of the Miocene bentonites has been documented by X-ray diffraction, and both optical and scanning electron microscopy; details describing the methods and data along with representative photomicrographs are presented elsewhere (Comer, 1972, 1974; Comer *et al.*, 1980; Lyew-Ayee, 1986). The Miocene bentonite beds consist mainly of the clay mineral montmorillonite and commonly are mixed with variable amounts of calcite as disseminated matrix or as limestone clasts (Figure 2A). Some beds contain small, but recognisable, amounts of chlorite, vermiculite, mica, kaolinite, halloysite and quartz. Halloysite was identified in scanning electron micrographs by its characteristic tubular morphology (Comer, 1974). Minor minerals identified optically include biotite, hornblende, devitrified glass shards, magnetite and zircon. In a few exposures black heavy minerals (principally magnetite) are concentrated along crude 'bedding' planes, and, locally, reddish concentric halos reminiscent of pisolites occur around some magnetite and altered hornblende grains. X-ray diffraction analysis of the insoluble residue from the limestones and the unlithified chalks reveals a mineral suite consisting of montmorillonite, mica, zeolite, chlorite, kaolinite, quartz and plagioclase (Figure 2B).

A variety of specific mineral alterations have been recognised. Biotite pseudomorphs have been identified by X-ray diffraction as hydrobiotite which exhibits characteristic swelling upon glycolation (Comer, 1974). Hornblende pseudomorphs are soft and disintegrate at a touch, having most likely converted to montmorillonite, chlorite, hematite and, perhaps, vermiculite. The glass shards have devitrified chiefly to montmorillonite with some of the excess silica forming quartz; some of the glass shards observed in scanning electron micrographs have altered to imogolite (Comer, 1974).

Bentonite beds in the railroad cut west of Queenhythe (section 72-2) mostly are greenish yellow at the base of the section and red at the top, and a few individual bentonite layers in the middle of the section grade upward from greenish yellow to red. The red colour represents amorphous iron oxide produced by alteration of the iron-bearing minerals magnetite, hornblende and, perhaps, biotite.

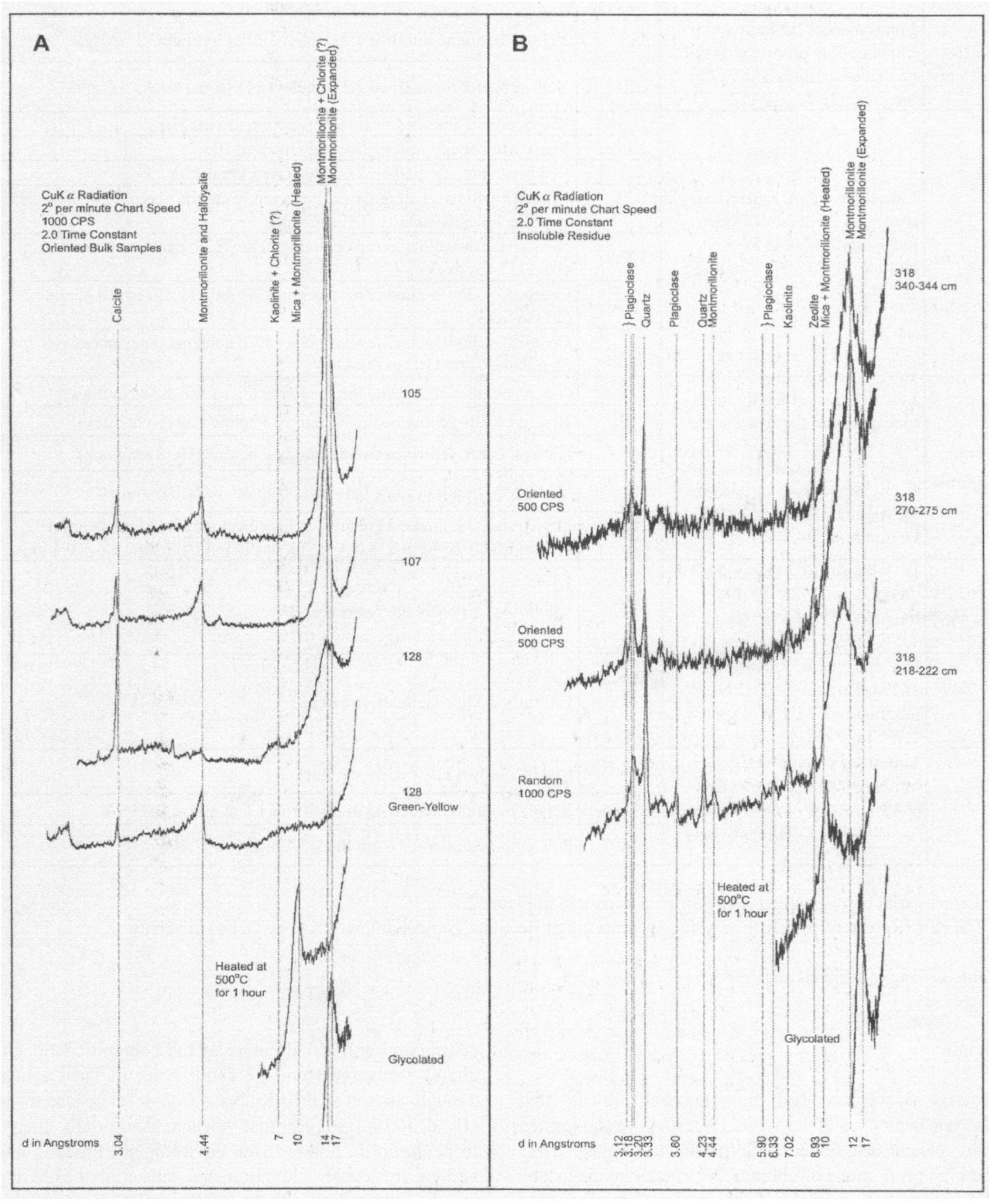


**Figure 2.** Representative X-ray diffraction patterns for Miocene bentonite; A -discrete bentonite beds; B - insoluble residue from unlithified Miocene (Montpelier) chalk.

The increase in redness is accompanied by a decrease in the abundance of altered biotite flakes and dark opaque minerals, and an increase in the sharpness and intensity of the 14 Angstrom peak, which most probably reflects an increase in the size and uniformity of the montmorillonite (Figure 2A, patterns 128 and 105). These changes may result from the increased effect of subaerial weathering upward in the section, including the oxidation of ferrous iron, the leaching of soluble cations (Mg, Ca, K, Na), and the growth and ordering of montmorillonite crystal lattices.

| Section | Location | Sample | Description |
|---|---|---|---|
| 72-4 (10 m) | Limestone cut 3.2 km west of Montego Bay on Adelphi road, St. James, latitude 18°27.7'N., longitude 77°53.3'W. | 111 | Yellow bentonite interbed 1.2 m above 112 (5 cm thick) |
| | | 112 | Yellow bentonite interbed 1.2 m below 111 (5 cm thick) |
| 72-2 (15 m) | Limestone cut on Kaiser Railroad ~1.5 km west of Queenhythe, northwestern St. Ann, latitude 18°26.1'N., longitude 77°25.3'W. | 106 | Red bentonite interbed near top of section (5 cm thick) |
| | | 104 | Marly Miocene limestone between 106 and 105 |
| | | 105* | Red bentonite interbed next below 104 (5 cm thick) |
| | | 128* | Greenish-yellow grading upward into red bentonite about 9 m below 105; contains limestone clasts (15 cm thick) |
| | | 127 | Next greenish-yellow to red bentonite below 128; contains limestone clasts (15 cm thick) |
| | | 126 | Greenish-yellow bentonite next below 127; only localized red alteration (15 cm thick) |
| | | 125 | Greenish-yellow bentonite next below 126; contains limestone clasts, but no red alteration (10 cm thick) |
| 72-3 (4 m) | Lowest bench in Kaiser limestone quarry at the first intersection of Kaiser Railroad and Discovery Bay-Stewart Town road in Discovery Bay, northwestern St. Ann, latitude 18°27.3'N., longitude 77°24.3'W. | 122 | Greenish-yellow bentonite interbed near top of bench (8 cm thick) |
| | | 119 | Next greenish-yellow bentonite interbed below 122 (8 cm thick) |
| | | 108 | Next greenish-yellow bentonite interbed below 119 (8 cm thick) |
| | | 103 | Marly Miocene limestone between bentonite beds 108 and 107 |
| | | 107* | Lowermost and thickest greenish-yellow bentonite interbed, below 103 (15 cm thick). K-Ar age: 8.6 ± 0.6 m.y.; Fission-track age: 8.6 ± 0.4 m.y. |
| 16318 (3.4 m) | R/V "Eastward"+ Station No. 16318, latitude 18°32.0'N., longitude 77°20.5'W. Depth 1,535 m | 318* | Unlithified Miocene marl, 30-344 cm |
| 16294 (1.3 m) | R/V "Eastward"+ Station No. 16294, latitude 18°32.2'N., longitude 77°24.2'W. Depth 1,735 m | 294 | Unlithified Miocene marl, 0-130 cm |
| JA | Limestone outcrop in Coral Spring quarry ~ 5 km west of Duncans, north-central Trelawny, latitude 18°28.5'N, longitude 77°35.4'W. | JA605A | Reddish brown interbed 10 cm thick |
| | | JA606 | Beige coloured interbed 4 cm thick and 1.6 m above JA605A |
| | | JA607 | Pink coloured interbed 4 cm thick 1.5 m above JA606 |

* Samples with corresponding X-ray diffraction pattern in Figure 2.
+ The R/V (Research Vessel) "Eastward" operated out of Beaufort, North Carolina USA, by Duke University.

**Table 1.** Sample locations and description.

## Origin

Mineral associations and grain textures indicate that Miocene bentonites of the White Limestone Group formed from volcanic ash. Euhedral biotite, abundant glass shards and high proportions of idiomorphic zircon are diagnostic of a volcanic ash origin, and the preservation of pristine crystal habits is indicative of direct air fall deposition with little or no subsequent resedimentation (Comer, 1974, 1984). In addition, montmorillonite, the major mineral constituent, is the commonest early alteration product of volcanic ash and zeolites, with few exceptions, are alteration products of volcanic materials. The fact that bentonite occurs in marine limestone indicates the volcanic ash was deposited on the sea floor. Furthermore, the deep sea floor setting and unlithified nature of the bentonitic Miocene chalks recovered from the south flank of the Cayman Trough, as well as their Sr, Na, $^{13}C$ and $^{18}O$ geochemistry (Land, 1979a), suggest that volcanic ash initially altered to bentonite in a submarine environment. Phreatic and vadose freshwater alteration and subaerial weathering mostly occurred after these marine rocks emerged from the sea. However, local resedimentation down the steep submarine slope may account for the breccia-like fabric of some bentonite layers. The red colour of some beds may have developed when volcanic ash deposited on nearby emergent parts of Jamaica experienced a period of subaerial weathering prior to being shed into the adjacent marine carbonate depositional environment.

| wt % | 1 | 2 |
|---|---|---|
| $SiO_2$ | 73.07 | 61.84 |
| $TiO_2$ | 0.16 | 0.44 |
| $Al_2O_3$ | 13.83 | 22.82 |
| $Fe_2O_3$ | 1.37 | 5.92 |
| MnO | 0.07 | 0.28 |
| MgO | 1.02 | 1.01 |
| CaO | 1.59 | 5.44 |
| $Na_2O$ | 3.07 | 1.06 |
| $K_2O$ | 5.39 | 0.48 |
| $P_2O_5$ | 0.04 | 0.74 |

1. Mean low Nb/Y Miocene ash from ODP Site 998, Leg 165. n=6
2. Mean Miocene bentonite from Jamaica. n=12

**Table 2.** Average major-element chemistry of (1) low Nb/Y Miocene ash from ODP Site 998 and (2) the Miocene bentonites of Jamaica (recalculated to volatile free).

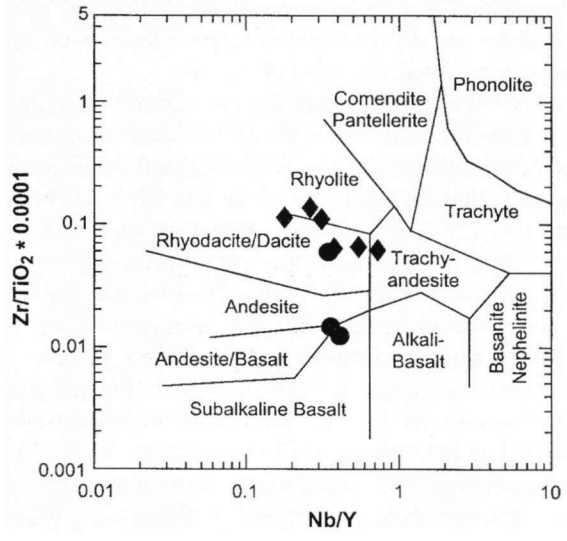


**Figure 3.** $Zr/TiO_2$-Nb/Y discrimination diagram after Winchester & Floyd (1977) showing plots of low Nb/Y ash beds from ODP Site 998 (closed diamonds) and Jamaican bentonites (closed circles).

## Chemistry

The bentonite beds contain an overall average concentration of approximately 62% $SiO_2$, 23% $Al_2O_3$, 6% $Fe_2O_3$ and 5% CaO (Table 2). Limestones that occur in the bentonitic interval contain an average of approximately 6% insoluble residue, 3% $SiO_2$, 1% $Al_2O_3$ and 0.5% $Fe_2O_3$ (Comer, 1974). Composition of the bentonitic limestones contrasts sharply with that of older non-bentonitic limestones in the White Limestone Group which contain an average of approximately 0.1% predominantly phosphatic insoluble residue, 0.03% $SiO_2$, 0.02% $P_2O_5$, 0.006% $Al_2O_3$ and 0.002% $Fe_2O_3$ (Comer, 1974).

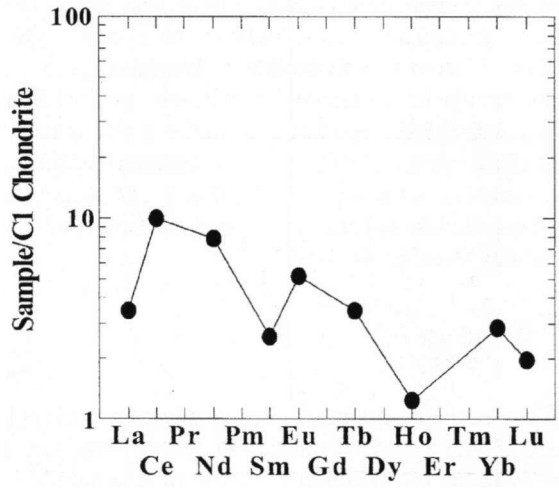


**Figure 4.** Chondrite-normalized REE pattern for Jamaican bentonite (JA605A). Analysis was determined via the semi-absolute method of neutron activation analysis using a SLOWPOKE reactor. All values are in ppm; La = 0.82, Ce = 6.1, Nd = 3.7, Sm = 0.39, Eu = 0.3, Tb = 0.13, Ho = 0.07, Yb = 0.48, Lu = 0.05.

| Sample No | JA605A | JA606 | JA607 |
|---|---|---|---|
| ppm | | | |
| Rb | 7 | 17 | 9 |
| Sr | 107 | 560 | 433 |
| Y | 7 | 8 | 16 |
| Zr | 104 | 30 | 96 |
| Nb | 3 | 3 | 6 |
| Th | 7 | 3 | 11 |
| Ga | 16 | 6 | 15 |
| Zn | 183 | 26 | 99 |
| Ni | 103 | - | 46 |
| wt% | | | |
| $SiO_2$ | 46.62 | 45.41 | 47.57 |
| $TiO_2$ | 0.91 | 0.21 | 0.17 |

**Table 3.** Trace element chemistry (in ppm) of bentonite beds in the Montpelier Formation, Coral Spring quarry, near Duncans, parish of Trelawny (Table 1, section JA). The trace elements were analyzed by X-ray fluorescence (XRF) spectrometry using pressed powder pellets. Major elements were determined by XRF spectrometry using fusion beads.

The trace elements, particularly those that are deemed to be immobile (Winchester & Floyd, 1977), provide useful information on the original source of volcanogenic clays. Spears & Duff (1984) and Huff *et al.* (1993) have successfully used immobile elements, especially Zr, Nb, Y and $TiO_2$, in tracing the original composition of bentonites. The Nb/Y ratios for the Jamaican bentonites (Table 3) are all less than 1.0 and, indeed, are below 0.5, which

indicates a subalkaline volcanic source, and when plotted versus the $Zr/TiO_2$ ratios, indicate rock compositions ranging from subalkaline basalt/andesite to dacite/rhyodacite (Figure 3). Furthermore, the low Zr and Nb values, and the chondrite-normalised rare earth element (REE) pattern, which shows enrichment of the light REEs relative to the heavy REEs (Figure 4), suggest that these subalkaline volcanics were erupted from a volcanic arc setting (Leat *et al.*, 1986).

## Age

The age range of the bentonites is interpreted to be between 25 and 8.5 Ma (Comer *et al.*, 1980). The younger limit is based on radiometric dating of a bentonite bed near the base of the youngest section studied during this investigation (Table 1; bed 107). Zircon concentrated from this bed gave a composite fission-track age of 8.6 + 0.4 Ma and K-Ar analysis of hydrobiotite from the same bed yielded an age of 8.6 + 0.6 Ma (Comer *et al.*, 1980). The radiometric age has confirmed that the bentonites in this section are Late Miocene (Tortonian), which would place them in the Coastal Group. The older age limit is based on fission-track analysis of zircon from bauxite and terra rossa, deposits that are interpreted to be subaerial facies equivalents of bentonite (Comer, 1974, 1984; Comer *et al.*, 1980). Zircon grains younger than 25 Ma are predominantly idiomorphic and thus indicate direct air fall deposition with volcanic ash, whereas zircon grains older than 25 Ma are mostly broken and angular, reflecting a complex history of recycling from older rocks (Comer, 1984).

## Source

The source of the Miocene volcanic ash was originally thought to be eruptive centres located along the Caribbean Plate boundary in the Cayman Trough and in central Hispaniola, north and east of Jamaica, respectively, with the ash being transported by the northeast trade winds (Comer, 1972; Lyew-Ayee, 1986). However, the trace element data in this paper suggest that the source of the ash may have been a volcanic arc region to the west of Jamaica, rather than the volcanic centres associated with extension.

Numerous Miocene volcanic ash and altered ash beds have been identified in cores recovered from the Ocean Drilling Program (ODP) Leg 165 in 1995-1996. These ash beds were identified from Sites 998, 999 and 1000, located relatively close to Jamaica, and have been described as generally silicic in composition. They represent major Miocene eruptive events that began 20-22 Ma and ended around 11 Ma. Based on the dispersal patterns, the source region is postulated to be in Central America (Sigurdsson *et al.*, 1997), thus implying eastward transport, a feature that is not unusual in the eruptions of present day volcanoes from that region where ash, transported in the upper troposphere, travels in the opposite direction to the trade winds. For example, McClelland *et al.* (1989) have described tephra clouds and plumes from satellite images that extended as far east as Haiti during the eruption of El Chichón, Mexico, in March 1982.

Analyses from Site 998, located on the Cayman Ridge, for which there are radiometric dates, show that there are similarities in the composition of several of these altered ash beds and the bentonites of the White Limestone Group (Figure 3). This is very evident in the trace-element chemistry of those ashes that were deposited during the period between 21.2 and 10.3 Ma, which have Nb/Y ratios less than 1. Ash beds of similar composition, but undated, have also been identified at Sites 999 and 1000. These ash beds have been divided into two distinct groups (Sigurdsson *et al.*, 1997), one of which has similarities to the Jamaican bentonites (Nb/Y<1) and another of which has Nb/Y ratios that are much greater than 1. Sigurdsson *et al.* (1997) regarded the two groups as being rhyolitic in composition, but speculated that the differences in geochemistry are either related to variable sources or minor post-depositional alteration of the ash.

The Miocene bentonites from the Coral Spring quarry near Duncans occur within the Lower Miocene sections of the deep water Montpelier Formation and are interpreted to fall within the age range of the low Nb/Y ash beds of Site 998 (21.2 to 10.3 Ma). However, there are some significant differences in the weight percentages of the major-element chemistry (Table 2) which may be due to post-depositional alteration. The alteration of volcanic glass to smectite through a combination of processes including ion exchange, diffusion, hydration and oxidation can account for the mobility of Si and the alkalis (Christidis & Dunham, 1993; Jeans *et al.*, 2000). In the Jamaican bentonites Si and the alkalis may similarly have been leached from the original volcanic ash, whereas $Fe_2O_3$ and CaO may have become more concentrated (Table 2). The higher values of calcium and iron in the Jamaican bentonites are attributed to the presence of calcite- and iron-bearing minerals.

Differences may also be attributed to a greater variation in the original magma composition of the Miocene ash falls over Jamaica compared to ODP samples, in that the data from the Coral Spring quarry indicate a variation in ash composition from basalt/andesite to dacite/-rhyodacite, whereas the ODP low Nb/Y ashes appear to be mostly silicic (Figure 3). Therefore, it is highly probable that the ash that formed the bentonites in the White Limestone Group originated from more than one volcanic centre during the Early to Middle Miocene. Numerous volcanic events are known to have existed and are illustrated in a palaeogeographic reconstruction of the Caribbean in the Miocene by Pindell (1994). This reconstruction shows volcanic arc activity extending along the Chortis block as well as the Sierra Madre Occidental

volcanic province where magma varied in composition from basalt to rhyolite (Donnelly *et al.*, 1990; Moore *et al.*, 1994).

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