

## CLAY PETROLOGY OF CAMBRO-ORDOVICIAN CONTINENTAL MARGIN, COW HEAD KLIPPE, WESTERN NEWFOUNDLAND

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**Abstract**—The sedimentary rocks of the Taconic Cow Head klippe contain three clay-mineral suites of progressively younger stratigraphic occurrence. An illite-14A chlorite suite is the oldest, occurring in the Middle Cambrian to early Lower Ordovician part of the 310-m Cow Head Breccia. These earliest clays were transported from the stable craton and shelf, slowly accumulating during  $70 \times 10^6$  yr on the continental slope in limestone breccia, green and gray shale, and argillaceous limestone. The illite and 14A chlorite are judged to be largely detrital. An illite-expandable chlorite suite is in early to late Lower Ordovician limestone breccia, green and gray shale, and argillaceous limestone of the Cow Head Breccia. A corrensite-illite-smectite suite of late Lower to Middle Ordovician age occurs in the Cow Head Breccia and throughout the overlying 200-m 'Red Shale' and the more than 400-m 'Green Sandstone' flysch sequence of volcanogenic sandstone and gray shale. Beginning in the early Lower Ordovician, increasing amounts of  $Mg^{2+}$ -rich volcanic detritus were rapidly transported westward from a developing volcanic island arc in central Newfoundland. During burial metamorphism, volcanic materials and their alteration products reacted to form the illite-smectite with 5–10% expandable layers plus corrensite or expandable chlorite found in the younger two clay-mineral suites.

### INTRODUCTION

This report presents the clay petrology of the Middle Cambrian to Middle Ordovician rocks in the Cow Head klippe in western Newfoundland (Figure 1). The klippe sequence consists of the Cow Head Breccia of Middle Cambrian to late Lower Ordovician age and the overlying Middle Ordovician 'Red shale' and 'Green Sandstone' flysch. The rocks accumulated on the western margin of the early Paleozoic Iapetus Ocean that lay between the North American and Baltic shields. The depositional site was in a carbonate belt at low paleolatitude.

The 310-m thick Cow Head Breccia is characterized by mass-flow limestone breccia, green and gray shale, calcarenite, and argillaceous limestone (Figure 1). There are small amounts of quartzose sandstone, yellow siltstone, gray marl and radiolarian-sponge spicule chert. These strata slowly accumulated on the stable continental slope for  $70 \times 10^6$  yr. As the Iapetus Ocean narrowed in the Middle Ordovician, the continental margin rapidly subsided, leading to deposition of 200 m of red shale in deeper water, followed by accumulation of more than 400 m of volcanogenic sandstone and gray shale in a flysch basin.

The autochthonous sequence beneath the klippe begins with the Precambrian basement which is overlain by the 1200-m Lower Cambrian Labrador Group composed of continental shelf sandstone, limestone and dolostone, the Lower Ordovician St. George

Dolomite, and the Middle Ordovician Table Head Limestone. Then follows 10 m of Middle Ordovician black shale and at least 100 m volcanogenic 'Green Sandstone' flysch.

As the Iapetus Ocean narrowed in the Middle Ordovician to create the Taconic Orogeny, the Cow Head klippe slide northwest down the paleoslope within the 'Green Sandstone' flysch basin (Hubert *et al.*, 1977). The klippe is a single structural slice resting on the autochthonous shelf sequence.

During the Middle Devonian Acadian orogeny, the autochthonous and klippe rocks were folded into major anticlines and synclines that resulted from drag on reverse faults in the klippe that strike parallel to the major reverse faults along the western margin of the Precambrian core of the Long Range Mountains. These faults and associated folds are the westernmost expression of the Acadian Orogeny, the effects of which are more intense in central Newfoundland where folding, intrusion and metamorphism occurred (Williams *et al.*, 1973). Metamorphic grade decreases westward, and the limestones in the Cow Head Breccia show no evidence of regional metamorphism and the shales throughout the klippe lack slaty cleavage.

### LABORATORY TECHNIQUES

The bulk chemical composition of the  $< 2 \mu\text{m}$  silicate fraction was determined for 34 samples that

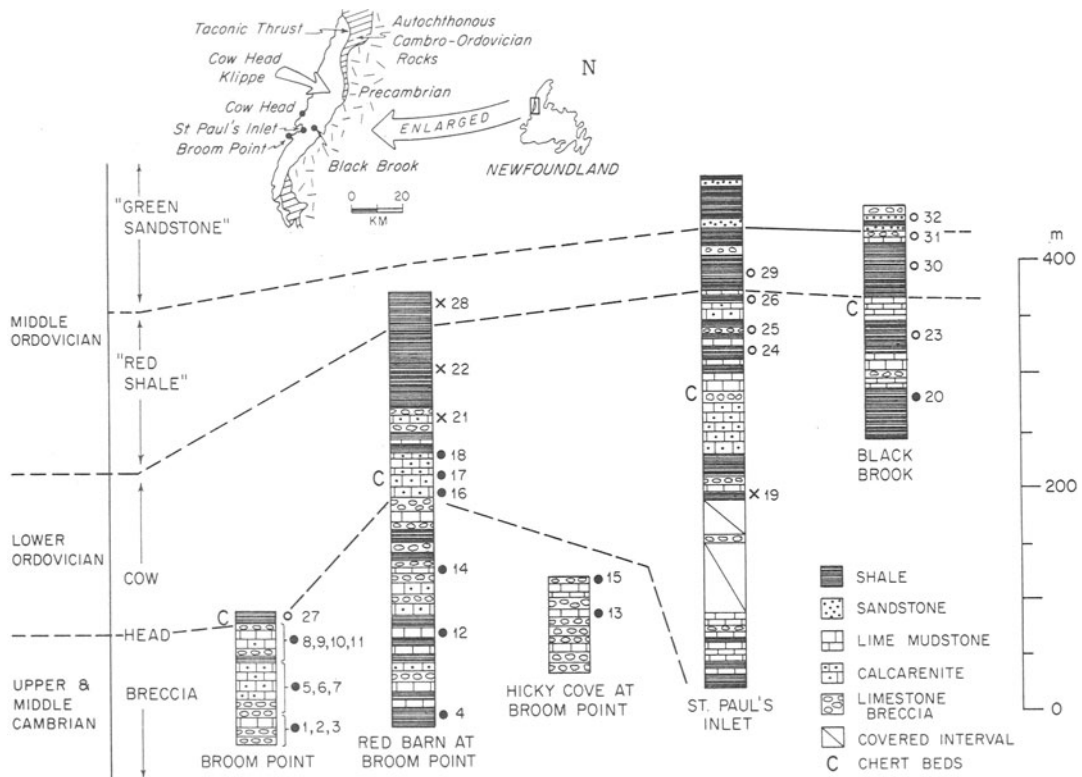


Fig. 1. Index map and stratigraphy of the Cow Head klippe. The location and number of each sample is shown by ● (illite-14A chlorite suite), × (illite-expandable chlorite suite), or ○ (corrensite-illite-smectite suite). Kindle and Whittington (1958, 1959) established the age relations using trilobite and graptolite biozones.

cover all the stratigraphic and lithologic varieties in the Cow Head klippe. They were collected at well-exposed sections at Broom Point, Inner Tickle of St. Paul's Inlet and Black Brook (Figure 1; Table 1). The composition of the clay-minerals of these 34 samples plus 11 other specimens were analyzed by X-ray powder diffraction (XRD).

Each sample was crushed into approximately 2–5-mm pieces and wet-sieved with distilled water to remove clay-sized particles artificially generated during crushing. The washed material was treated with a NaOAc–HOAc solution, buffered to a pH of 5.0, to remove carbonate (Jackson, 1966), and then ultrasonically disaggregated. The resulting bulk silicate fraction was washed in distilled water and separated into the <1- and >1- $\mu\text{m}$  fractions by repeated centrifugal sedimentation in distilled water. Oriented specimens of the <1- $\mu\text{m}$  fraction were prepared by centrifugal sedimentation on to porous ceramic tiles for XRD analysis (Kinter and Diamond, 1956). Relative peak intensities were calculated on ethylene-glycol solvated specimens. Air-dried oriented specimens were heated for 1 hr at 350 and 550°C for XRD analysis. Portions of the <1- $\mu\text{m}$  fraction were treated with 1 N HCl to determine the presence or absence of kaolinite, and 1 N  $\text{MgCl}_2$  and glycerol to determine the interlayer charge characteristics of the corrensite (Walker, 1961). The proportion of smectite layers in

the illite-smectites were determined by the methods of Reynolds and Hower (1970).

Chemical analyses were performed on washed <2- $\mu\text{m}$  silicate fractions by X-ray fluorescence (XRF) techniques. Loss on ignition was measured by heating the ground sample at 950°C. The ignited sample was then mixed and fused at 950°C with a 1:1 dilution of  $\text{Li}_2\text{B}_4\text{O}_7$ . The resulting glass bead was fractured and fragments were mounted in epoxy resin and polished for XRF analysis on an automated ETEC electron microprobe with a 20- $\mu\text{m}$  beam diameter. Each analysis reported represents an average of five individual analyses of the same glass bead. Matrix correction was performed by Bence-Albee computer iterative calculation.

#### CLAY-MINERALOGY PETROLOGY

The clay minerals in the rocks of the Cow Head klippe are illite, mixed-layer illite-smectite, 14A chlorite, expandable chlorite and corrensite. Kaolinite was not detected in any of the samples. They occur in three clay-mineral suites named for the dominant clay minerals. The suites are (1) illite-14A chlorite; (2) illite-expandable chlorite; and (3) corrensite-illite-smectite (Figure 2).

Table 1. Samples analyzed by XRD and XRF

Age	Sample No.	Suite	Location	Lithology
Middle Ordovician	32	3	Black Brook	Green sandstone
	31	3	Black Brook	Red shale
	30	3	Black Brook	Red shale
	29	3	St. Paul's Inlet	Red shale
	28	2	Broom Point	Red shale
Late Lower Ordovician	27	3	Broom Point	Green shale
	26	3	St. Paul's Inlet	Green shale
	25	3	St. Paul's Inlet	Clay matrix of breccia
	24	3	St. Paul's Inlet	Clay matrix of breccia
	23	3	Black Brook	Green shale
	22	2	Broom Point	Green shale
	21	2	Broom Point	Lime mudstone with black shale laminae
	20	1	Black Brook	Gray shale
Early Lower Ordovician	19	2	St. Paul's Inlet	Lime mudstone with green shale laminae
	18	1	Broom Point	Dolostone with gray shale laminae
	17	1	Broom Point	Gray shale
	16	1	Broom Point	Lime mudstone with gray shale laminae
Upper Cambrian	15	1	Broom Point	Clay matrix of breccia
	14	1	Broom Point	Lime mudstone with gray shale laminae
	13	1	Broom Point	Lime mudstone with green shale laminae
	12	1	Broom Point	Lime mudstone with green shale laminae
	11	1	Broom Point	Lime grainstone with gray shale
	10	1	Broom Point	Clay matrix of breccia
	9	1	Broom Point	Clay matrix of breccia
	8	1	Broom Point	Clay matrix of breccia
	7	1	Broom Point	Clay matrix of breccia
	6	1	Broom Point	Lime mudstone with gray shale laminae
	5	1	Broom Point	Lime mudstone with gray shale laminae
	4	1	Broom Point	Gray shale
	3	1	Broom Point	Lime mudstone with gray shale laminae
Middle Cambrian	2	1	Broom Point	Clay matrix of breccia
	1	1	Broom Point	Lime mudstone with gray shale laminae

The samples are in chronological order from oldest (1) to youngest (32). Clay-mineral suites are illite-chlorite (1), illite-expandable chlorite (2), and corrensite-illite-smectite (3). Cow Head Breccia: samples 1-27. 'Red Shale': samples 28-31. 'Green Sandstone' flysch: sample 32.

#### Illite-14A chlorite suite

**Clay minerals.** The oldest suite occurs in green and gray shale, argillaceous limestone and limestone breccia in the Middle Cambrian to late Lower Ordovician part of the Cow Head Breccia. The suite consists of illite with subordinate 14A chlorite plus traces of mixed-layer illite-smectite with 5-10% expandable layers. Corrensite was not detected on the XRD patterns.

Illite was identified by characteristic XRD peaks at 10 and 5 Å that remain unmodified after ethylene-glycol solvation. The proportions of 1Md and 2M polytypes of illite were determined by XRD of non-oriented clay mounts using the method of Velde and Hower (1963). The ratios of 2M/(2M + 1Md) in the illite-14A chlorite suite suggest that about three-quarters of the illite is detrital, high-temperature mica (2M polytype).

The chlorite phase was identified by the characteristic (001) 14 Å peak and its higher order XRD peaks. It is judged to be mostly detrital chlorite by the position of the 14 Å peak which is not modified by heat-treatment or ethylene-glycol solvation, and by

its association with abundant 2M mica. In a few samples 14.2-14.4 Å peak shifted to >15 Å after ethylene-glycol solvation, suggesting minor amounts of additional expandable chlorite phase. This phase

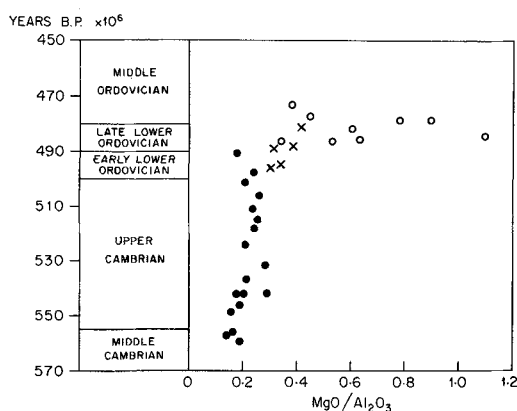


Fig. 2. Scatter diagram of  $MgO/Al_2O_3$  ratio of the  $<2\text{-}\mu\text{m}$  silicate fraction plotted against age. Samples are a ● (illite-14A chlorite suite), × (illite-expandable chlorite suite) or ○ (corrensite-illite-smectite suite).

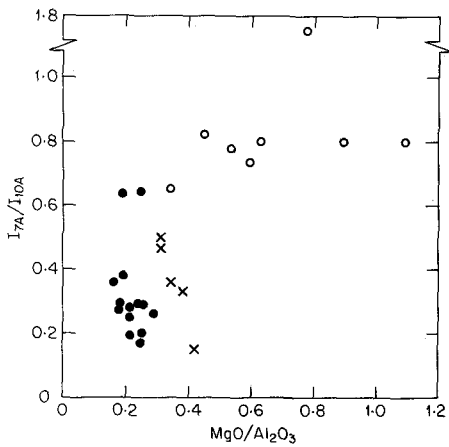


Fig. 3. Scatter diagram of  $MgO/Al_2O_3$  ratio for the  $<2\text{-}\mu\text{m}$  silicate fraction plotted against the  $I_{7A}/I_{10A}$  peak ratio of each sample. Symbols for the clay-mineral suites as in Figure 2.

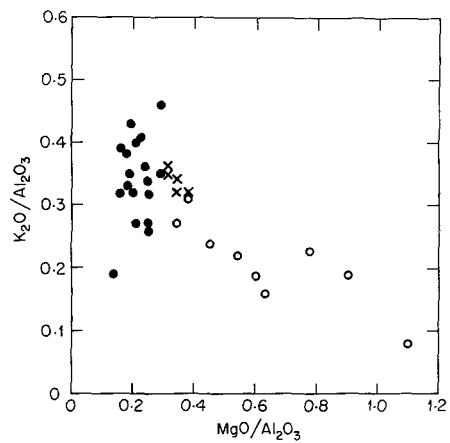


Fig. 4. Scatter diagram of  $MgO/Al_2O_3$  ratio plotted against  $K_2O/Al_2O_3$  ratio for the  $<2\text{-}\mu\text{m}$  silicate fraction of each sample. Symbols for clay-mineral suites as in Figure 2.

could be a mixed-layer chlorite-expandable layer clay, where the expandable layer consists of  $Mg^{2+}$ -deficient interlayers incorporated into the chlorite structure (MacEwan *et al.*, 1961). In this paper, the

term expandable chlorite is used for mixed-layered chlorites which do not exhibit the low-angle superlattice peak characteristic of an ordered mixed-layer chlorite (corrensite).

Table 2. Chemical analyses of  $<2\text{-}\mu\text{m}$  silicate fraction in wt % of oxides. See Table 1 for stratigraphic formation, clay-mineral suite, location, and lithology

Age	Sample no.	Fe <sub>2</sub> O <sub>3</sub>	MnO	TiO <sub>2</sub>	CaO	K <sub>2</sub> O	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	Loss on ignition
Middle Ordovician	32	5.78	0.12	0.92	0.11	4.90	58.40	15.79	6.14	0.41	7.44
	31	8.22	0.15	0.78	0.02	1.94	68.94	8.20	3.72	0.79	7.24
	30	6.07	0.12	0.59	0.13	2.40	55.78	12.69	11.48	0.40	10.34
	29	5.42	0.08	0.96	0.08	1.49	71.53	8.00	4.81	0.56	7.07
	28	8.38	0.05	0.93	0.07	4.87	55.76	15.38	6.50	0.27	7.79
Late Lower Ordovician	27	14.92	0.05	0.79	0.06	2.71	52.88	11.73	9.17	0.22	7.48
	26	5.43	0.03	0.62	0.04	0.58	67.30	7.66	8.43	0.31	9.60
	25	5.91	0.04	0.60	0.12	1.99	61.69	12.08	7.65	0.35	9.57
	24	4.61	0.08	0.74	0.10	2.82	61.77	12.56	6.78	1.13	9.41
	23	6.45	0.07	0.92	0.32	4.47	56.31	16.37	5.54	0.58	8.97
	22	11.40	0.16	1.12	0.13	4.47	56.00	13.83	5.24	0.16	7.49
	21	4.05	0.02	0.69	0.05	3.19	75.61	8.86	2.75	0.21	4.57
	20	6.85	0.02	1.12	0.20	6.21	56.22	17.14	3.08	0.21	8.84
Early Lower Ordovician	19	4.58	0.03	1.27	0.09	5.83	56.55	16.45	5.11	0.28	9.81
	18	10.96	0.02	1.37	0.03	5.37	50.98	15.65	5.30	0.19	10.12
	17	3.56	0.06	1.24	0.14	6.16	57.74	16.97	4.08	0.57	9.48
	16	4.45	0.11	1.03	0.20	6.60	59.66	16.62	3.46	0.48	7.38
Upper Cambrian	15	6.79	0.04	1.22	0.23	5.28	57.29	16.47	4.13	0.21	8.34
	14	10.75	0.06	0.93	0.07	4.04	54.68	15.44	3.89	0.70	9.44
	13	5.33	0.04	1.02	0.10	4.66	58.07	17.24	4.27	0.37	8.90
	12	6.92	0.12	1.07	0.06	5.95	54.76	17.66	4.40	0.72	8.34
	11	7.21	0.08	1.08	0.12	6.22	58.40	15.47	3.30	0.18	7.94
	10	7.74	0.03	0.81	0.94	5.32	54.81	15.35	2.80	0.18	12.01
	9	6.86	0.01	0.79	0.84	4.54	55.24	16.87	3.49	0.25	11.11
	8	9.23	0.13	1.07	0.13	5.10	55.98	15.83	3.18	0.16	9.17
	7	13.62	0.08	1.08	0.65	6.06	49.90	16.06	2.87	0.21	9.47
	6	7.50	0.08	1.08	0.20	7.73	55.11	16.87	4.44	0.23	7.54
	5	7.14	0.04	1.12	0.10	6.13	55.25	17.59	3.38	0.18	9.07
4	1.70	0.07	0.64	0.06	3.52	73.09	11.02	1.79	0.81	7.31	
3	7.80	0.12	0.92	0.13	6.16	54.25	15.98	2.60	0.17	11.81	
Middle Cambrian	2	10.91	0.06	1.05	0.33	3.64	46.34	19.47	2.78	0.55	14.72
	1	8.99	0.04	1.14	0.10	6.74	54.54	16.25	3.06	0.25	8.67

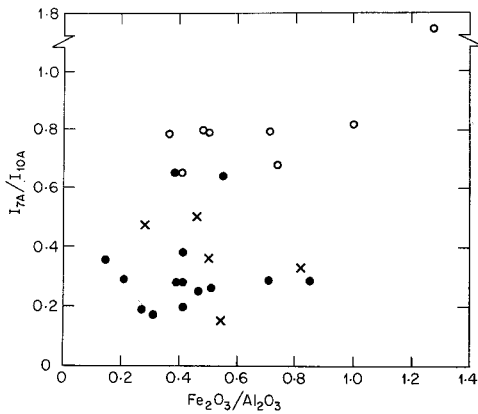


Fig. 5. Scatter diagram of  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$  ratio of the  $<2\text{-}\mu\text{m}$  silicate fraction plotted against  $I_{7A}/I_{10A}$  peak ratio of each sample. Symbols for clay-mineral suites as in Figure 2.

**Bulk chemical composition of the  $<2\text{-}\mu\text{m}$  silicate fraction.** The samples of the detrital illite–A14A suite are distinguished from the illite–expandable chlorite suite and the corrensite–illite–smectite suite by relatively low ratios of  $\text{MgO}/\text{Al}_2\text{O}_3$  and high ratios of  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  (Figures 3, 4; Table 2). These ratios reflect the relatively greater abundance of illite in the illite–14A chlorite suite. The relative proportions of illite and 14A chlorite in the illite–14A chlorite suite are shown by the ratio of  $I_{7A}/I_{10A}$ ; most samples are relatively rich in illite (Figure 3).

The  $\text{MgO}/\text{Al}_2\text{O}_3$  ratios for the illite–14A chlorite suite vary from 0.14 to 0.29 (Figure 3); a narrow range of relatively low values maintained for  $70 \times 10^6$  yr from Middle Cambrian through early Lower Ordovician.

For the three clay-mineral suites, there is an inverse relationship between  $\text{MgO}/\text{Al}_2\text{O}_3$  and  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ , because the illite–14A chlorite suite is rich in  $\text{K}^+$  whereas the corrensite–illite–smectite suite is rich in  $\text{Mg}^{2+}$  and the illite–expandable chlorite suite is of intermediate composition (Figure 4). The abundant illite and high  $\text{K}_2\text{O}$  values are related to a continental weathering provenance whereas the higher  $\text{MgO}$  values are indicative of a volcanic influence.

The illite–14A chlorite and illite–expandable chlorite suites have lower  $I_{7A}/I_{10A}$  ratios than the corrensite–illite–smectite suite, but the three suites show nearly complete overlap in  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$  ratios (Figure 5). The lack of correlation of clay-mineral suites with amount of  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$  in the bulk composition of the  $<2\text{-}\mu\text{m}$  silicate fraction is probably due to ferric oxide surface coatings on clays of the red shales and contamination by pyrite in gray and green shales.

#### Illite–expandable chlorite suite

**Clay minerals.** This suite contains major amounts of illite, 14A chlorite, and expandable chlorite plus lesser amounts of illite–smectite with 5–10% expandable layers. The suite is stratigraphically restricted to

limestone breccia, green and gray shale and argillaceous limestone in the early and late Lower Ordovician part of the Cow Head Breccia and to the lower part of the Middle Ordovician 'Red Shale'.

The expandable chlorite has a 14 Å peak that shifts to 14.4–15 Å after ethylene-glycol solvation and the 7 Å peak shows a definite broadening to the low-angle (higher  $d$ -spacing) side (Figure 6). The expandable chlorite phase does not exhibit the low-angle superlattice peak that would be indicative of corrensite. Either the mixed-layering in the chlorite phase is truly random, or alternatively, the mixed-layered phase is indeed corrensite. Perhaps we cannot detect a low-angle superlattice peak due to the much lower abundance of the mixed-layered chlorite phase in the illite–expandable chlorite suite as compared to the corrensite–illite–smectite suite. Intuitively, we suspect that the mixed-layer chlorite phase may be a corrensite that is present in relatively minor amounts.

**Bulk chemical composition of the  $<2\text{-}\mu\text{m}$  silicate fraction.** The  $\text{MgO}/\text{Al}_2\text{O}_3$  ratios for the illite–expandable chlorite suite vary from 0.31 to 0.42, a narrow range between lower values of the illite–14A chlorite suite and higher values of the corrensite–illite–smectite suite (Figure 3).

The ratios of  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ , and  $I_{7A}/I_{10A}$  in the illite–expandable chlorite suite are similar to those of the illite–14A chlorite suite, but the illite–expandable chlorite suite has consistently higher ratios of  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  and lower ratios of  $I_{7A}/I_{10A}$  than the corrensite–illite–smectite suite (Figures 3, 4).

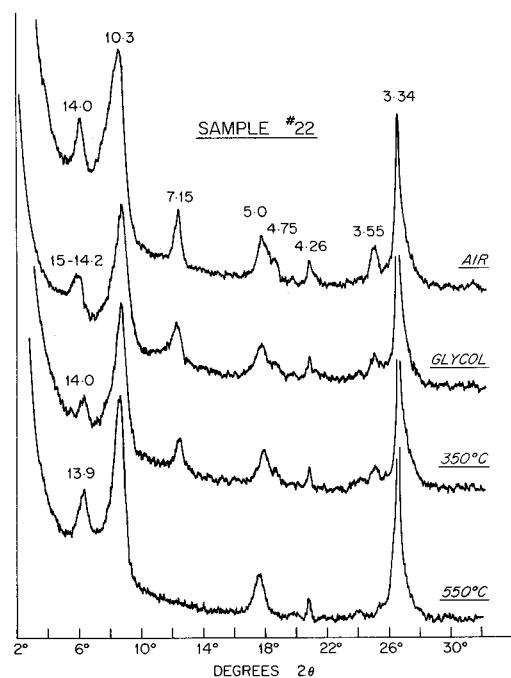


Fig. 6. Representative XRD patterns for the illite–expandable chlorite suite using oriented  $<1\text{-}\mu\text{m}$  clay mounts and  $\text{CuK}_\alpha$  radiation.



*Corrensite-illite-smectite suite*

**Clay minerals.** The suite is defined by the presence of abundant corrensite in every sample. Also abundant is an illite-smectite with 5–10% expandable layers. Discrete illite and 14A chlorite phases were not positively identified, perhaps because their concentration in the sample is too low for detection.

Abundant corrensite occurs only in late Lower to Middle Ordovician rocks. These include thin-bedded green and gray shale, argillaceous limestone, and limestone breccia of continental-slope facies in the upper part of the Cow Head Breccia and occurrences in the overlying deeper water 'Red Shale' and gray shale and volcanogenic sandstone of the 'Green Sandstone' flysch.

Corrensite is a trioctahedral  $Mg^{2+}$ -rich clay composed of an ordered 1 : 1 interstratification of chlorite and smectite where  $Fe^{2+}$  can substitute in trioctahedral positions and in the brucite interlayers of chlorite (Early *et al.*, 1956; Kubler, 1973). The corrensite was identified by the strong 31–32 Å superlattice reflection after ethylene-glycol solvation, together with shifting of the (002) peak from 14.6–14.9 to 15.4–15.8 Å due to the rational series of reflections of paired 14 Å and 17 Å units (Figure 7). The remaining higher order reflections change correspondingly. The corrensite identified in this study is a mixed-layer chlorite-smectite (Early *et al.*, 1956) rather than the mixed-layered chlorite-vermiculite (Bradley and Weaver, 1956). Upon Mg-saturation and glycerol solvation, expansion of the interlayer sites still occurs, indicating a low-charge, smectite-type expandable layer rather than a high-charge vermiculite-type layer.

Kaolinite is absent; no 7 Å peaks remain following treatment by 1 N HCl.

The amount of illite and illite-smectite in the corrensite-illite-smectite suite is consistently much less than in the illite-14A chlorite suite. The corrensite-illite-smectite suite in the younger rocks contains less of the illite, but two-thirds of the illite is of low-temperature, diagenetic origin (1Md polytype), whereas the older illite-14A chlorite suite has much more of

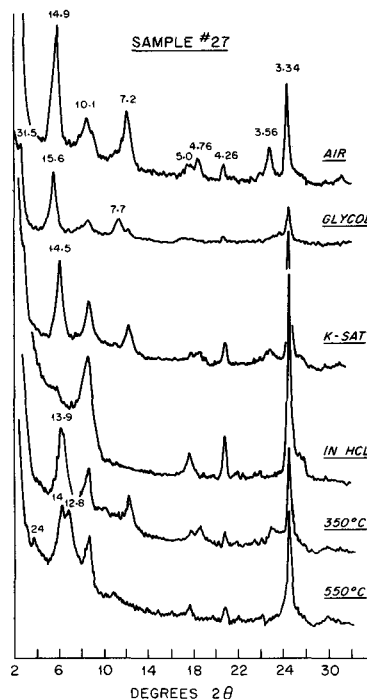


Fig. 7. Representative XRD patterns for the corrensite-illite-smectite suite using oriented <1-µm clay mounts and  $CuK_{\alpha}$  radiation.

the illite phase, but three-quarters is of detrital, high-temperature origin (2M polytype).

**Bulk chemical composition of the <2-µm silicate fraction.** The distinguishing chemical feature of the corrensite-illite-smectite suite of late Lower and Middle Ordovician age is that it is much richer in  $Mg^{2+}$  than the two older suites (Figure 2). Correspondingly, the  $K_2O/Al_2O_3$  ratios are lower (Figure 4), and the  $I_{7A}/I_{10A}$  ratios are higher (Figure 3).

**DISCUSSION**

*Stratigraphic control of clay-mineral suites*

The clay minerals are mostly illite and 14A chlorite in the gray and green shale, argillaceous limestone

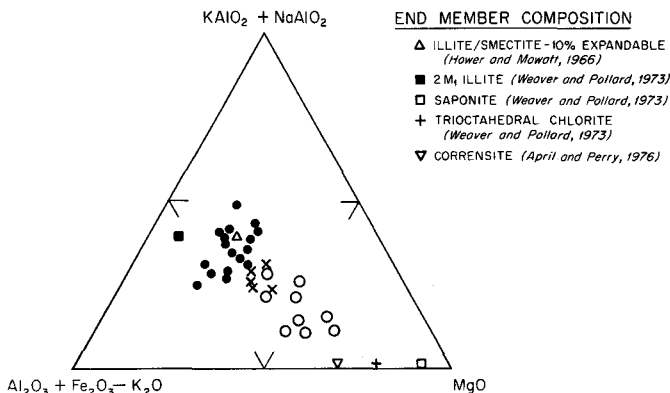


Fig. 8. Chemical composition of the <2-µm silicate fraction plotted in the system  $(KAIO_2 + NaAlO_2) - (Al_2O_3 + Fe_2O_3 - K_2O) - MgO$ . Symbols for the Cow Head claymineral suites as in Fig. 2.

and limestone breccia of Middle Cambrian through early Lower Ordovician age in the Cow Head Breccia. About two-thirds of the illite is the high-temperature polytype. The bulk chemical composition of the < 2- $\mu\text{m}$  fraction has relatively high  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  ratios and low  $\text{MgO}/\text{Al}_2\text{O}_3$  ratios. The clay petrology and chemistry reflect slow accumulation on the stable continental slope of weathered terrigenous clay (high  $\text{K}_2\text{O}$ , low  $\text{MgO}$ ) from the North American craton and shelf.

Concomitant with narrowing and subduction of the oceanic crust along the western margin of the Iapetus Ocean in the Lower Ordovician, a volcanic island arc rapidly developed in central Newfoundland (Williams *et al.*, 1973; Hubert *et al.*, 1977) and a change began in the provenance of the clay minerals. Initially green, gray and red mud, and then gray mud and volcanogenic sandy debris spread westward from the volcanic area. The volcanic detritus may have been Mg-rich clays formed in the weathering environment (less likely) or volcanic glass and ferromagnesian minerals which altered to Mg-rich smectites at the depositional site during early diagenesis in the pore water-sediment system (Perry *et al.*, 1976). As discussed below, the expandable chlorite and corrensite seem to be the result of alteration of smectite and/or the volcanic detritus during burial metamorphism.

#### *Origin of illite-smectite*

The bulk chemical compositions of the < 2- $\mu\text{m}$  silicate fraction are plotted on the triangle ( $\text{KAlO}_2 + \text{NaAlO}_2$ )-(Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> - K<sub>2</sub>O)-MgO (Figure 8). Assuming that the bulk compositions of the clays remained relatively unchanged except for addition of potassium from coarser size fractions during burial metamorphism, the original corrensite-illite-smectite suite of clays were Mg<sup>2+</sup>-rich, similar to Mg-rich smectites. Some samples are sufficiently high in Mg<sup>2+</sup> that their bulk compositions approach that of a saponite (the Mg end-member of the smectite group of clay minerals).

During burial metamorphism, smectite can be progressively converted to mixed-layer illite-smectite and ultimately illite (Perry and Hower, 1970; Hower *et al.*, 1976). The conversion results in the fixation of potassium into interlayer positions as the burial temperature increases. The abundance of 1Md illite in the corrensite-illite-smectite suite suggests a history of this type of burial metamorphism. Potassium was derived from K-feldspar and/or K-mica detrital silt in the shale.

The conversion of smectite to illite-smectite involves loss of magnesium and iron from the growing illite-smectite (Hower *et al.*, 1976). In Tertiary rocks of Texas Gulf Coast, the magnesium and iron are incorporated into 14A chlorite. The illite-smectite in the Cow Head rocks occurs in association with expandable chlorite and corrensite and relatively insignificant amounts of 14A chlorite, probably because

the Cow Head rocks contain much more magnesium and iron than the Tertiary rocks of Texas Gulf Coast.

#### *Origin of corrensite*

Corrensite seems to be a diagenetic clay mineral that requires ready availability of Mg<sup>2+</sup> in order to form (Kubler, 1973). A qualitative sequence of diagenetic events is suggested by the Mg-rich bulk chemical compositions of the < 2- $\mu\text{m}$  silicate fraction, the association of corrensite, expandable chlorite, and illite-smectite in Lower and Middle Ordovician strata, and the Mg-rich character of the expandable chlorites. During burial metamorphism, Mg<sup>2+</sup>-rich smectites which may have formed during early diagenesis (Perry *et al.*, 1976), and/or volcanic detritus, are altered to dioctahedral illite-smectite of low expandability (as discussed above) and a trioctahedral mixed-layer clay, corrensite or expandable chlorite. The corrensite can continue to exist with a higher proportion of expandable layers than the illite-smectite because of its trioctahedral character. The symmetrical arrangement of the octahedral cations about the central hydroxyl ion allows the O-H axis to be nearly normal to the (001) crystallographic plane and allows for greater electrostatic repulsion between potential interlayer cations and the hydroxyl hydrogen ion. The larger hydration energy of Mg vs K would also contribute to the higher thermal stability of trioctahedral expandable phases (corrensites) as contrasted to dioctahedral illite-smectites having a comparable proportion (~ 50%) of expandable layers.

#### SUMMARY

The Cow Head klippe in western Newfoundland contains three stratigraphically restricted suites of clay minerals. The oldest is an illite-14A chlorite suite found in green and gray shale, argillaceous limestone, and mass-flow carbonate breccia in the Middle Cambrian through late Lower Ordovician part of the Cow Head Breccia. These predominantly detrital illite and 14A chlorite clays were transported eastward from the North American craton and shelf to the stable continental slope.

Beginning in the early Lower Ordovician, Mg<sup>2+</sup>-rich volcanic detritus was transported westward from a developing volcanic island arc in central Newfoundland. The volcanic influence first appears in continental slope green and gray shale and argillaceous limestone in the late Lower Ordovician part of the Cow Head Breccia. As the continental margin rapidly foundered in the Middle Ordovician, volcanic material accumulated in the 'Red Shale' and overlying gray shale-volcanogenic sandstone of the 'Green Sandstone' flysch. We infer that during burial metamorphism, the Mg-rich volcanogenic materials of late Lower to Middle Ordovician age altered to a corrensite (expandable chlorite) and illite-smectite assemblage, with illite-smectite now approaching a non-expandable illite composition.

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