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GEOCHEMISTRY AND PETROLOGY OF LOWER PALEOZOIC PLATFORM-EQUIVALENT SHALES, WESTERN NEWFOUNDLAND

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ABSTRACT

A total of 274 shale samples have been collected from a variety of lower Paleozoic tectonostratigraphic settings in western Newfoundland. Thick shale units of particular interest occur in the Humber Arm and Hare Bay allochthons, and within the Table Head Group at the top of the autochthonous Cambro-Ordovician platformal sequence. Preliminary results of shale analyses indicate localized, anomalous concentrations (roughly 300 ppm) of Zn, Cu, Pb and Ni. In part of the Humber Arm Allochthon (Cow Head Group) these anomalies occur throughout the Middle Cambrian to Middle Ordovician stratigraphic sequence, and are related to the early precipitation of sulphides associated with organic carbon. In the laterally equivalent Northern Head group (Bay of Islands area) sulphide precipitation is localized in Arenigian rocks at the base of the flysch sequence, and may be related to: 1) early diagenetic mobilization of metals during oxidizing marine conditions or 2) subsequent burial history. Shale of the Middle Ordovician Black Cove Formation contains sphalerite associated with early precipitated pyrite.

INTRODUCTION

The objective of this project is to evaluate the potential of lower Paleozoic shale in western Newfoundland as a source of base-metal mineralization in nearby platform carbonates of similar age, and as hosts of sedimentary exhalative base-metal deposits.

Sixty-one base-metal mineral occurrences within the carbonate platform of western Newfoundland have been documented in a recent study conducted as part of the Canada-Newfoundland Mineral Development Agreement (Saunders and Strong, 1986). These occur throughout the Middle Cambrian to Middle Ordovician carbonate rocks from the Port au Port Peninsula to the tip of the Great Northern Peninsula. Many, including the Daniels Harbour ore body, are hosted by the Lower Ordovician St. George Group.

Shale units of equivalent age are disposed in several tectonostratigraphic settings in western Newfoundland. These shales occur as: 1) interbedded units within the Lower Cambrian to Middle Ordovician carbonate-dominated platformal sequence; 2) a black shale-dominated interval (Black Cove Formation) of Middle Ordovician age, which occurs at the top of the platformal sequence and is thought to be related to margin collapse; and 3) thick shale intervals within Lower Cambrian to Lower Ordovician deep-water equivalents of the platformal sequence, which occur in the Humber Arm and Hare Bay allochthons.

Objectives of this project are:

1) to identify anomalous metal concentrations in shales and document the nature of their occurrence through the use of the SEM/EDAX;

2) to establish if significant trends in major and/or trace element chemistry occur and if they vary with stratigraphic position or tectonic setting;

3) to characterize the depositional and early diagenetic conditions indicated by organic carbon/sulphur relationships;

4) to identify potential temporal changes in oceanic conditions, which may have governed the transportation or precipitation of metals, through the examination of pyritic sulphur isotopic signatures in a representative subset of samples (of known age); this will be augmented with determination of sulphur isotopic signatures of localized sulphate occurrences; and

5) to characterize the burial diagenetic history of individual sedimentary sequences through the determination of illite crystallinity index for a representative subset of samples.

This project is a contribution to the Canada–Newfoundland Mineral Development Agreement, 1984–1989; project carried by the Geological Survey of Canada, DSS contract 23233-7-0223/01-ST.

TECTONOSTRATIGRAPHIC SETTING OF WESTERN NEWFOUNDLAND SHALES

Regional Setting

The Humber Zone of western Newfoundland (Williams, 1979) records 1) the establishment of a passive continental margin in the late Precambrian/Early Cambrian, 2) continental margin sedimentation spanning the Cambrian to Middle Ordovician, 3) the destruction of the margin during Middle Ordovician Taconic orogenesis and 4) subsequent deformation during Acadian orogenesis.

A mixed siliciclastic–carbonate Lower Cambrian sequence (Labrador Group) overlies rifted Grenvillian basement, and is overlain by a thick (roughly 1500 m) platformal carbonate sequence (Port au Port Group, St. George Group) spanning the Middle Cambrian to Lower Ordovician (Figure 1). Equivalent deep-water strata are preserved in two major allochthons, the Humber Arm Allochthon in the south and the Hare Bay Allochthon in the north (Figure 4). Block-faulting and foundering of the platform is recorded by the deposits of the Middle Ordovician Table Head Group atop the platformal sequence (Klappa *et al.*, 1980; Stenzel and James, 1987). It preceded the structural emplacement of the allochthons onto the platform.

Autochthonous Platformal Sequence

The autochthonous platformal sequence (Figure 1) was dominated by shallow-water sedimentation, and is generally poor in shale.

The Lower to Middle Cambrian Labrador Group (James and Stevens, 1982; Knight and Boyce, 1987) comprises: 1) sandstone of the basal Bradore Formation, overlain by 2) shale, siltstone, minor sandstone and carbonate of the Forteau Formation that is in turn overlain by 3) the Hawke Bay Formation which is dominated by quartzitic sandstone with locally developed shale and limestone units.

The Middle to Upper Cambrian Port au Port Group (Chow and James, 1987) consists of the March Point, Petit Jardin and Berry Head formations, all having shallow-water carbonate lithologies containing minor shale interbeds. The Lower to lower Middle Ordovician St. George Group (Knight and James, 1987) comprises shallow-water carbonates of the Watts Bight, Boat Harbour, Catoche and Aguathuna formations. The Aguathuna Formation straddles the Lower/Middle Ordovician boundary and contains several depositional breaks indicated by stratiform breccias.

Locally, an unconformity separates the St. George Group from the overlying Middle Ordovician Table Head Group (Klappa *et al.*, 1980; Ross and James, 1987). The Table Head Group consists of: 1) peritidal to subtidal carbonates in the lower part (Table Point Formation), followed by 2) local hemipelagic slope sediments deposited in response to differential subsidence (Table Cove Formation), and 3) rapid collapse, resulting in the deposition of mud of the Black Cove Formation across a block-faulted submarine topography.

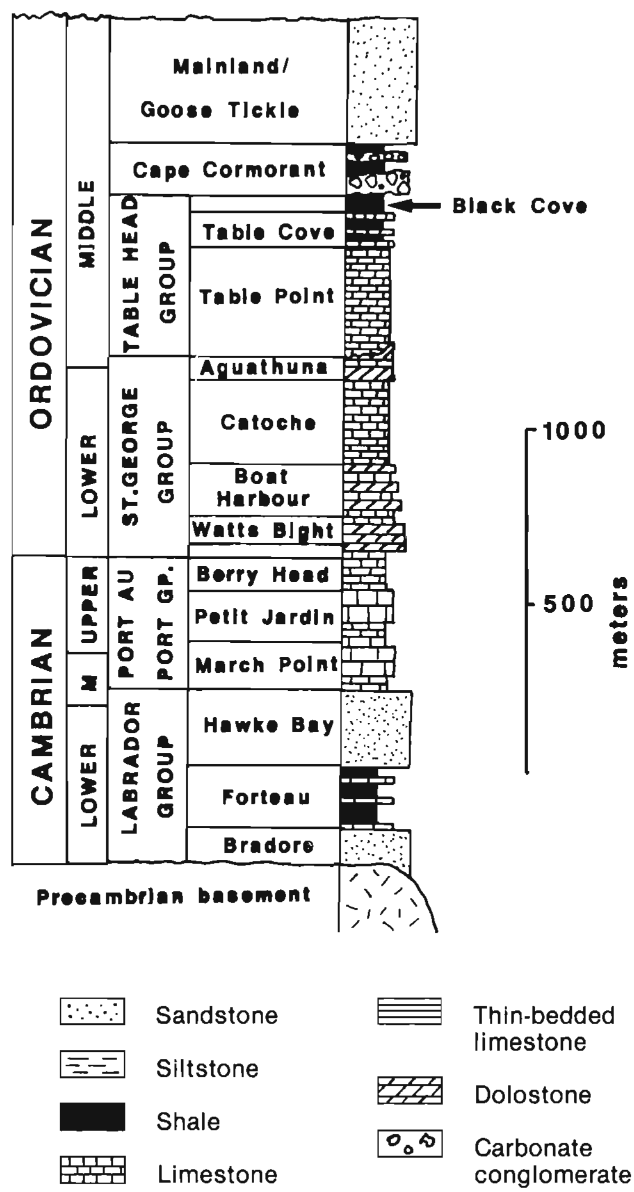

Figure 1. *Schematic summary of Lower Paleozoic autochthonous, platformal sequence, western Newfoundland. St. George Group contains unnamed unit at base.*

This topography was progressively overlain by Middle Ordovician flysch (Mainland sandstone and Goose Tickle Formation) comprising sandstone, siltstone and shale. This was commonly preceded or punctuated by carbonate debris flows (Cape Cormorant Formation) derived from erosion of Table Head and older carbonates (Stenzel and James, 1987).

Allochthonous Deep-Water Sequences

The Humber Arm and Hare Bay allochthons are broadly similar in that they comprise thrust slices of predominantly sedimentary lithologies in the lower part, overlain by volcanic and igneous slices of oceanic affinity, and capped by ophiolite complexes; all are separated by m lange zones of variable thickness. Both allochthons structurally overlie the autochthonous platformal sequence and are bounded by mélange. The internal stratigraphy and structure of the Humber Arm Allochthon is presently better understood than the Hare Bay Allochthon.

Humber Arm Allochthon

The Humber Arm Allochthon is centred on the Bay of Islands and extends from the Port au Port Peninsula to Portland Creek (Figure 4).

A succession of deep-water sedimentary units, equivalent to the platformal sequence described above, is exposed in the lower part of the Humber Arm Allochthon (Figure 2) and is termed the Humber Arm Supergroup (Stevens, 1970). At the base, red and green shale and sandstone of the ?Lower Cambrian Summerside Formation occur. These lithologies pass upward into the Lower to Middle Cambrian Irishtown Formation which contains quartzitic sandstone, conglomerate and shale. These units are the deep-water equivalents of the Labrador Group.

The Irishtown Formation is overlain by Middle Cambrian to Lower Ordovician deep-water carbonate slope deposits, which reflect the style of carbonate sedimentation on the platform (James and Stevens, 1986; Botsford, 1987). In the Bay of Islands area, this sequence is informally termed the Northern Head group (Botsford, 1987), whereas laterally equivalent strata to the north are termed the Cow Head Group (James and Stevens, 1986) (Figure 2). Although both sequences comprise carbonate gravity deposits and shale, differences between them reflect an irregular platform margin morphology that has controlled their deposition and local paleoceanographic conditions (Botsford, 1987) (see below).

Both units are conformably overlain by flysch, termed the Eagle Island formation (Botsford, 1987) in the Bay of Islands area, and the Lower Head formation in the Cow Head area (Williams *et al.*, 1985). These units are regarded as facies equivalents of the autochthonous Mainland sandstone. The Humber Arm Allochthon is structurally thin at its northern and southern extremities, and only the Cow Head Group and Lower Head formation are preserved, in imbricate slices, in the Cow Head area.

Hare Bay Allochthon

The Hare Bay Allochthon is centered on Hare Bay, and extends from Canada Bay, in the south, to the northeast tip of the Great Northern Peninsula (Figure 4).

Six major structural slices have been mapped (Williams and Smyth, 1983), and are generally separated by shaly mélange. Several of these slices contain sedimentary lithologies, including shale units, and are described here.

The Northwest Arm Formation is exposed on the western margin of the allochthon and consists of thinly interbedded black and green shale, minor carbonate conglomerate, sandstone and chert. The formation has yielded Lower Ordovician graptolites (Tuke, 1968). Strong similarities with the upper part of the Northern Head group (Middle Arm Point formation) and an apparently conformable relationship with overlying sandstones of the Goose Tickle Formation have been noted by the writer, and a similar depositional setting is considered likely.

The Maiden Point Formation is contained in the structurally overlying thrust slice. It comprises a thick sequence of unfossiliferous, bedded quartzose sandstone and shale interbeds, plus minor mafic volcanics. The age of the Maiden Point Formation is uncertain, but it is tentatively regarded as Early Cambrian (Williams and Smyth, 1983). The Maiden Point Formation is similar to portions of the Summerside and Irishtown formations of the Humber Arm Allochthon.

The structurally overlying Milan Arm Mélange is similar to other mélange zones in the allochthon, but it appears to occupy a consistent structural position and contains huge rafts of predominantly volcanic blocks. These are surrounded by a black and green shale matrix.

The Cape Onion Formation occurs in an overlying thrust slice and is confined to the northern part of the allochthon. It consists of basaltic pillow lavas and black, pyritic shale that has yielded Lower Ordovician (Tremadoc) graptolites (Erdtmann, 1971; Williams and Smyth, 1983).

Eastern Margin of the Humber Arm Allochthon

In the complex zone immediately east of the Humber Arm Allochthon, several fault-bounded, variably deformed rock units have been identified, but are still of uncertain age and affinity. Both parautochthonous slices of the platformal sequence, possibly representative of a more easterly, shale-rich facies, and equivalents of parts of the Humber Arm Allochthon are thought to occur (Figure 3).

The Reluctant Head Formation comprises thin-bedded limestone and limestone breccia with grey, dolomitic shale (locally phyllite) and is regarded as Cambrian in age (Lilly, 1963; Williams and Cawood, 1986).

The Whale Back formation (Williams and Cawood, 1986) contains green sandstone, siltstone and shale; the formation resembles and is tentatively correlated with the Middle Ordovician Goose Tickle Formation.

The Pinchgut group (Williams and Cawood, 1986) occurs in faulted contact with the Irishtown Formation. It contains thin-bedded limestone, grey-green dolomitic shale and thick-bedded carbonate conglomerate. The age and depositional setting is uncertain. Williams and Cawood (1986) have suggested that the Pinchgut group represents an eastern facies of the platformal carbonate sequence. However, lithologically, the unit resembles the lower part of the Cooks Brook Formation in clast composition of conglomerate, and bedding style of conglomerate and shale (personal observations, 1987). This, and the proximity to the Irishtown Formation, suggests

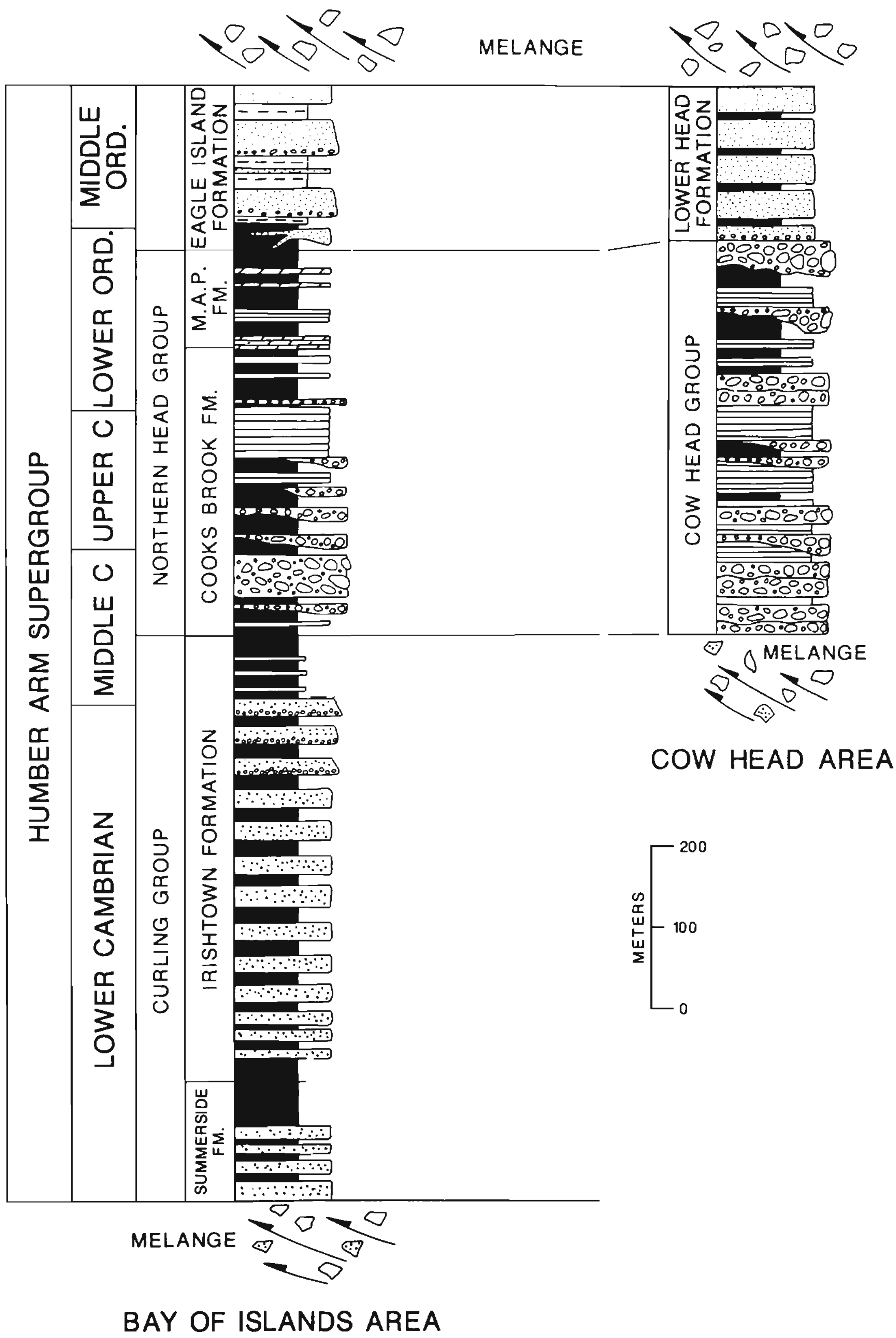

Figure 2. *Schematic summary of the Humber Arm Supergroup, in the Humber Arm Allochthon, illustrating the relationship of the Bay of Islands and Cow Head areas. M.A.P. Fm. is Middle Arm Point formation; see Figure 1 for Legend.*

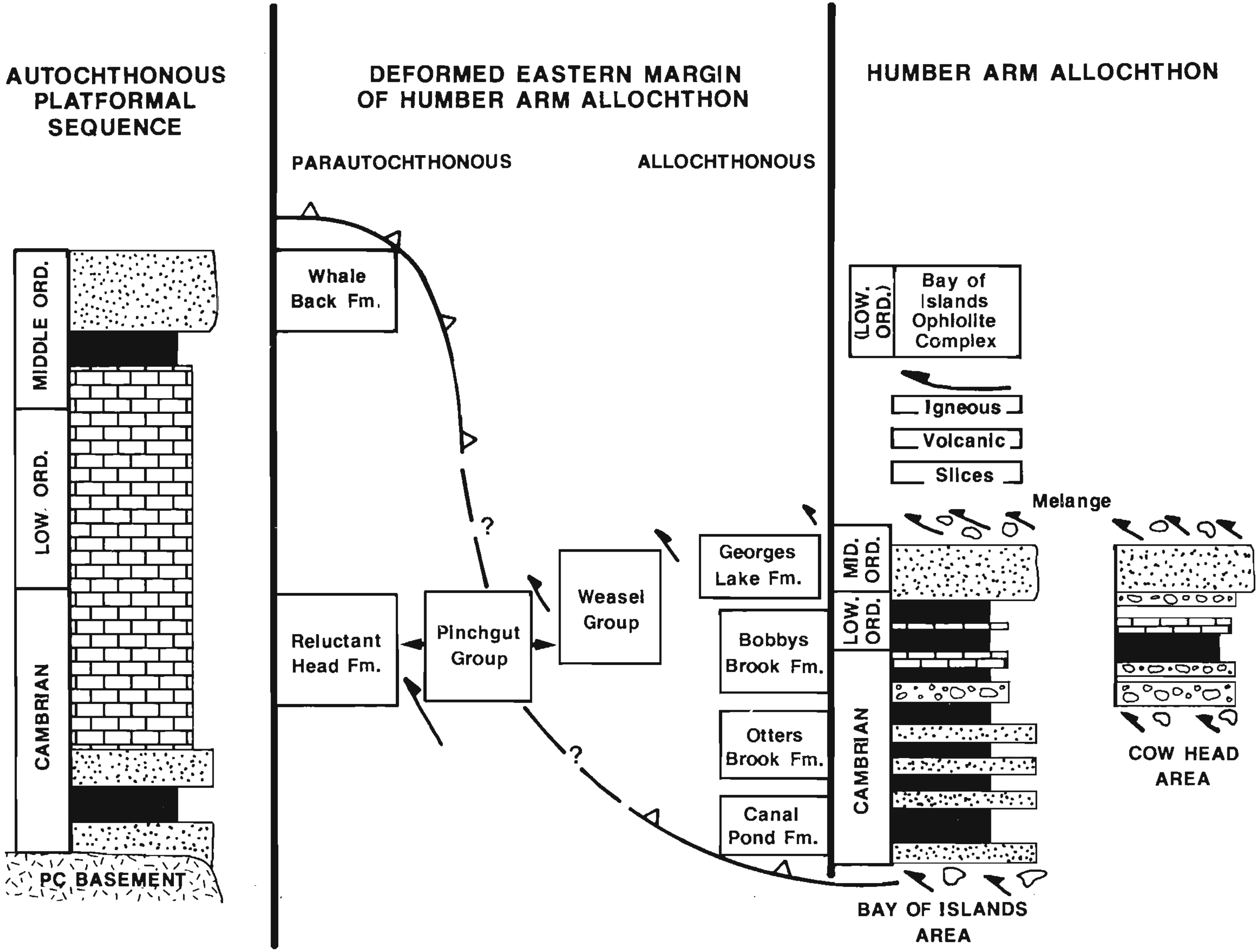

Figure 3. *Schematic summary indicating the inferred tectonostratigraphic settings of units sampled at the deformed eastern margin of the Humber Arm Allochthon, relative to platformal sequence and the allochthon; see Figure 1 for Legend.*

the alternative view that the Pinchgut is part of the Humber Arm Allochthon.

The thrust-bounded Weasel group occurs to the north in the vicinity of Old Mans Pond and is situated structurally atop the platformal sequence (Williams *et al.*, 1982; Nyman *et al.*, 1984). It contains grey shale, thin-bedded limestone and carbonate conglomerate. The age and depositional setting of the unit are uncertain, since it displays similarities with both the Reluctant Head Formation and the (allochthonous) Northern Head group. The author collected poorly preserved ?Ordovician brachiopods this summer and samples are currently being processed for conodonts.

In a separate structural slice, red and green slates of the Canal Pond formation are clearly correlatives of the Summerside Formation. Nearby, black and grey shale and quartzitic sandstone of the Otter Brook formation, are similarly correlated with the Irishtown Formation. Likewise, black and grey shale and carbonate of the Bobby's Brook formation closely resemble the Northern Head group.

The Georges Lake formation (Williams and Cawood, 1986) separates the margin of the Humber Arm Allochthon from the structurally underlying platformal sequence. The Georges Lake formation comprises grey to black, pyritic shale and calcareous and quartzose siltstone and sandstone. Shaly mélange zones are prominent. The unit has been related to wildflysch sedimentation and deformation during emplacement of the Humber Arm Allochthon (Williams and Cawood, 1986).

SAMPLING

Areas of Sampling

Shale samples from all of the tectonostratigraphic units described above have been collected in eight principal geographic areas (Figure 4).

Port au Port Area. Samples were collected from the Table Head Group, the overlying Mainland formation and the structurally overlying Humber Arm Allochthon.

Bay of Islands Area (Humber Arm Allochthon). A large suite of samples spans the sedimentary sequence here, including the Summerside and Irishtown formations, but focussing on the Northern Head group and overlying Eagle Island formation. Mélange zones within the allochthon were also sampled, and altered shales (Middle Arm Point and Eagle Island formations) were collected from the base of the Bay of Islands ophiolite complex.

Humber Arm Area (Deformed margin of the Humber Arm Allochthon). Representative shale samples were collected from the variably deformed and metamorphosed units described above, from the Georges Lake area northward to the vicinity of Old Man's Pond (Figure 4).

Bonne Bay—Cow Head Area (Autochthonous sequence and Humber Arm Allochthon). The Lower Cambrian Forteau Formation and Middle Ordovician Goose Tickle Formation were examined and sampled in the Bonne Bay area. The basal mélange of the Humber Arm Allochthon was also sampled, and altered shale samples were collected from the base of the Bay of Islands ophiolite complex.

A suite of shale samples, spanning the Middle Cambrian to Middle Ordovician Cow Head Group has been assembled. These were collected from several stratigraphic sections, which include both proximal and distal depositional settings.

Table Point Area. The author sampled from a coastal section immediately north of Bellburns. This section contains excellent exposures of the Table Head Group and overlying flysch (Goose Tickle Formation).

Canada Bay Area. The margin of the Hare Bay Allochthon lies within this region. Deformation and metamorphism of platformal sediments increases progressively toward the margin of the allochthon, and sampling of platformal shales transects this gradient. Transported and platformal sediments were also sampled in the Main Brook area to the north.

Pistolet Bay—northern Hare Bay Area. Shale units and mélange zones of the Hare Bay Allochthon (Northwest Arm Formation, Maiden Point Formation, Milan Arm Mélange, Cape Onion Formation) and exposures of the Table Head Group and Goose Tickle Formation were sampled in this region.

Jackson's Arm Area (White Bay). Deformed and metamorphosed equivalents of parts of the lower Paleozoic carbonate sequence occur in the most easterly, 'external' setting in the Jackson's Arm area. Phyllitic units, commonly rich in pyrite, were sampled here.

Status of Samples

Samples collected and analysed prior to the 1987 field season, mostly from the Humber Arm Supergroup, provide major and trace element data for 160 samples; organic carbon—sulphur content has been determined for 97 of these. Major- and trace-element analyses of the 114 samples collected during 1987 are presently being conducted by the Newfoundland Department of Mines and organic carbon—sulphur analysis for all remaining samples is underway at the Geologic Survey of Canada.

In total, these analyses will provide a basic geochemical database of 274 shale samples. Subsets of this collection have been selected for sulphur isotope analysis and determination of illite crystallinity index (see below).

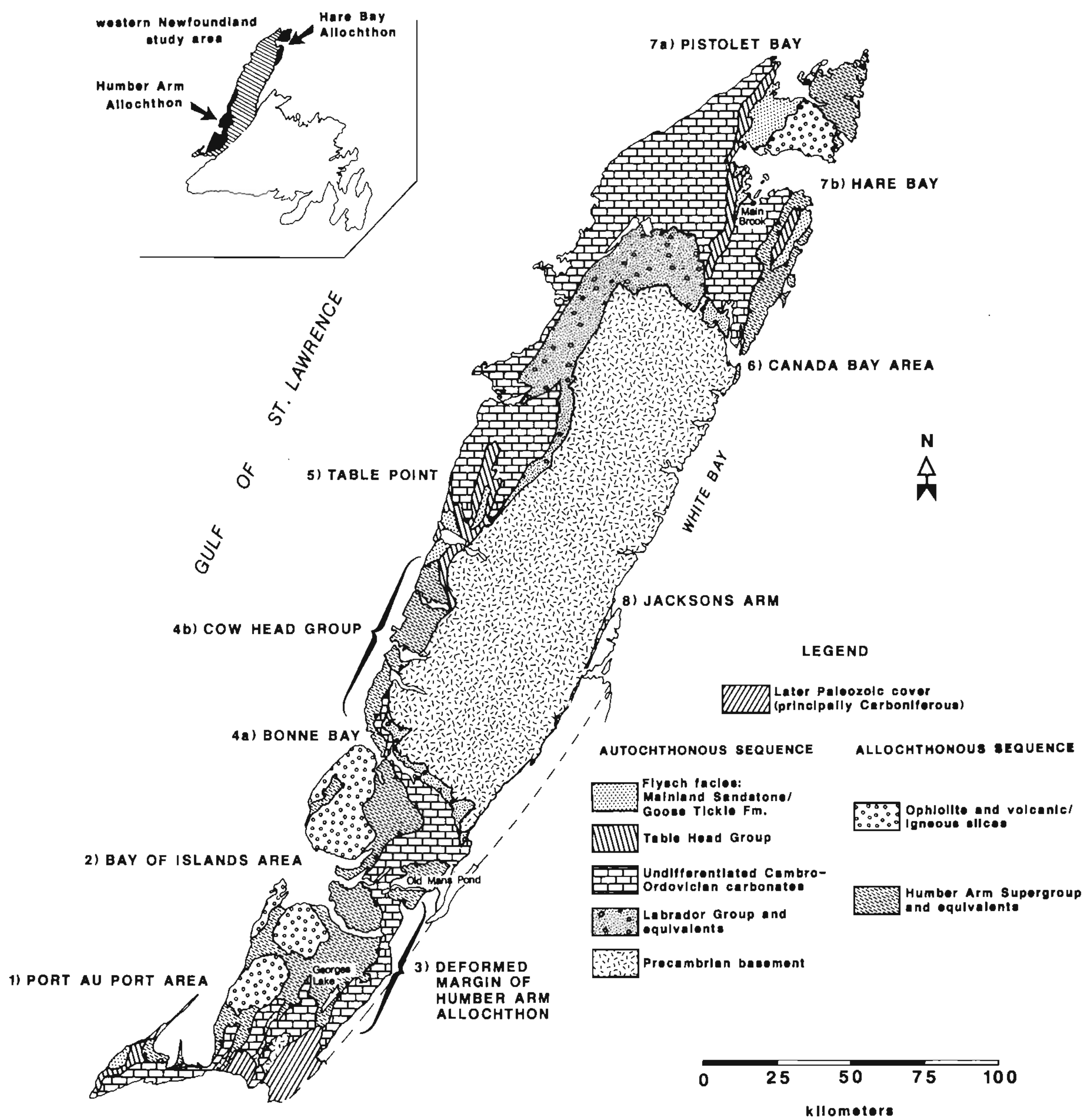

Figure 4. *Generalized geology of western Newfoundland indicating the principal areas of sampling.*

INTERIM RESULTS

Variation in deep-water depositional–early diagenetic conditions and possible temporal oceanic changes

In the Bay of Islands area, the Humber Arm Supergroup records a marked change, in the late Tremadoc, from near-anoxic depositional and early diagenetic conditions to a better-oxygenated, suboxic setting in the Arenig. Near-anoxic conditions predominated from at least the late Middle Cambrian to the Late Tremadoc, and are characterized by: 1) relatively abundant organic carbon, 2) paucity of bioturbation, 3) absence of Mn and Ba in shale, 4) presence of early precipitated pyrite, and 5) apparent absence of ferric Fe compounds. All of these are consistent with the early onset of anoxic diagenetic conditions, at, or very close to the seafloor. These conditions spanned deposition of the Irishtown and Cooks Brook formations and are sharply transitional, through the base of the Middle Arm Point formation. The subsequent suboxic setting then prevailed during deposition of the the Middle Arm Point and Eagle Island formations. The suboxic setting is characterized by: 1) abundant bioturbation and diminished organic carbon, 2) widespread occurrence of diagenetic Mn-carbonate, 3) presence of hematite, and 4) the precipitation of authigenic barite within shale. These features are thought to reflect early diagenesis under redox gradients that existed at shallow depths in the sediment as a result of increased oxygen levels in the depositional environment (Botsford, 1987).

Whereas this Lower Ordovician transition into more oxidizing deep-water conditions is dramatic in the Northern Head group, the change is much more subdued in the Cow Head Group, where proximal facies are relatively rich in organic carbon throughout. This difference has been ascribed to variability in the carbonate margin and slope morphology, which influenced local paleoceanographic conditions, and resulted in the more extensive and continuous deposition of biogenic debris in the Cow Head area (Botsford, 1987).

Notwithstanding these lateral variations, the relative abundance of organic carbon within the Middle Cambrian to Lower Ordovician interval described above is consistent with a worldwide episode of extensive black mud deposition, suggestive of poorly aerated, deep-marine bottomwater (cf. Leggett *et al.*, 1981). Likewise, the appearance of more oxidizing conditions in the late Tremadoc of the Northern Head and Cow Head groups is roughly coincident with a widespread Lower Ordovician interval sparse in black shale, suggesting that it may reflect, in part, global oceanic conditions. This temporal change in oceanic conditions is of interest in this study, as it bears on the potential mobilization and precipitation of base metals in shales, and may be partly responsible for the distribution of sulphides discussed below.

The most widespread subsequent mud deposit is represented by the Middle Ordovician Black Cove Formation, which is generally well-laminated and relatively rich in organic carbon. This is consistent with deposition in restricted, fault-bounded basins created by differential collapse of the carbonate platform (Stenzel and James, 1987).

SULPHIDE OCCURRENCE AND BASE-METAL CONCENTRATIONS

Pyrite-rich Horizon at the Base of the Cooks Brook Formation (late Middle Cambrian)

Abundant pyrite characterizes the base of the Northern Head group (Irishtown–Cooks Brook formation boundary) and is particularly well developed at Middle Arm in the Bay of Islands. Here, over a roughly 10 m shale-dominated unit, several beds of what was originally carbonate-pebble conglomerate, ranging in thickness from 2 to 40 cm, are partially to completely replaced by pyrite (Plate 1). The only lithology that is never replaced is black, phosphatized shale, which comprises up to 10 percent of individual beds. Where replacement is complete, field textures suggest detrital pyrite, but petrographic examination indicates that this is a relatively fine-crystalline (30 micrometers), pebble-by-pebble replacement of an original carbonate host exhibiting interstitial ferroan carbonate cement. No associated base-metal sulphides were observed.

This pyrite-rich layer overlies a roughly 40-m-thick, black shaly unit at the top of the Irishtown Formation. This is indicative of widespread anoxic deep-water conditions, conducive to sulphate reduction and the resultant early precipitation of sulphides.

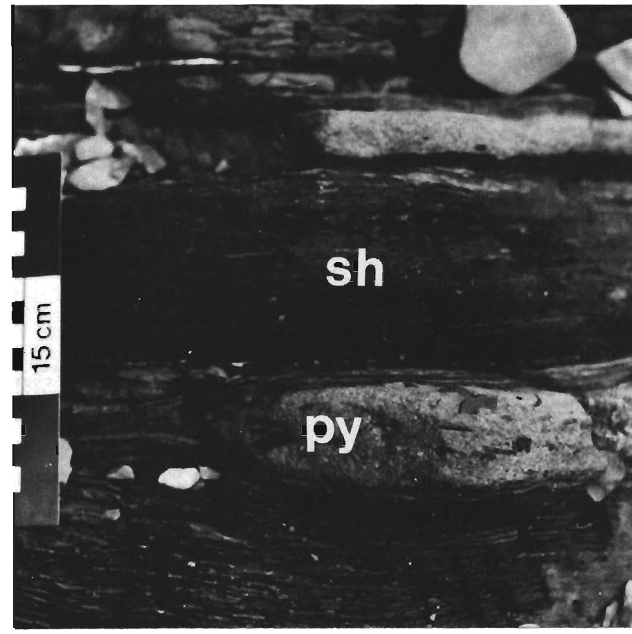

Plate 1. *Thin beds of carbonate conglomerate completely replaced by pyrite (py) within laminated black shale (sh); base of the Cooks Brook Formation (late Middle Cambrian), Middle Arm, Bay of Islands.*

Base-Metal Concentrations

Humber Arm Allochthon. The distribution of Zn, Pb, Cu and Ni concentrations in shale of the Northern Head and Cow Head groups is shown in Figure 5 and indicates the presence of anomalous concentrations of these metals in several samples. Individual metals occur in concentrations up to 300 ppm compared to 'background' values of 20 to 50 ppm. Preliminary results indicate that the stratigraphic distribution and nature of these anomalies differ between the Northern Head and Cow Head groups.

Northern Head Group

The stratigraphic distribution of Pb, Zn, Cu and Ni within the Northern Head group is shown in Figure 6 and indicates the pronounced enrichment of these metals in shales of Early Ordovician (Arenig) age at the base of, and within, the Eagle Island sandstone.

Petrographic and SEM/EDAX examinations of individual shale samples indicate the presence of chalcopyrite, galena, sphalerite and locally pentlandite, occurring as highly disseminated blebs and grains, 10 to 50 micrometers in size, and within very thin veinlets.

Sulphide blebs commonly demonstrate irregular, intergrown and locally replacive boundaries with the surrounding clay matrix. Intergrown galena–sphalerite and galena–chalcopyrite also occur in euhedral cubic habit (Plate 2), where they may have replaced pyrite. Where sulphides

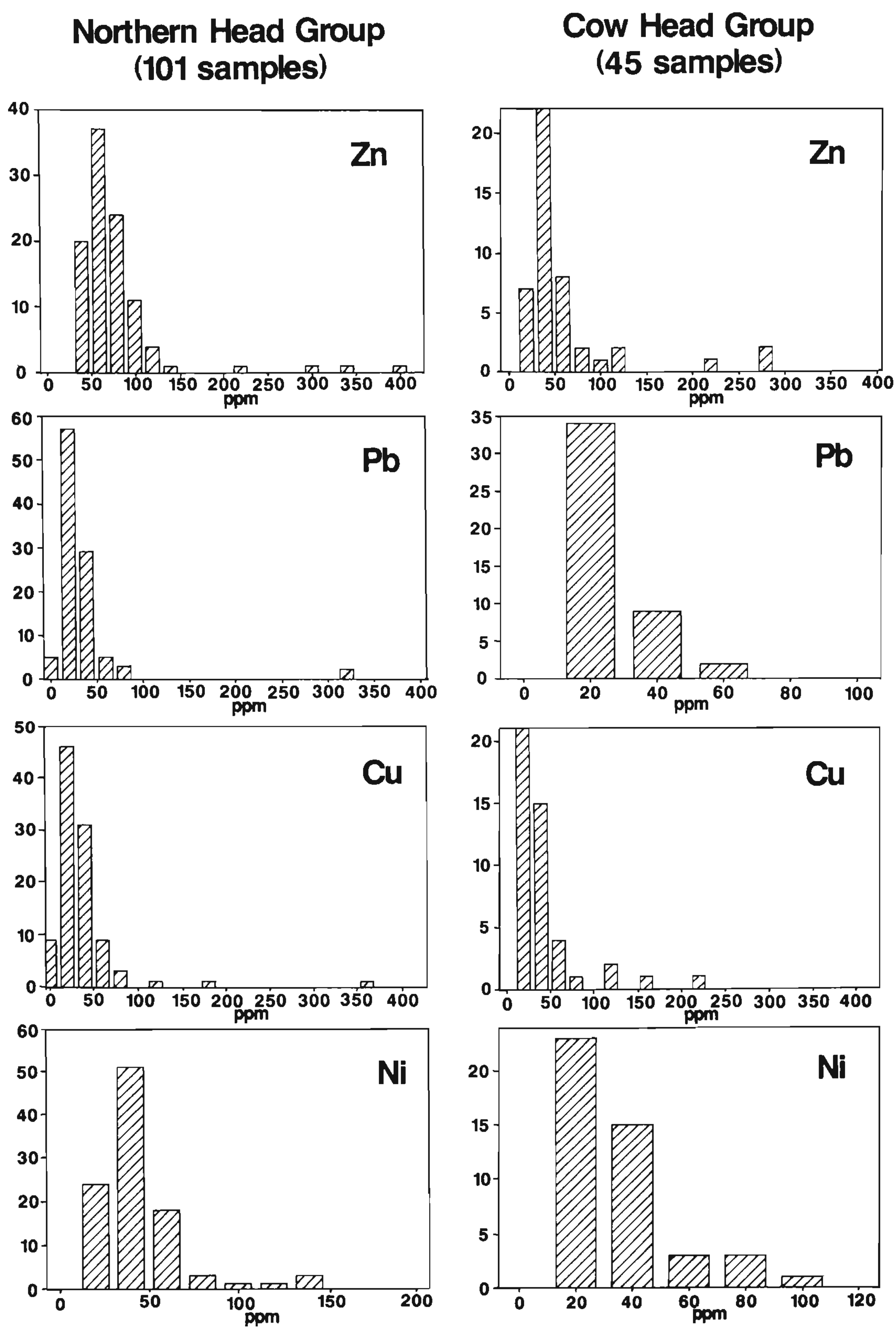

Figure 5. *The distribution of Zn, Pb, Cu and Ni in shale of the Northern Head and Cow Head groups within the Humber Arm Allochthon.*

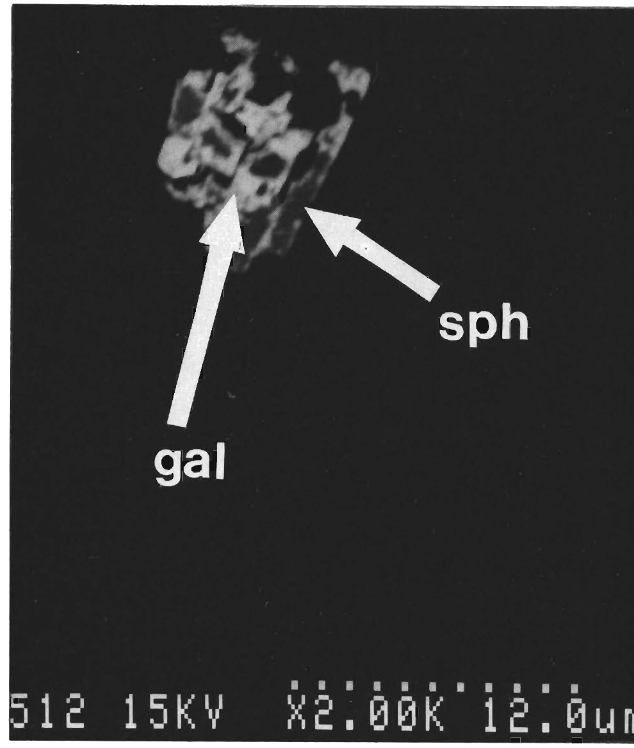

Plate 2. *SEM/EDAX photomicrograph (backscatter mode) illustrating intergrown galena (gal)/sphalerite (sph) grain within (opaque) shale matrix; Middle Arm Point formation, Bay of Islands area; magnification and scale in micrometers at lower right.*

have been noted within adjacent thin sandstones, they occur as late pore fillings, surrounding detrital grains and locally replacing interstitial matrix and cement (Plate 3).

Veinlets range up to 0.25 mm in width. Some contain galena, others, chalcopyrite. Both sulphides occur intergrown with vein-filling K-feldspar and quartz (Plate 4).

Cow Head Group

In contrast to the Northern Head group, zinc and copper anomalies within Cow Head Group shales are not concentrated at one stratigraphic horizon, but are scattered from the Upper Cambrian to the Lower Ordovician. Concentrations of lead and nickel are consistently low in shales of the Cow Head Group.

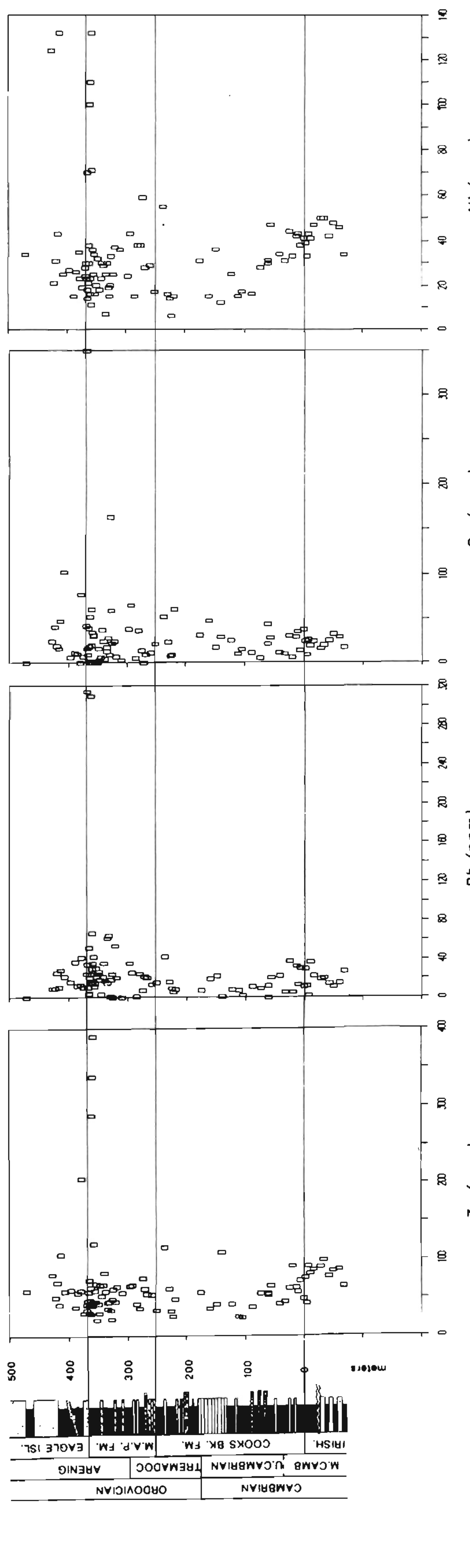

Figure 6. *Stratigraphic distribution of Zn, Pb, Cu and Ni within shale of the Northern Head group and adjacent units. The stratigraphic interval spans: 1) the Irishtown Formation, at the base, through 2) the Cooks Brook and Middle Arm Point formations (Northern Head group) and 3) the overlying Eagle Island sandstone. This diagram displays the anomalous concentration of these elements in sulphides localized at the base of the Eagle Island sandstone.*

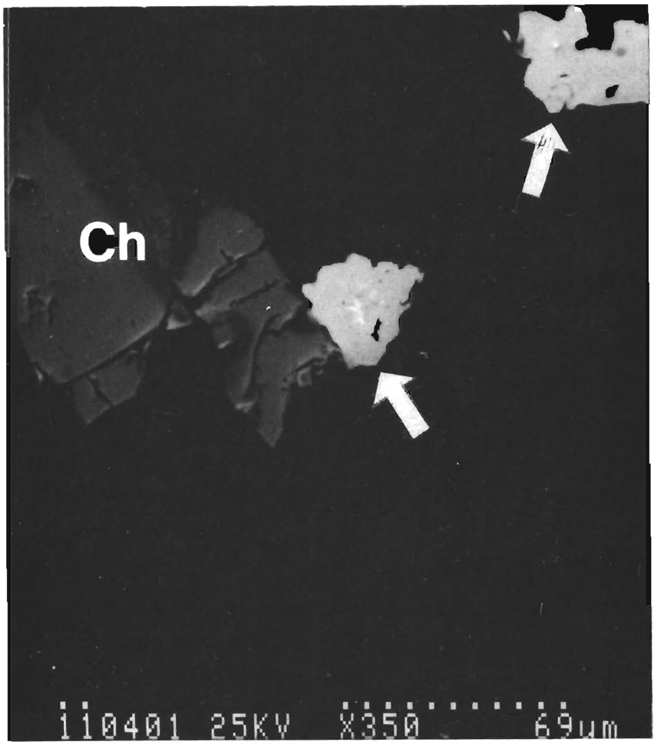

Plate 3. *SEM/EDAX photomicrograph (backscatter mode) illustrating pore-filling chalcopyrite blebs (arrows), with small inclusions of galena (bright areas), within thin sandstone bed at base of Eagle Island sandstone. Surrounding silicate grains are opaque in backscatter mode but adjacent detrital chromite grain (Ch) can be seen; Eagle Island formation, Bay of Islands area; magnification and scale in micrometers at lower right.*

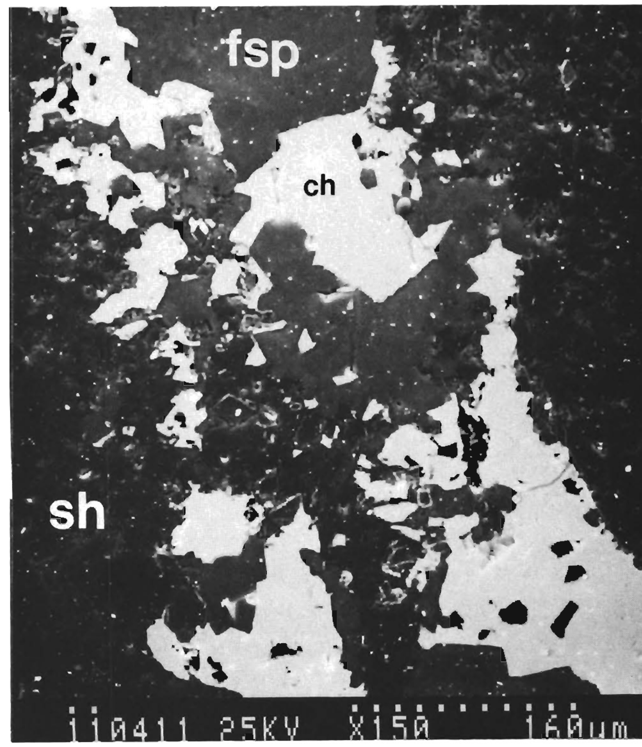

Plate 4. *SEM/EDAX photomicropgraph (scanning mode) of thin veinlet within Middle Arm Point formation shale illustrating intergrown chalcopyrite (ch) and K-feldspar (fsp) crosscutting shale matrix (sh); magnification and scale in micrometers at lower right.*

Although sulphides in these shales have not yet been well documented, sphalerite, chalcopyrite and ?pyrrhotite appear to be associated with delicate framboidal pyrite (Plate 5), which is, in turn, related to the presence of organic matter. All of these sulphides appear to have been precipitated relatively early in the diagenetic history of the shales. Copper and zinc anomalies are commonly associated with elevated concentrations of vanadium, which displays a good correlation with organic carbon content.

Existing trace element data comes from samples collected from the distal (depositional) portion of the Cow Head Group. The proximal, more organic carbon-rich facies was sampled during 1987.

Platformal Sequence: Black Cove Formation. Geochemical data presently available for shales of the Black Cove Formation has been provided by S. Stenzel. This unit was extensively sampled during 1987 and geochemical analyses are in progress. The data of Stenzel indicate anomalous concentrations of Zn (ranging from 200 to 366 ppm) in several Black Cove shales, from both the Port au Port and Pistolet Bay areas (Figure 4). These are all thinly laminated black shales with abundant siliciclastic and carbonate silt grains.

Sulphides are dominated by pyrite containing localized association of sphalerite. Pyrite occurs as disseminated subhedral to euhedral grains 10 to 30 micrometers in size and as interlocking masses of similar crystals, up to 2 mm in size (Plate 6). Sphalerite appears to occur generally as a replacement of pyrite, commonly close to the margin of interlocking masses (Plate 6). Precipitation of both sulphides appears to be relatively early, predating sediment compaction, and commonly localized by fragments of organic material.

Discussion

The mechanism of metal concentration in shale of the Northern Head group and Cow Head Group contrasts in timing and style. In the first case, precipitation of Zn, Cu, Pb and Ni(?) sulphides appears to have been a stratigraphically confined, relatively late event, through vein and pore filling and replacement, and not directly related to the presence of organic carbon. On the other hand precipitation in the Cow Head Group appears to have been relatively early and does not demonstrate evidence of extensive remobilization. This contrast in sulphide mineralization may be related to several factors.

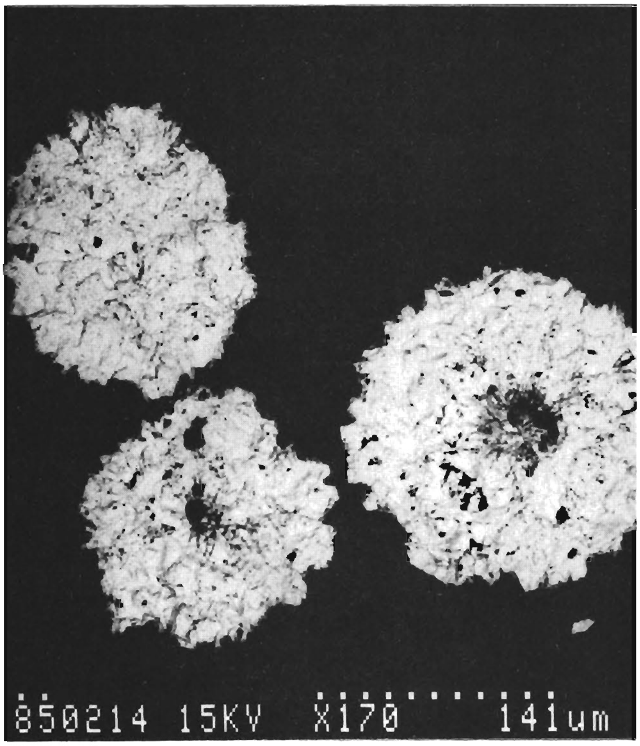

Plate 5. *SEM/EDAX photomicrograph (scanning mode) illustrating framboids comprising intergrown chalcopyrite and pyrrhotite within Cow Head Group shale; Western Brook Pond; magnification and scale in micrometers at lower right.*

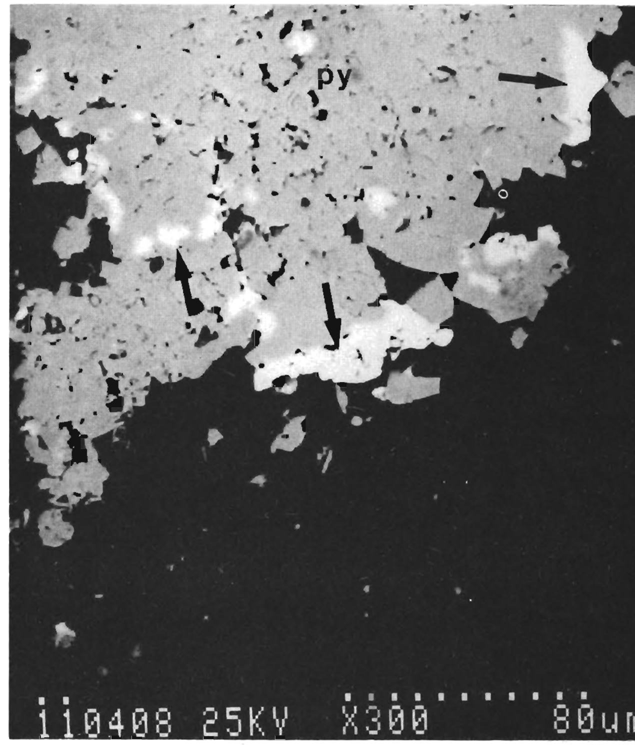

Plate 6. *SEM/EDAX photomicrograph illustrating interlocking mass of early-precipitated pyrite (py) with associated sphalerite (arrowed lighter areas) near margins; Black Cove Formation shale, Pistolet Bay area; magnification and scale in micrometers at lower right.*

The mobility of transition metals generally increases under oxidizing conditions, while reducing conditions generally result in precipitation as sulphides in the presence of reduced sulphur (Jacobs and Emerson, 1982; Maynard, 1983). Transport mechanisms may include the formation of complexes involving chloride or organic matter. Concentration of metals in organic material may commence during the life-cycle of organisms, and combined with the behaviour of these metals outlined above, is thought to account for the common association of sulphide mineralization with (organic-rich) black shale (Vine and Tourtelot, 1970; Calvert and Price, 1970; Maynard, 1983).

Preliminary evidence suggests that these processes of metal enrichment, related to the presence of organic carbon, controlled sulphide precipitation in Cow Head Group shales. This does not, however, appear to be the principal factor controlling the anomalous occurrence of Pb, Zn, Cu and Ni in the Northern Head group, since this enrichment appears in an interval that has undergone the most oxidizing depositional and early diagenetic conditions (as outlined above).

Factors responsible for this localized enrichment may include: 1) the transport of metals, within detrital grains or as complexes, during deposition of the Eagle Island sandstone, 2) the *in situ* mobilisation of metals during oxidizing-early diagenetic conditions (cf. Klinkhammer *et al.*, 1982), and 3) contrasting burial and deep-diagenetic history. Determination of illite crystallinity indices is directed toward assessing the last factor.

SULPHUR ISOTOPES

Samples selected for pyritic sulphur isotope determination are of known or readily inferred age and span the entire stratigraphic sequence under consideration. Temporal trends in sulphur isotopic signature may be used to identify episodes of oceanic stagnation having associated widespread reducing conditions, and ventilated, relatively oxidizing conditions. These may have been a factor in controlling base-metal mobility (cf. Goodfellow and Jonasson, 1984).

The nature of the sulphur reservoir present in bottom-water at any given time is most directly indicated by early diagenetic pyrite (or its metastable precursor), precipitated at the onset of bacterial sulphate reduction during shallow burial. Ensuing generations of pyrite tend to be coarser crystalline and more euhedral and may incorporate sulphur of uncertain isotopic history. A chemical technique recently developed at the Geological Survey of Canada (Hall *et al., in press)* facilitates the extraction, separation and sulphur isotope determination of highly disseminated, early precipitated pyrite like that in the shale samples of this study.

The majority of isotopic analyses are being carried out using samples most likely to contain pyrite of this type, but the isotopic signature of other styles of pyrite is also being determined for comparison.

The sulphur isotopic signature of authigenic barite from the Northern Head and Cow Head groups is also being determined.

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