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Article abstract

The bajada-playa sequence of terrestrial Upper Carboniferous redbeds of the Hopewell Group at Dorchester Cape, New Brunswick, hosts innumerable reduction spheroids in fine- to coarse-grained clastic sedimentary rocks, paleosols and caliche beds. The spheroids are grey-green, typically 2 to 3 cm in diameter, and may contain a dark, mineralized central core and less commonly one or more mineralized rings, concentric about the core. They decrease progressively in average diameter from 2.75 cm at the base to 0.85 cm at the top of an overall upward-fining 250 m thick measured stratigraphic section.

Conditions controlling the genesis of the spheroids were established shortly after sedimentation. Development was subtly controlled by groundwater flow patterns and by various sedimentary structures. The enclosing redbeds provide an adequate source for the metals contained in the mineralized spheroids. Low-temperature chloride complexes originating from evaporative fluids concentrated during redbed formation are believed to have been responsible for transport of the metals to reduction sites. Precipitation probably occurred as a result of a change in redox potential governed by electrical self-potentials of various detrital and early diagenetic grains, particularly pyrite and/or Fe-Ti oxides.

Electron microprobe analyses reveal Cu, Ag, Fe, Ti, U, V and REE enrichments in reduction spheroid cores. Mineralized rings are less enriched in these elements but contain slightly greater concentrations of Ti-oxide minerals. Minerals observed other than bulk redbed constituents include: chatcoteite, covellite, cuprite, pyrite, ilmenite, rutile, mottramite, rooseelite, xenotime, monazite, native copper, azurite and native silver with trace amounts of alloyed Hg.

Reduction spheroids from the Upper Carboniferous Hopewell Group, Dorchester Cape, New Brunswick: notes on geochemistry, mineralogy and genesis

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The bajada-playa sequence of terrestrial Upper Carboniferous redbeds of the Hopewell Group at Dorchester Cape, New Brunswick, hosts innumerable reduction spheroids in fine- to coarse-grained clastic sedimentary rocks, paleosols and caliche beds. The spheroids are grey-green, typically 2 to 3 cm in diameter, and may contain a dark, mineralized central core and less commonly one or more mineralized rings, concentric about the core. They decrease progressively in average diameter from 2.75 cm at the base to 0.85 cm at the top of an overall upward-fining 250 m thick measured stratigraphic section.

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Electron microprobe analyses reveal Cu, Ag, Fe, Ti, U, V and REE enrichments in reduction spheroid cores. Mineralized rings are less enriched in these elements but contain slightly greater concentrations of Ti-oxide minerals. Minerals observed other than bulk redbed constituents include: chalcocite, covellite, cuprite, pyrite, ilmenite, rutile, mottramite, roscoelite, xenotime, monazite, native copper, azurite and native silver with trace amounts of alloyed Hg.

La séquence de bajadas-playas des formations rouges terrestres du Carbonifère supérieur du groupe de Hopewell à Dorchester Cape, Nouveau-Brunswick, abrite d'innombrables sphéroïdes de réduction dans des couches de caliche, de paléosol et de sédiments clastiques à grain fin à gros. Les sphéroïdes sont de couleur gris-vert, ils ont généralement 2 à 3 cm de diamètre et ils peuvent renfermer un noyau central minéralisé de teinte foncée de même que, moins couramment, un ou plusieurs anneaux minéralisés concentriques au noyau. Leur diamètre moyen diminue graduellement, passant de 2,75 cm à la base à 0,85 cm au sommet d'une section stratigraphique à affinement généralement ascendant d'une épaisseur mesurée de 250 m.

Les conditions ayant régi l'origine des sphéroïdes ont été établies peu après la sédimentation. Leur développement a été subtilement gouverné par les configurations d'écoulement des eaux souterraines et par diverses structures sédimentaires. Les formations rouges encaissantes constituent une source adéquate des métaux que renferment les sphéroïdes minéralisés. On croit que les complexes chlorurés de basse température provenant des fluides volatils concentrés pendant la constitution des formations rouges ont causé le transport des métaux à des points de réduction. Des précipitations sont probablement survenues par suite d'un changement du potentiel d'oxydoréduction gouverné par les polarisations spontanées électriques de divers grains diagénétiques détritiques et anciens, en particulier de la pyrite ou des oxydes de fer-titane.

Les analyses par microsonde électronique révèlent des enrichissements de Cu, d'Ag, de Fe, de Ti, d'U, de V et d'éléments des terres rares dans les noyaux des sphéroïdes de réduction.

Les anneaux minéralisés renferment des proportions moindres de certains de ces éléments, mais des concentrations légèrement plus fortes d'oxyde de titane. Outre les composants bruts des couches rouges, les minéraux observés comprennent de la chalcocite, de la covellite, de la cuprite, de la pyrite, de l'ilménite, du rutile, de la mottramite, de la roscoélite, du xénotime, du monazite, du cuivre natif, de l'azurite et de l'argent natif avec des quantités infimes de mercure allié.

[Traduit par la rédaction]

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INTRODUCTION

Reduction spheroids are widespread in continental and marine redbed sediments. Typically, mineralization by Cu, U and V in the dark central cores of spheroids (cf. Carter, 1931) in redbed sequences is accompanied by dissolution of hematite from the immediately surrounding reduced area; the result is a grey-green halo of bulk composition similar to the host rock (Parnell, 1988; Hofmann, 1991a, b). The reducing agent/mechanism has been variously suggested to be detrital organic matter (Prest *et al.*, 1969; van de Poll and Sutherland, 1976; Mykura and Hampton, 1984), migrating hydrocarbons (Hofmann, 1992; Curiale *et al.*, 1993), bacterial activity (Prest *et al.*, 1969; Hofmann, 1991a, b, c, 1993), meteoric water/brine mixing (Parnell, 1988), and electrochemical activity (Tilsley, 1980, personal communication 1995; Dyck and McCorkell, 1983). At Dorchester Cape, fully developed reduction spheroids are typically 2 to 3 cm in diameter, range to a maximum of 25 cm, and have a dark mineralized core surrounded by a grey-green halo of reduced sedimentary rock and, less commonly, one or more mineralized rings about the central core.

The occurrence of mineralized reduction spheroids has much in common with sediment-hosted stratiform Cu deposits in which important amounts of other metals may occur. As summarized by Rose (1989) and Brown (1992), these deposits form at temperatures <100°C at oxidation-reduction interfaces by the introduction of mineralizing fluids into rocks containing pyrite and/or organic materials. Favoured transportation media are low-temperature metal-chloride brines under the near-neutral oxidizing conditions reportedly prevalent in hematitic redbeds (Brown, 1992). Concerning possible source and transport of Cu, van de Poll and Sutherland (1976) showed that redbeds of the Hopewell Group contain between 22 and 56 ppm Cu, and that no more than 20 ppm of the total Cu in the redbeds is present in the cores of reduction spheroids (cf. Fischer and Stewart, 1961). The matter of source and availability of Cu is thus less problematic than the nature of the processes, geochemical and otherwise, that led to the very high (to 17%) concentrations of Cu and associated elements in the cores. Here we examine the distribution and morphology of the reduction spheroids, document their mineralogy and geochemistry, and suggest a plausible genetic model.

STRATIGRAPHIC SETTING

The shoreline at Dorchester Cape, New Brunswick (Fig. 1), exposes approximately 275 m (true thickness) of conglomerates, sandstones, mudstones and several well developed, dominantly calcareous paleosols. Fining-upward sequences are prevalent and reduction spheroids, although present in all lithologies, are generally more abundant in the lower half of the measured section (Fig. 2). The lower conglomeratic portion contains one limestone unit interpreted by van de Poll and Sutherland (1976) as a playa lake bed. Higher in the sequence are numerous gleyed horizons and calcretes.

A dominantly siliceous paleosol about 30 m below the base of the Boss Point Formation was chosen to mark the top of the measured section. The upper 25 m of the formation was not described due to poorer exposures and the sparse development of reduction spheroids.

These beds are equivalent to Hopewell Group strata, according to van de Poll (1994), who referred to the section as the Dorchester Cape Beds and suggested that they may be included with the Maringouin Formation, given Member status at the top of the Maringouin Formation, or designated a formation or group distinct from the Hopewell Group. The Hopewell Group occupies the stratigraphic interval at the base of the Cumberland Group (cf. Ryan *et al.*, 1991) overlying the Windsor Group, and is Late Visean-Early Namurian in age (H.W. van de Poll, personal communication, 1995).

MORPHOLOGY AND DISTRIBUTION OF SPHEROIDS

In conglomeratic units toward the base of the measured section, reduction haloes in some cases surround pebbles and large clasts (Fig. 3). Here, the haloes tend to mimic the shape of the clast, influenced perhaps by its self-potential (Tilsley, 1980; Hamblin, 1958, p. 25). Elsewhere, bedding planes and foreset beds served as preferred domains for reduction (Figs. 4, 5). In some instances, spheroids are so abundant on bedding planes that they coalesce, forming continuous grey-green layers. As shown in Figure 6, narrow bleached layers are also found perpendicular to bedding, especially in areas of crack fills and flame structures (Fig. 7). Hamblin (1958) described bleached zones along joints at high angles to bedding and attributed these bleached zones to increased permeability along the fractures. The ellipsoidal shape (see Fig. 5) of some reduction spheroids may also be attributed to preferential transmission of aqueous fluids, or from lower resistivity, along anisotropic planes such as bedding contacts. Uncompacted (circular in cross-section) burrows, filled with fine grained and/or coarse grained sediment (Figs. 8, 9), may occur in the same bed with both ellipsoidal and spherical reduction spheroids, suggesting that the ellipsoidal shape of some spheroids resulted not from compaction but from preferential transmission of fluids. Burrows, which in some extensively bioturbated units range from 0.65 to 1.0 cm in diameter, are typically devoid of reduction spheroids, implying that bioturbation may retard spheroid development on a local scale.

Overall, the average size (Table 1) of reduction spheroids decreases from 2.75 cm (average diameter) in the relatively coarse grained sediments at the base to 0.85 cm (average diameter) in the mudstones near the top of the measured section (see Fig. 2). The average core size ranges from 1% (in a siltstone) to 4% (in a mudstone) of the total volume of the spheroid, suggesting a relationship between grain size, its associated effects (e.g., porosity, permeability), and spheroid development.

Reduction spheroids are fairly common in the paleosols of the upper 160 m of the section. Typically, they are small (ca. 0.5 cm in average diameter) and contain black cores.

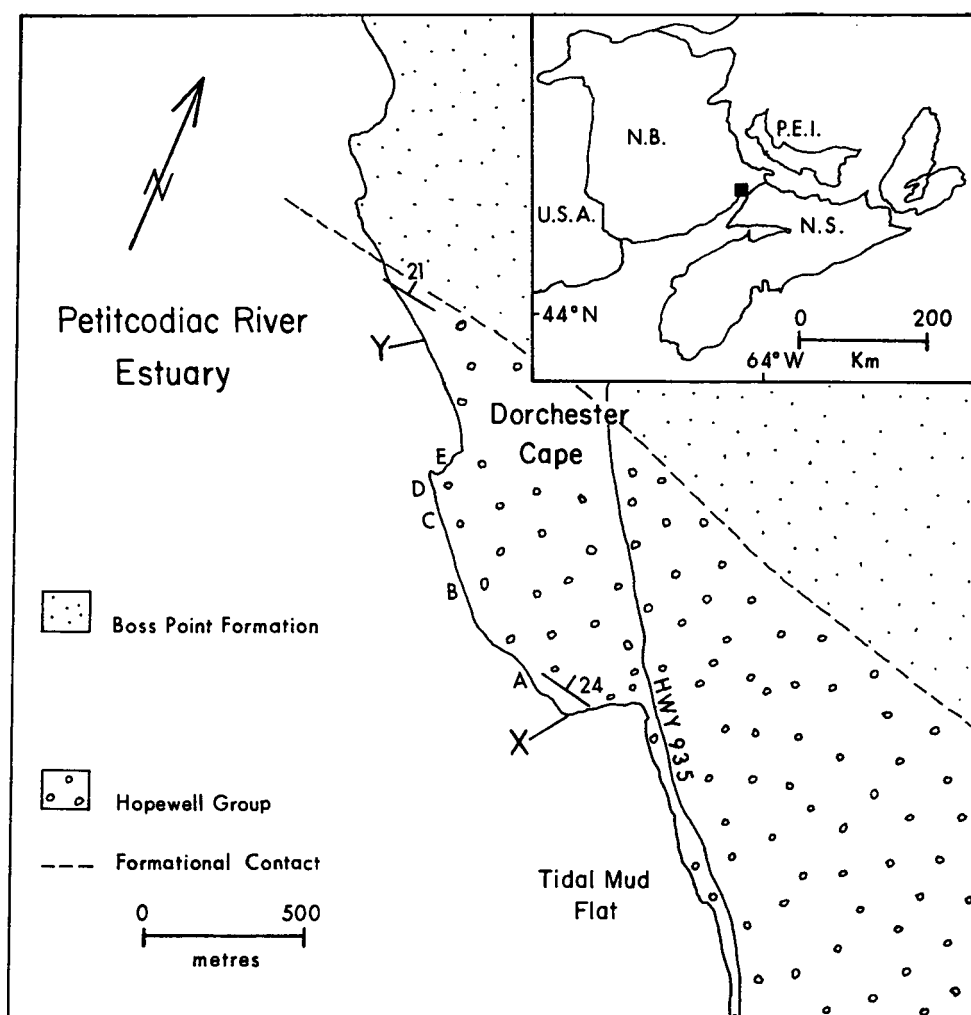


Fig. 1. Index and location maps for the Dorchester Cape Beds of the Hopewell Group. Points "A" through "E" are locations of photos presented in this paper. Locations "X" and "Y" represent the beginning and end, respectively, of the measured section. (Redrawn after van de Poll and Sutherland, 1976.)

Elsewhere, black mineralized rings surround the cores of some spheroids (Fig. 10).

ANALYTICAL PROCEDURE

Petrographic observations were made in reflected light and transmitted light on 20 polished thin sections containing reduction spheroids. Portions of the samples were mounted on aluminum discs, coated with carbon and examined using a JEOL-733 electron microprobe at an operating voltage of 15 keV, using a beam diameter of 1 μ m and a beam current of 15 to 25 nA. Examination was undertaken in backscattered mode, in which minerals exhibit an image intensity proportional to their atomic mass; hence heavy metal phases are prominent and readily distinguishable.

MINERALOGY AND GEOCHEMISTRY OF THE SPHEROIDS

All the cores examined showed an enrichment in V, present as the mineral roscoelite (Table 2a), as first reported by van

de Poll and Sutherland (1976). Roscoelite occurs particularly as a replacement of the cement/matrix of the rocks. Where replacement has been most intense, a mesh of thread-like roscoelite extends through the rock, and rims of detrital grains are replaced. Hofmann (1991b) pointed out that roscoelite is primarily responsible for the green colouration of the cores of reduction spheroids.

Although uranium minerals are reportedly common in the cores of reduction spheroids (Hofmann, 1991b), they are by no means ubiquitous in spheroids from Dorchester Cape. Traces of carnotite have been noted at several locations. Electron microprobe analysis of one sample (float) matches that of mottramite (Table 2b), with a formula of $[(\text{Cu}_{0.95}\text{U}_{0.05})_{0.24}\text{Pb}_{0.91}(\text{VO}_4)(\text{OH})]$ obtained by averaging seven analyses of the same sample. These two uraniferous-vanadiferous minerals, and the commonly occurring malachite and/or azurite, are probably late diagenetic minerals in spheroid cores. Lead at Dorchester Cape occurs as traces of galena in sparsely mineralized specimens containing little or no Cu or Ag (see also Fig. 2), or in mottramite, as noted above. Mottramite occurs as micrometre-scale intergrowths

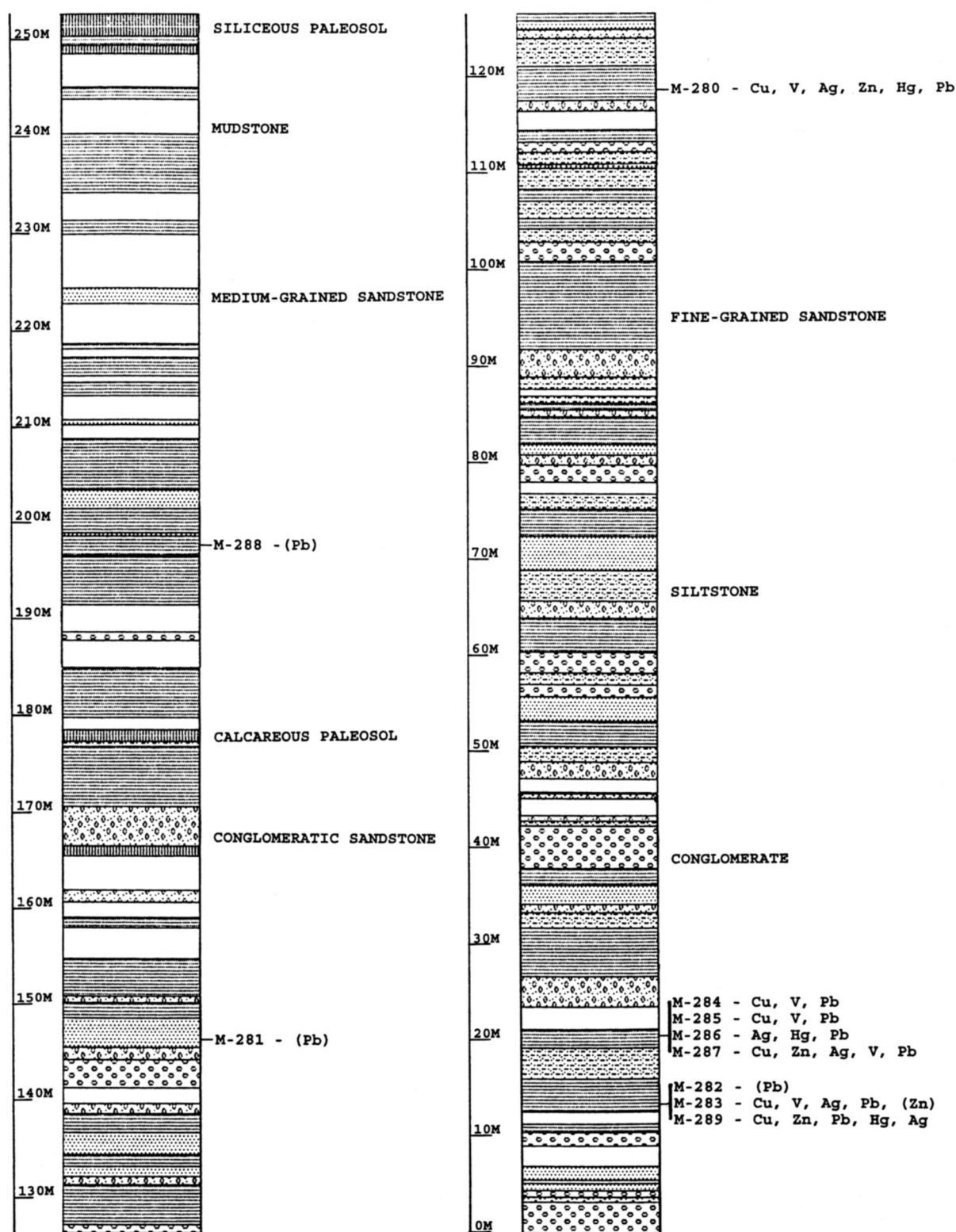


Fig. 2. Stratigraphic column of a portion of the Dorchester Cape Beds of the Hopewell Group at Dorchester Cape, New Brunswick. Chemical symbols indicate element enrichment in samples taken at that level. Symbols in brackets indicate minor elements. M numbers refer to samples housed in the Department of Physics, Engineering and Geoscience, Mount Allison University.

in a clay matrix. Consequently, electron microprobe analysis also incorporated Si and Al, which were deliberately omitted from the element list (Table 2b), as is (OH). Similarly, the Fe-bearing native silver is a fine grained intergrowth with roscoelite; therefore Al, Si, K and V are omitted from the

element list (Table 2c). These omissions account for the low totals for these analyses.

In addition to Cu sulphide minerals and native copper, van de Poll and Sutherland (1976) reported alloys of Ag and Hg at Dorchester Cape. We confirm Ag phases in sev-

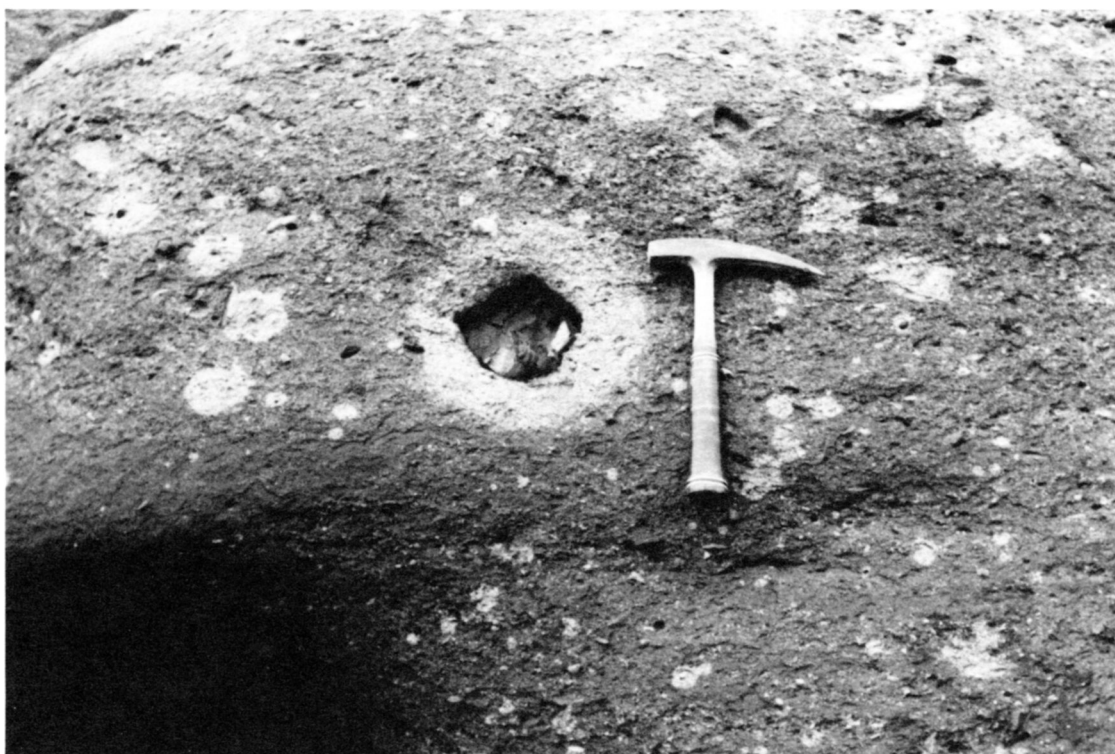


Fig. 3. Reduction halo surrounds large (15 cm diameter), angular clast in conglomerate. The reduction halo is between 3 and 5 cm in width and mimics the shape of the clast. A thin black mineralized coating (not shown in photo) on the clast lacks organic matter and consists mainly of an unidentified Cr-V-Al-silicate. Location on Figure 1: F. Stratigraphic position: 165 m.



Fig. 4. Reduction spheroids developed along bedding planes and foreset beds in a fine grained sandstone unit. Reduction spheroids (centre of photo) parallel to bedding planes. Location on Figure 1: E. Stratigraphic position: 127 m.

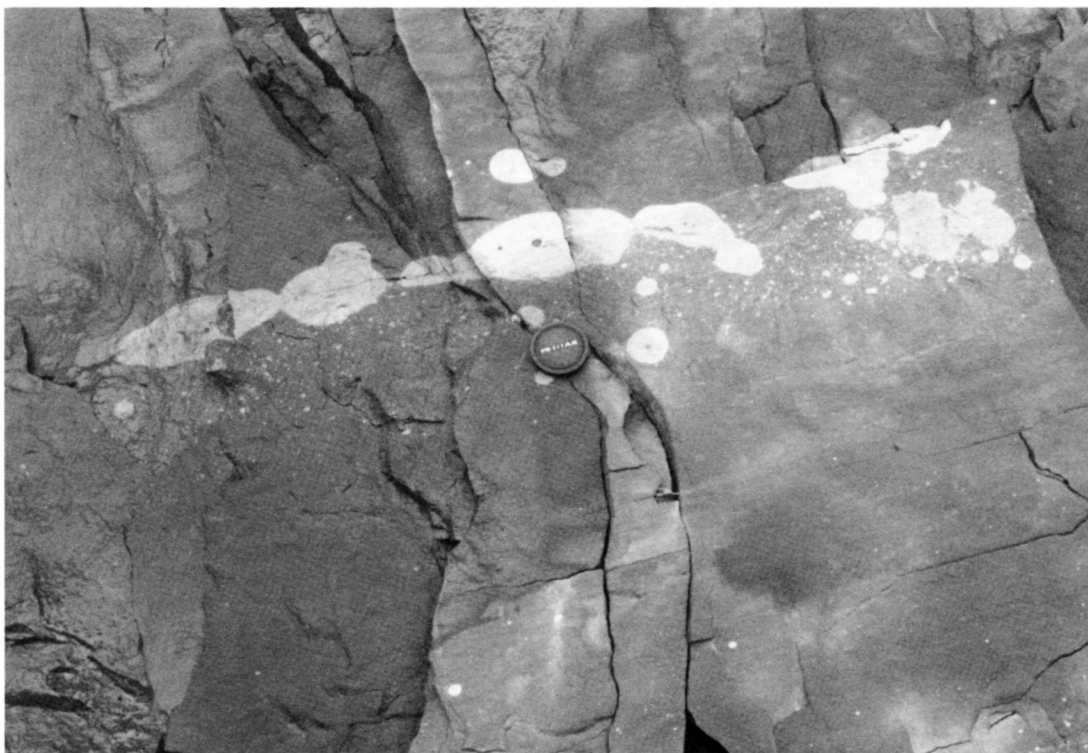


Fig. 5. Oblate ellipsoidal reduction spheroids in sandstone, coalescing along poorly-defined bedding plane. Reduction spheroids above and below the bedding plane are nearly spherical, suggesting that compaction of the unit was not the dominant factor in the elongation of the spheroids. Location on Figure 1: G. Stratigraphic position: 175 m.



Fig. 6. Crack fill in sandstone, infilled by material from overlying conglomerate. Reduced material in the vertical body surrounds clasts of igneous and carbonate material. Reduced material occurs parallel to bedding planes. Location on Figure 1: B. Stratigraphic position: 38 m.



Fig. 7. Flame structures in a siltstone unit containing numerous small reduction spheroids. Sharp peaks on the flame structures imply little compaction of unit after dewatering. Location on Figure 1: A. Stratigraphic position: 17 m.



Fig. 8. Burrow in mudstone unit filled with coarser sediment from the overlying coarse sandstone. Burrow is approximately 6.5 mm in diameter and almost perfectly round in cross-section. Location on Figure 1: D. Stratigraphic position: 115 m.



Fig. 9. Burrows in a mudstone unit containing numerous reduction spheroids. Spheroids are absent within the confines of the burrows or have grown into the burrows. Location on Figure 1: A. Stratigraphic position: 17 m.

Table 1. Average diameters and volumes for reduction spheroids with a visible core in several fine grained units (based on measurement of 50 to 70 examples from each unit).

Lithology and Stratigraphic Position	Average Sphere Diameter	Average Core Diameter	Ratio	Average Sphere Volume	Average Core Volume	Ratio
Mudstone @ 245 m	0.85 cm	0.24 cm	0.28	0.32 cm ³	0.01 cm ³	0.02
Mudstone @ 188 m	1.48 cm	0.48 cm	0.32	1.70 cm ³	0.06 cm ³	0.04
Siltstone @ 108 m	1.79 cm	0.43 cm	0.24	3.00 cm ³	0.04 cm ³	0.01
Mudstone @ 22 m	2.75 cm	0.88 cm	0.32	10.89 cm ³	0.36 cm ³	0.03

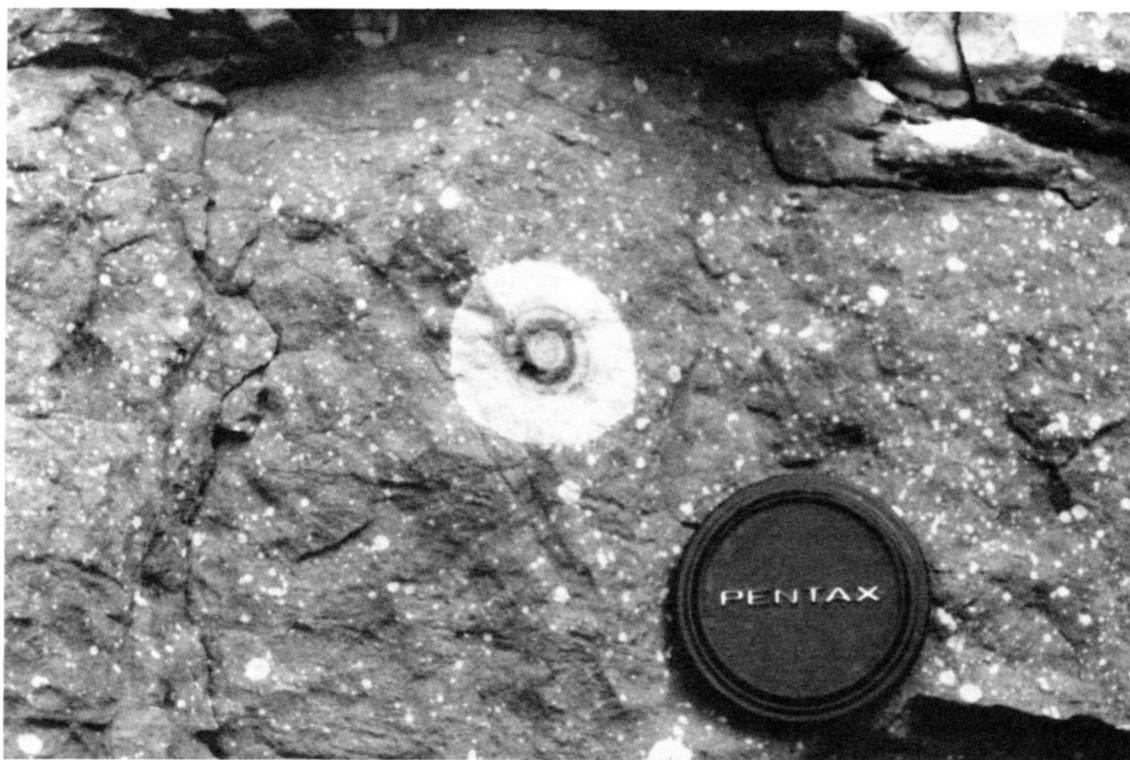


Fig. 10. Reduction spheroid showing rings developed around a mineralized core. Location on Figure 1: A. Stratigraphic position: 17 m.

eral samples (Table 2c). They consistently yield traces of alloyed Hg, but only at levels of a few atomic percent. A single Hg-rich phase was encountered, which detailed analysis proved to be a sub-micrometre intergrowth of Hg-rich and Hg-poor phases (Table 2c). However, it was not possible to determine whether the Hg-rich phase is a Ag alloy or a Ag-free phase. The native silver consistently contains traces (up to 5 atomic %) of Cu or Fe. Within a given sample, one of these metals is the predominant trace. A mean of 10 analyses from one sample yielded 1.30 atom % Hg and 4.14 atom % Cu in native silver, indicating that in general, Hg occurs only in trace quantities. In Ag-rich cores, native silver may be the predominant authigenic phase, occurring as replacement masses up to 50 μm wide (Fig. 11) after both detrital grains and carbonate cement.

In some samples, detrital titanomagnetite, ilmenite and rutile are partially replaced by limonite and pyrite in reduction spheroid haloes (cf. Miller, 1957). The Ti oxides here, as elsewhere in the Hopewell Group, may have their provenance in a buried Ti-P ferrogabbro complex about 15 km north-northwest of Dorchester Cape (Bell, 1984; Boyle and Stirling, 1994). Probably the oxides served to initiate the formation of reduction spheroids due to their relatively high self-potentials. To some extent the oxide phases have replaced feldspar grains (see Fig. 12A) and occur as a cement which post-dates, and may replace, normal calcite cement (Fig. 12B).

In Cu-rich cores, native copper, cuprite, chalcocite and covellite also occur as replacement and/or as pore (space) fillings. The intensity of Cu replacement is divisible into

progressive stages: (i) coating and/or replacement of the outer portions of detrital grains (Fig. 13A); (ii) replacement of cement/matrix to form millimetre-scale masses of Cu mineralization. The thread-like mesh of roscoelite is also replaced by Cu minerals. The margins of the Cu enrichment zones (Fig. 13B) show a sharp limit to the distribution of Cu-replaced grains, passing into roscoelite-replaced grains and matrix in the outer parts of cores (Fig. 13C). At the boundary between V-rich and Cu-rich zones, the Cu minerals appear to have replaced earlier growths of roscoelite (Fig. 13D).

A special effort was made to map chemical differences between core and ring of several samples (see Fig. 10). Native silver, roscoelite and mottramite show no difference in occurrence between core and rings. The only notable distinction recognized is a relatively greater concentration of Ti-oxide minerals in the rings.

Rare earth element (REE) phosphates occur in some samples, generally on a scale of tens of micrometres, and most are referable to monazite. In many cases it is difficult to discriminate authigenic from detrital REE phosphates in sediments. However, the authors' experience is that reduction spheroids from other localities commonly contain abundant REE phosphates, which exhibit fractionation of REE. Therefore, the xenotime recorded at Dorchester Cape (see Fig. 14) is probably authigenic.

Reduced organic carbon is notably lacking in these rocks (cf. Kemp *et al.*, 1994). This is not to imply that organic matter could not have influenced the development of reduction spheroids. Root structures have been observed at sev-

Table 2. Electron microprobe analyses of: (a) roscoelite, (b) mottramite, and (c) native silver in reduction spheroids from the Dorchester Cape Beds of the Hopewell Group.

(a) Roscoelite			
	1	2	
V	15.41	7.19	
K	7.49	4.78	
Al	9.11	7.26	
Si	20.31	16.50	
O	44.88	64.27	
Total	97.20	100.00	
(b) Mottramite			
	1	2	
Pb	43.15	12.96	
V	10.72	14.18	
Cu	9.56	11.28	
U	1.52	0.63	
O	16.86	60.95	
Total	81.81	100.00	
(c) Native silver			
	1	2	3
Ag	93.01	94.56	61.16
Hg	3.13	1.30	5.24
Cu	3.07	4.14	0.19
Fe	0.00	0.00	6.94
Total	99.21	100.00	73.53

Analyst J. Parnell. 1. Typical composition (wt. %); 2. Mean composition (atomic %) (n=10); 3. Typical composition of Fe-rich native silver (wt. %). Oxygen calculated by stoichiometry.

eral locations, although there does not seem to be any spatial relationship between them and the reduction spheroids. Whether syngenetic (e.g., plant remains) or transitory (e.g., fluid hydrocarbons), organic matter could have been lost during diagenesis (Adams *et al.*, 1974; Brown, 1992).

DISCUSSION AND CONCLUSIONS

Sedimentological and morphological evidence support the concept that the metals enriched in reduction spheroids were supplied via groundwater. The occurrence of ellipsoidal reduction spheroids in the same bed with circular bur-

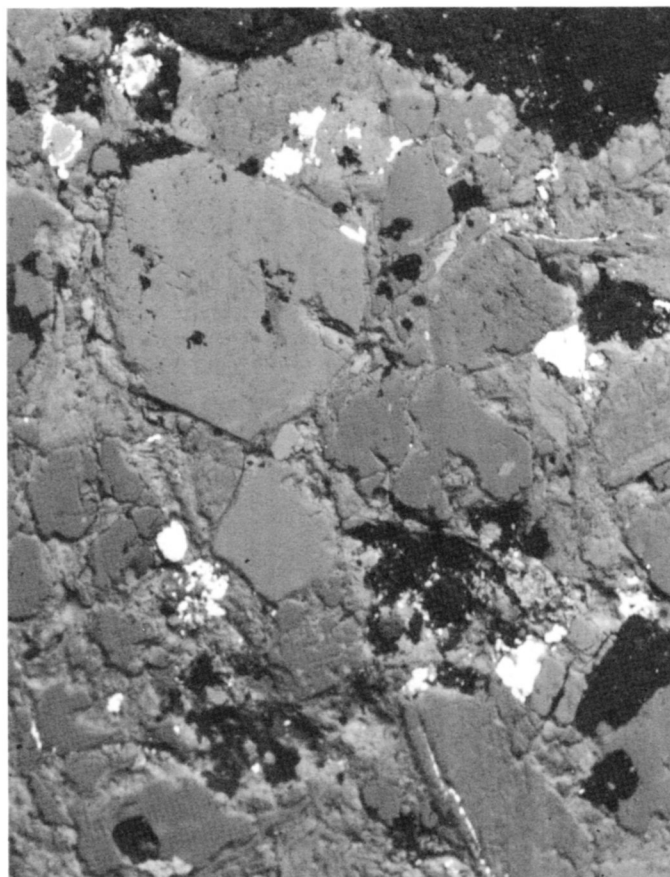


Fig. 11. Reflected-light photomicrograph, showing disseminated crystals of native silver (bright) in reduction spheroid. Ag replaces grains and matrix (the dark colour is mounting resin). Field width 1.2 mm.

rows (especially burrows filled with easily compactable fine grained sediment) indicates that the ellipsoidal shape of some spheroids is not due to compaction, but preferential growth along one axis. The occurrence of reduced layers and coalescing reduction spheroids along bedding planes, foreset beds, joints (Hamblin, 1958) and other zones of heightened permeability (e.g., crack fills) implies that fluid flow influenced the reduction process. The groundwater which contributed to the development of the spheroids may have originated within the redbeds and/or evolved as pore fluid from the underlying Windsor Group. In addition to the redbed sandstones, some igneous clasts in the conglomerates in the lower part of the Dorchester Cape Beds were probably derived from the Coverdale Ti-P ferrogabbro complex (Boyle and Stirling, 1994). These constituents would have been potentially important contributors of Ti and V, as well as REE and P, to the development of the reduction spheroids. Clearly, an adequate source of metals for the spheroids is not a problem.

According to Rose (1989) and Brown (1992), low-temperature chloride-rich brines are the most common ore fluids in redbeds. Under intermediate oxidizing conditions, cuprous chloride results in significant Cu solubility. At Dorchester Cape, the chloride may have migrated from the Windsor Group, or more likely from the evaporative fluids (evidenced by presence of caliche beds) concentrated during redbed

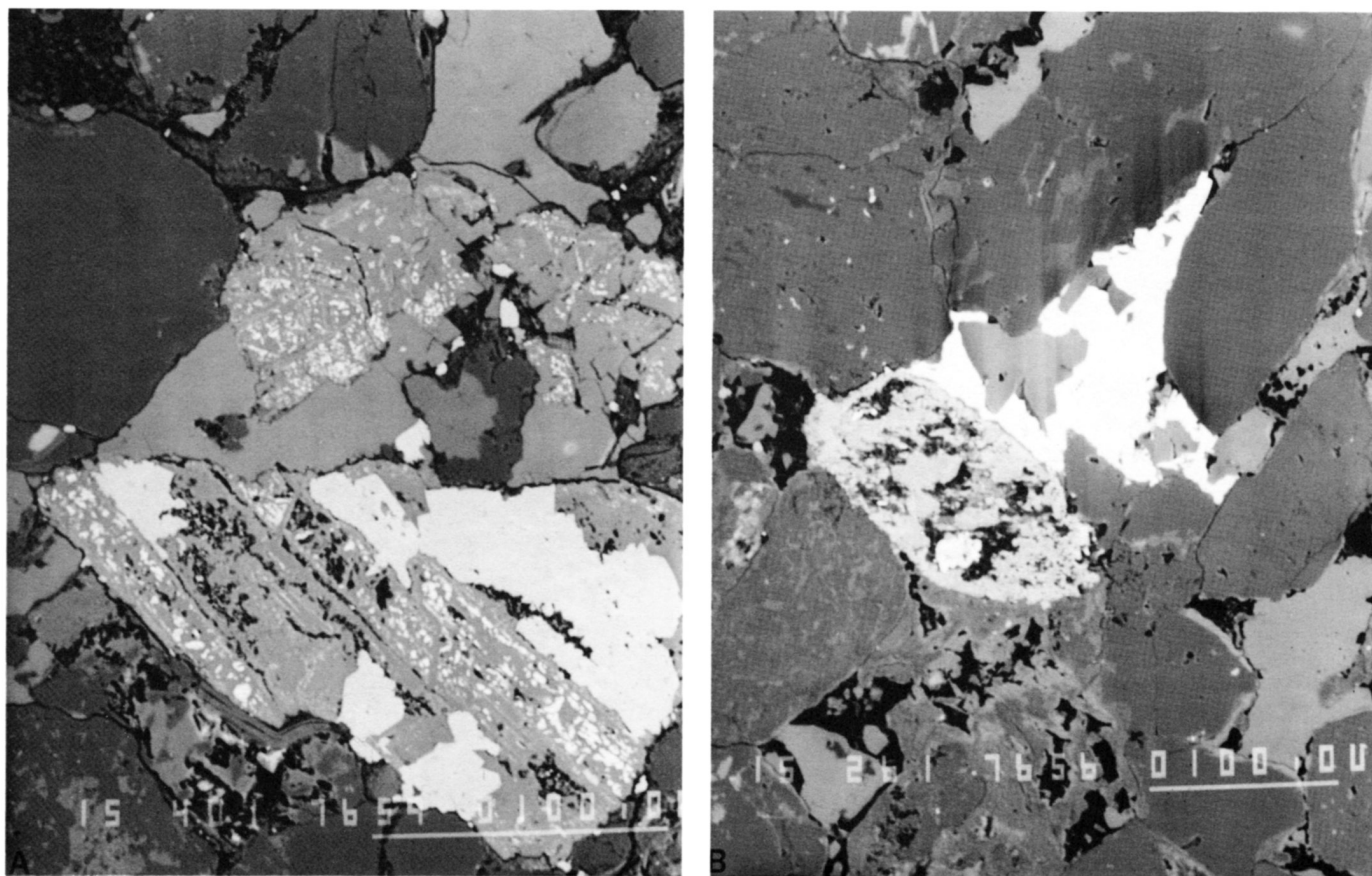


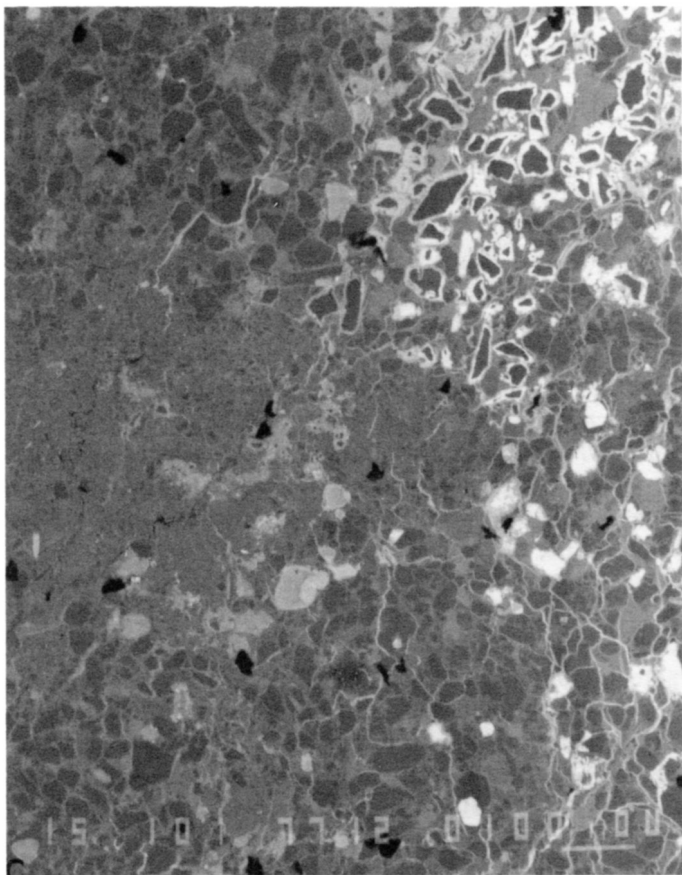
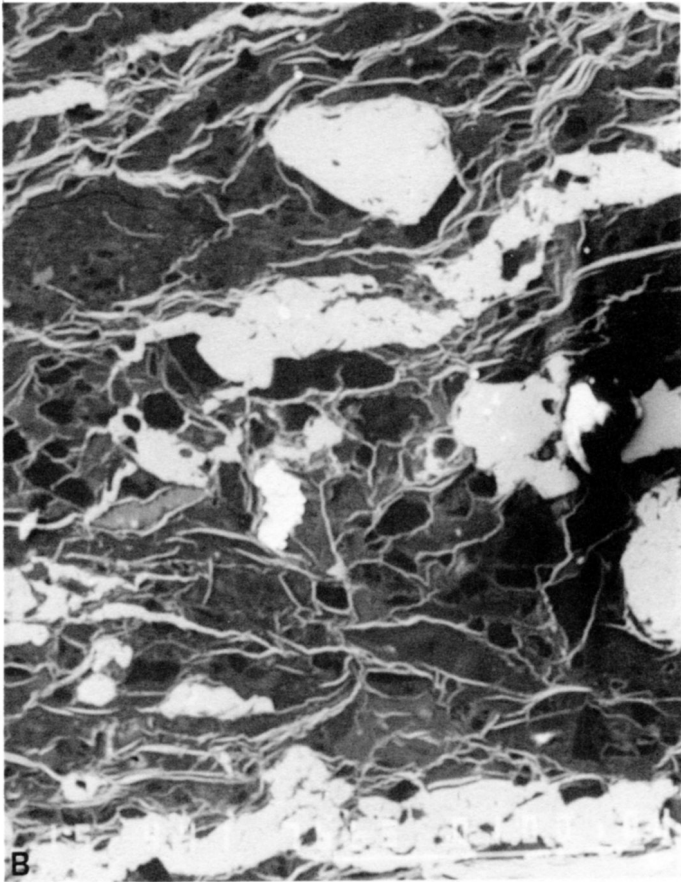
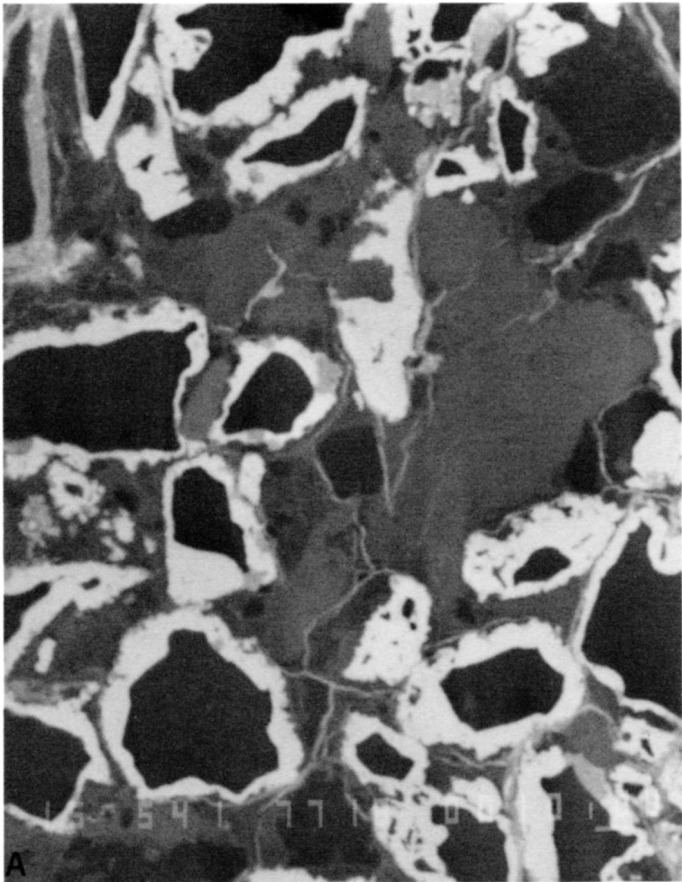
Fig. 12. Reflected-light photomicrographs showing Ti-oxide phases (bright) in sandstone hosting reduction spheroids. (A) as replacement of feldspar grains, (B) as cement between detrital grains following calcite (light grey) cement; the large rounded grain "I" is a heavily altered detrital Fe-Ti oxide. Field widths: (A) 280 microns, (B) 440 microns.

deposition. A slightly alkaline pH common to groundwater and pore fluids at low temperatures might account for the lack of Co and Zn and the paucity of Pb in the reduction spheroids (Rose, 1976). Furthermore, under near-neutral pH conditions, Co, Zn and Pb are unlikely to have as mobile as Cu and Ag due to their selective adsorption upon Fe oxides and other minerals present in the redbeds (Zelinski *et al.*, 1983; Rose, 1989).

A general decrease in grain size of the sediments upward in the measured section suggests a relatively slower rate of burial. As a result, fluid transport, and hence metal supply, was probably relatively constrained in the top part of the section. This correlates well with the reduced number and size of reduction spheroids in the upper beds. The increased development of paleosols towards the top of the section hints at long diastems in the depositional record. Alternatively, a facies change from channel sands to flood plain muds might increase the likelihood of paleosol formation. In either case, early processes, otherwise instrumental in reduction spheroid formation, may have been suppressed. Consequently, slow burial would allow the degradation of organic materials before anoxic conditions are attained (Thompson *et al.*, 1989). The fact that reduced organic matter is lacking in the Hopewell Group does not, of course, preclude its having perhaps played a part in the reduction process at some earlier stage. During early diagenesis, humic

acid-bearing solutions, derived from organic matter, may have caused the widespread alteration of detrital Fe-Ti oxides (Fig. 12B) in these rocks (Adams *et al.*, 1974). Elsewhere in New Brunswick and Nova Scotia there is much evidence of the preservation of plants in Late Visean and in Namurian fluvial sequences. A host of factors including water table fluctuations and seasonal climatic changes can influence the growth and preservation of plants, the former presence of which can be inferred from bioturbation such as root structures, which have been noted in the Dorchester Cape beds.

Groundwater flow was the mechanism by which metals were supplied to local reduction centres (e.g., early diagenetic pyrite, detrital oxide grains and/or organic matter). Dewatering may also have played a role at a very early stage (cf. Brown, 1992). Mineralized rings in reduction spheroids have been attributed to changes in water chemistry, redox potential or temperature conditions under which a spheroid is developing (Hofmann, 1990), to mixing between fluids of different redox status (Metcalf *et al.*, 1994), and to counter-diffusion of mineral species which produces Liesegang rings (Harrison, 1975; Hofmann, 1990). In the Hopewell Group, the dominant factor may have been changes in redox potential. Restriction of rings to only certain spheroids in some beds suggests that they are the result of subtle changes and/or differences on a very local scale.



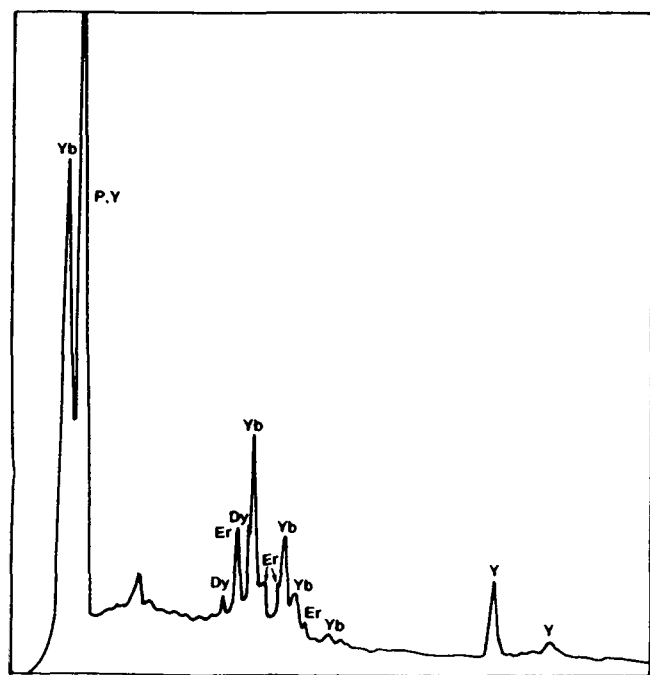


Fig. 14. Qualitative electron microprobe peak plot for xenotime variety (dominated by ytterbium and yttrium).

In summary, we conclude that:

- (1) Metal-enriched groundwater was the supply of metal ions to growing reduction spheroids. Relatively high permeabilities and related changes in resistivity along bedding planes and other anisotropic zones account for the ellipsoidal shape of some spheroids and for their intimate relationship with various primary structures. This has important implications for the use of reduction spheroids in structural studies, which assume any deviation from an original spherical shape is due to strain.
- (2) Metals were derived from the oxidation of igneous clasts and detrital grains within the conglomerates and sandstones of the Dorchester Cape Beds, and also from the dissolution of hematite from within the reduced halo of the spheroid itself.
- (3) Progressive reduction in the size and abundance of reduction spheroids, upwards in the section, corresponds to an overall fining upward sedimentary pattern. Key controls of the size diminution of spheroids in the uppermost 80 m of the measured section were the changing rate of burial and decreased permeability.
- (4) Mineralization was less controlled by reduced organic matter than by local self-potentials of detrital and early diagenetic mineral grains.
- (5) Minerals present in reduction spheroids at Dorchester Cape include: chalcocite, covellite, cuprite, pyrite, il-

menite, rutile, mottramite, carnotite, roscoelite, native silver, native copper, malachite, azurite, monazite and xenotime. Ti oxides are relatively concentrated in the rings of spheroids as compared to their cores.

- (6) The most varied geochemistry of the spheroids occurs in the lower 80 m of the 250 m measured section. Authigenic REE phosphate mineralization is sparse throughout the section.

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Fig. 13. Reflected-light photomicrographs showing Cu mineralization in reduction spheroid cores. (A) detrital grains (dark) replaced in outer parts by Cu minerals (bright), in matrix of roscoelite (grey); (B) Cu mineral masses (bright) representing replacement of whole detrital grains. Thread-like mesh of Cu minerals cutting roscoelite-rich matrix; (C) Cu mineral (bright) replacing roscoelite (grey) grain coatings and matrix; (D) close-up of boundary in (C). Field widths: (A) 210 microns, (B) 260 microns (C) 1.1 mm, (D) 160 microns.

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