Black shale geochemistry: A possible guide to Ordovician oceanic water masses

By WILLIAM B. N. BERRY

Most modern oceanic plankton faunas are circumscribed in their occurrence by the distribution of the water mass in which they live. Even in shelf seas, water mass properties exert such a control on plankton distribution that certain taxa may be used to recognize the presence of a particular water mass. Distribution of different but seemgly coeval Ordovician graptolite faunas suggests that water mass characteristics played the same role in plankton distribution in the past as they do today. Geochemical analyses of selected Ordovician graptolite-bearing shales indicate that each shale bears trace metals in combinations and abundances unique to each. Trace metals in coeval Late Ordovician shales in New York and the western United States differ in a manner consistent with variations in graptolitic fauna. Modern ocean water masses also have trace metal contents unique to each. Plankton tissues take up these metals which may be transported relatively rapidly to the sea floor by zooplankton faecal pellets. If the pellets fall into anoxic environments, the sediment will reflect the trace metal composition of the waters in which the plankton lived because the metals will remain essentially in place as sulphides. The distribution of water masses may therefore be traced by using the trace metal geochemical signatures of black shales.

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Distribution patterns exhibited by Ordovician graptolites have attracted considerable attention (e.g. Berry 1979; Bulman 1971; Skevington 1974). The Ordovician graptolite faunal regions and provinces are characterized by unique, primarily endemic taxa. For example, isograptids and pseudisograptids typify the Pacific faunal region. These taxa are not found in the Atlantic faunal region. Coeval Atlantic region faunas typically include pendent (tuning fork shape) didymograptids of the *D. murchisoni* group. Skevington (1974) suggested that temperature difference in Ordovician oceanic surface waters may have been a major factor in development of the two Ordovician graptolite faunal regions.

Another, subtle pattern in graptolite faunal associations may be recognized within the context of the faunas that characterize the regions and provinces. Dover *et al.* (1980) described such a pattern in an analysis of coeval sets of Middle Ordovician graptolite collections from stratigraphic sections in thrust belts in central Idaho. The faunas from the Trail Creek section are typified by the presence of distinctive pseudisograptids whilst apparently coeval faunas from the Little Fall Creek section, are characterized by the presence of glyptograptids of the *G. austrodentatus* group. Pseudisograptids are rare in the latter section. Certain isograptid taxa are common to both areas. The stratal sequences in both areas have been sampled extensively over a number of years by several different collectors and sampling bias does not seem to be a significant factor in the faunal difference.

In Bruton, D. L. (ed.), 1984. *Aspects of the Ordovician System.* 177–181. Palaeontological Contributions from the University of Oslo, No. 295, Universitetsforlaget.

An explanation for the small scale differences in Ordivician graptolite associations

The small scale differences among seemingly coeval Ordovician graptolite faunas in a number of localities have remained despite intensive collecting and are clearly real rather than due to preservational or sample bias.

One approach to understanding the reasons for these differences among plankton faunas from ancient oceans is to seek comparable or analogous patterns among plankton faunas in modern oceans. Controls on distribution of modern plankton faunas may be recognized. Potentially, distribution of plankton faunas in ancient seas may have been controlled by similar environmental factors.

Russell (1952), Bradshaw (1959) and Fager & McGowan (1963) documented the relationship that major modern oceanic plankton faunas are limited to specific oceanic water masses. Whereas these reflect plankton fauna-oceanic water mass relationships at a relatively broad scale, more detailed analysis of plankton faunas has revealed similar relationships but at a smaller scale. Fraser (1965) recognised eight plankton associations in the North Sea and found that each of these was limited in its distribution by the limits of the water mass in which it existed and the unique physical and chemical properties of the water. Temperature and salinity are the primary properties involved in the differences between water masses.

Johnson & Nigrini (1980, 1982) described radiolarian associations in surface sediments of the western and eastern parts of the Indian Ocean and found that the distribution of the tests of these planktonic organisms in the surface sediments closely reflects water mass distribution. Thus, not only may the plankton living in a water mass, but also their remains in surface sediments reflect control on their distribution by the water mass in which they live.

Those faunal associations found in the present North Sea and especially those in the Indian Ocean surface sediments that reflect water mass control over their distribution, suggest a possible explanation for the small scale differences cited among coeval Ordovician graptolite faunas. The differences described may indicate that specific graptolite associations were restricted to particular oceanic water masses.

Patterns similar to those described for Ordovician graptolites have been recorded among Palaeogene and Neogene plankton faunal associations (Sancetta 1978, 1979). These faunas, obtained from cores in the Pacific Deep Sea drilling programme (Keller 1978) have proved useful in documenting palaeooceanographic and palaeoclimatic changes through time.

Trace metal geochemistry of Ordovician graptolitic shales

As an aid in tracing rock units that bear a unique graptolite association, and to more fully explore the possibility that water mass properties did influence the distribution of Ordovician graptolite associations, trace metal compositions of selected Ordovician graptolite-bearing strata have been examined. This approach to an understanding of small scale Ordovician graptolite biogeography has developed from results of studies of trace metal associations in modern oceanic water masses. Bewers *et al.* (1976) and Campbell & Yeats (1982) noted that "biological uptake of metals" takes place near the surface in present-day oceanic water masses and that some have unique trace metal associations. Certain plankton appear to have trace metals in their tissues that reflect the trace metal species present in the water. When these plankton are preserved in ocean floor sediment such that decay of their tissues is retarded and release of contained metals inhibited, then the chemistry of the sediments and rocks formed from them, will reflect the trace metal composition of the surface waters at the time the plankton lived.

The unique chemical characteristics of the *Dictyonema flabelliforme sociale*-bearing phyllites at Nordaunevoll, eastern Trøndelag, Norway enabled Gee (1981) to trace these phyllites in the field. Gee (1981: 93) stated that "trace element (V, Mo, U) analysis of the Nordaunevoll phyllites has demonstrated a chemistry that is strikingly similar to that of sediments of similar type and age on the Baltoscandian Platform in Skåne and Östergötland". He suggested that it might be "possible to identify similar tectono-stratigraphic levels in the Swedish Caledonides of northern Jämtland and Västerbotten, and elsewhere in the mountain belt".

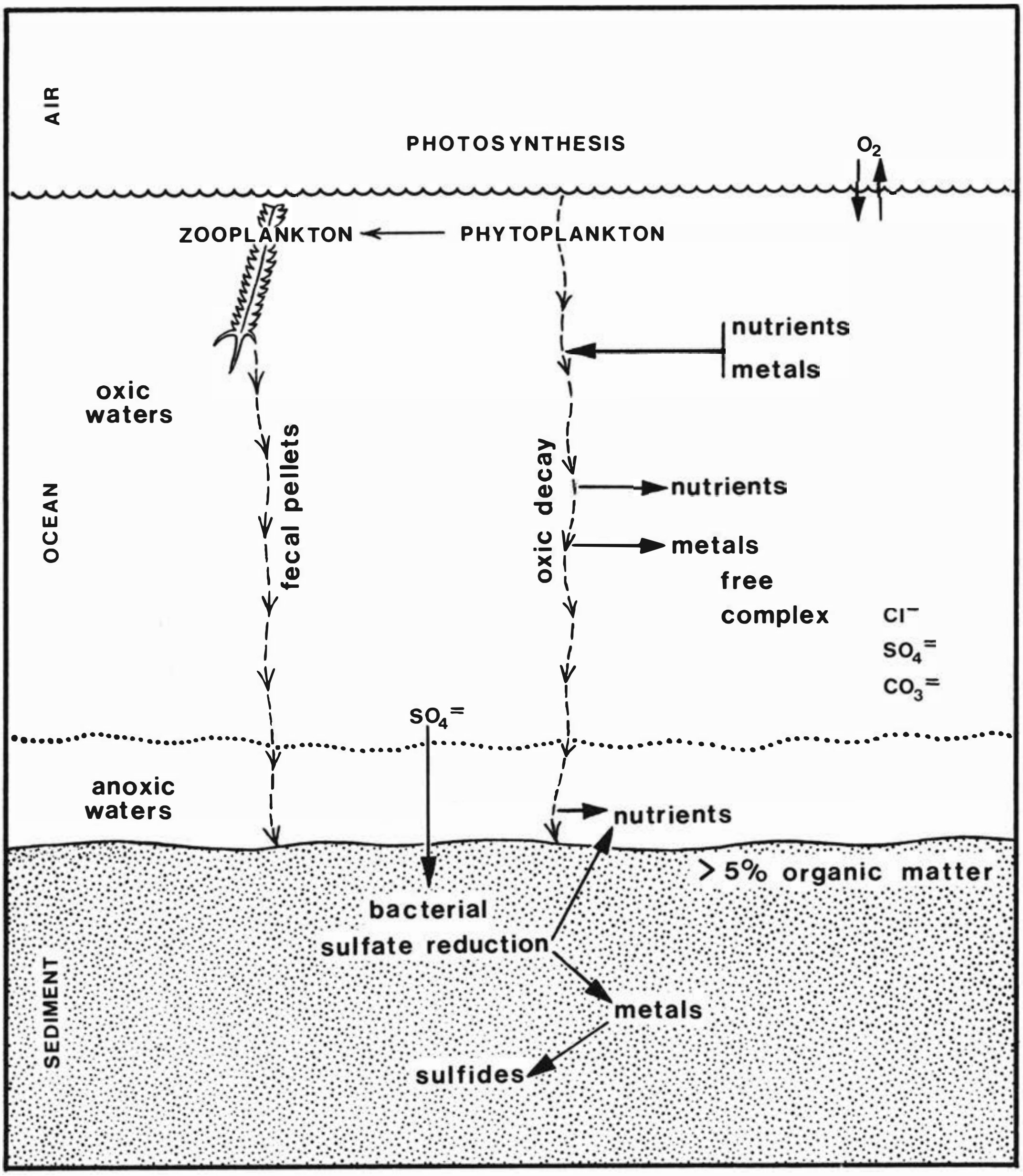

Fig. 1. Schematic diagram of an Ordovician oceanic environment in which graptolites may have lived. The diagram suggests that phytoplankton tissues may be "packaged" into zooplankton faecal pellets, thus providing a mechanism for rapid deposition of metal-bearing organic material. Anoxic bottom waters will result in sulphate reduction which may lead to metals being preserved essentially "in place" as sulphides.

Gee also noted that not only may trace metal geochemistry of the *Dictyonema*-bearing shales play a role in tracing them from area to area, but also it may be useful in biogeographic and palaeogeographic reconstructions as a consequence of identifying these shales in remote areas by their geochemical signature.

Poole & Desborough (1981) and Gee (1981) drew attention to the relatively high (more than 5 percent) organic carbon content of (Lower?) Palaeozoic black shales that bear significant quantities of metal sulphides. Anoxic depositional environments in which organic matter is not fully decomposed by oxidation is important to the preservation of trace metals contained in plankton that fall partly decayed to the sea floor. Under anoxic conditions, many metals tend to form sulphide complexes and to remain in place.

Plankton tissues bearing trace metals may accumulate on the sea floor relatively rapidly by incorporation in faecal pellets (Fig. 1). Smayda (1971) and Porter & Robbins (1981) noted that zooplankton faecal pellets may preserve planktonic organisms in a partially decayed condition both by "packaging" them in pellets that drop relatively quickly to the sea floor and by protecting the organic matter with an organic (probably mucous) rind on the outside of the pellets. The rind retards decomposition by oxidation in oxygenerated waters. Porter & Robbins (1981) examined samples of dark, organic-rich shales of different ages from a number of localities and suggested that faecal pellets were the most abundant organic particles in the shales that they studied and that such pellets appear to be a major source of organic matter.

The trace metal composition of late Ordovician (approximate equivalent of the *Dicranograptus clingani* Zone of Britain), Snake Hill Shale in eastern New York state and approximately coeval black, graptolite-bearing Vinini Shale in Nevada has been determined using neutron activation (see Perlman & Asaro 1969; Alvarez *et al.* 1982, for technique). Poole & Desborough (1981) also recorded geochemical analyses of samples from the Vinini Shale. Analyses of these coeval late Ordovician shales from eastern and western North America that have somewhat different graptolite faunas, show the Vinini Shale, to have relatively greater quantities of chromium, molybdenum, uranium, and vanadium than does the Snake Hill Shale whilst the latter bears significant quantities of cobalt, iron, manganese, and titanium. The difference in trace metals between the shales is consistent with differences in graptolitic faunas of each. Potentially, the trace metal composition of the Snake Hill Shale reflects the influence of waters from the deltaic environments in eastern New York and adjacent areas described by Bretsky (1970) and Dennison (1976).

Conclusion

Trace metal composition of Ordovician graptolite-bearing shales may provide a useful tool in correlations (Gee 1981), and it may reflect differences in water mass chemistry in ancient oceans as is indicated by the analyses of trace metals in the Snake Hull and Vinini Shales. Poole & Desborough (1981) and Trudinger (1981) noted the possibility that Lower Palaeozoic organic rich shales may bear metals in sufficient quantities to make them potentially valuable ore deposits. Trace metal analyses of Ordovician graptolite-bearing strata, though seldom carried out to date, may therefore prove to be economically important as well as significant in correlation and in understanding graptolite biogeography.

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