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Nutrient-enriched waters and the early skeletal fossil record

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Abstract: This paper examines the role of stratified, oxygen-depleted and nutrient-enriched water masses (NEW) in transforming the fossil record over the Precambrian–Cambrian boundary interval. The following may serve as markers for the encroachment of NEW over low-latitude cratons: trace-element enriched black shales, 'stone coals' and hydrocarbon source rocks, phosphorites, phosphatized shells and organic matter, sponge spicule cherts, early appearance of silica and phosphatic skeletons, appearance of *Anabarites* and *Coleoloides* biofacies, peak diversity of phosphatic species, occurrence of black shale lagerstätten and light $\delta^{13}C$ values of carbonates. Nutrient-depleted waters (NDW) are inferred over inner cratonic areas, and nutrient-starved waters (NSW) may well have developed over deeper waters at times through the later Cambrian, related to the effects of sea-level rise and salinity stratification. Carbon isotopic fluctuations are suggested to record the history of these water masses, with major changes in carbon burial and palaeoproductivity. The latter may well imply episodes of 'greenhouse' climate, with globally raised levels of carbon dioxide and relatively high ocean temperatures.

The aim of this paper is to examine the influence of stratified, nutrient-enriched waters (NEW) on the biosphere over the late Precambrian–Cambrian interval, using evidence from the skeletal fossil record and carbon isotopes. Changes in nutrient supply would influence both marine productivity and ocean-atmosphere chemistry, and may have played a role in the increased invertebrate biomass and fossil diversity during the 'Cambrian explosion'. On the practical side, an attempt must be made to understand the influence of nutrient supply upon fluctuations in stable carbon isotopes, an important new tool for Precambrian–Cambrian event stratigraphy (e.g. Aharon *et al.* 1987; Brasier *et al.* 1990; Kirschvink *et al.* 1991), now being tested within IGCP Project 303.

Many explanations have been put forward to explain the 'Cambrian explosion' (*see* Stanley 1976; Brasier 1979, 1981; Conway Morris 1987; McMenamin & McMenamin 1990). Of these, the 'nutrient-stimulus scenario' has the potential to explain a wide variety of phenomena. This hypothesis has arisen gradually from evidence for widespread evaporites, anoxia and stable isotopic changes, plus the occurrence of diverse and abundant phosphatic shells contemporaneous with phosphatic sediments over the boundary interval (e.g. Rhodes & Bloxam 1971; Degens & Stoffers 1976; Holser 1977; Chamberlain & Marland 1977; La Barbera 1978; Brasier 1980; 1990*a*,*b*, 1991*a*; Cook & Shergold 1984, 1986; Donnelly *et al.* 1990). Briefly stated, it infers a build-up of PO_4, Si, trace elements and dissolved organic matter in stratified marine reservoirs along the rifting margins of low-latitude continents during the latest Precambrian (*c.* Kotlinian) regression. These elements were later delivered into surface waters, broadly contemporaneous with the widespread secretion of phosphatic or siliceous skeletons, and the massive deposition of phosphorites in shallow embayments. Such phosphatic events were episodic, associated with sea-level pulses through the Cambrian (Notholt & Brasier 1986; Shergold & Brasier 1986), and enhanced the early fossil record through localized taphonomic windows (Brasier 1990*a*). They may also have exerted an ecological influence on early skeletal assemblages, favouring those dominated by *Anabarites trisulcatus* and associated forms. Evidence is now beginning to emerge for relative nutrient-depletion landward of the outer platform margins, where archaeocyathan 'reefs' and endemic trilobites flourished during the early Cambrian (see below; Brasier 1990*b*, 1991*a*).

This paper looks more closely at this scenario. It begins with a theoretical discussion of the biological carbon cycle and the role played by phosphorus and other nutrients.

Phosphorus and the biological carbon cycle

Figure 1 provides a simple model for the biological carbon cycle in late Precambrian and Cambrian times. By analogy with the present day, carbon dioxide occurred mainly as dissolved marine bicarbonate in the oceans and interacted with three other reservoirs that involved the biosphere: (1) $CaCO_3$ minerals (precipitated by inorganic or microbial processes or by biomineralization), leading to carbonate sediments; (2) organic carbon of primary producers (mainly cyanobacteria, benthic algae and phytoplankton), a proportion of which was buried in sediments as particulate organic matter but a large part may have remained in the water column as dissolved organic matter; (3) organic carbon of heterotrophic consumers (as bacteria, protists and metazoans) which may also have led to particulate and dissolved organic matter.

The further subdivisions of reservoirs into boxes (Fig. 1) draws attention to evolutionary changes over the boundary interval, in each case towards the right-hand box (i.e. biominerals, metazoans, benthic algae and phytoplankton). The possible effects of these changes upon the carbon and nutrient cycles will be examined in a separate paper.

Several processes of organic synthesis are known to result in disequilibrium fractionation of carbon isotopes. Thus photosynthesis by primary producers shows a preference for the lighter isotope (^{12}C), leaving surface waters relatively enriched in ^{13}C. Heterotrophic organisms consume this light carbon, releasing lighter carbon dioxide back into the ocean. In the case of methanogenic and sulphate-reducing bacteria, their anaerobic metabolism results in a further fractionation towards lighter organic carbon (e.g. Schidlowski *et al.* 1983).

Where light and temperature are optimal, availability of dissolved nutrients (mainly P, Fe or nitrate) controls the limits of primary production and hence of carbon isotope fractionation. Thus a trend towards heavier carbon isotopes cannot

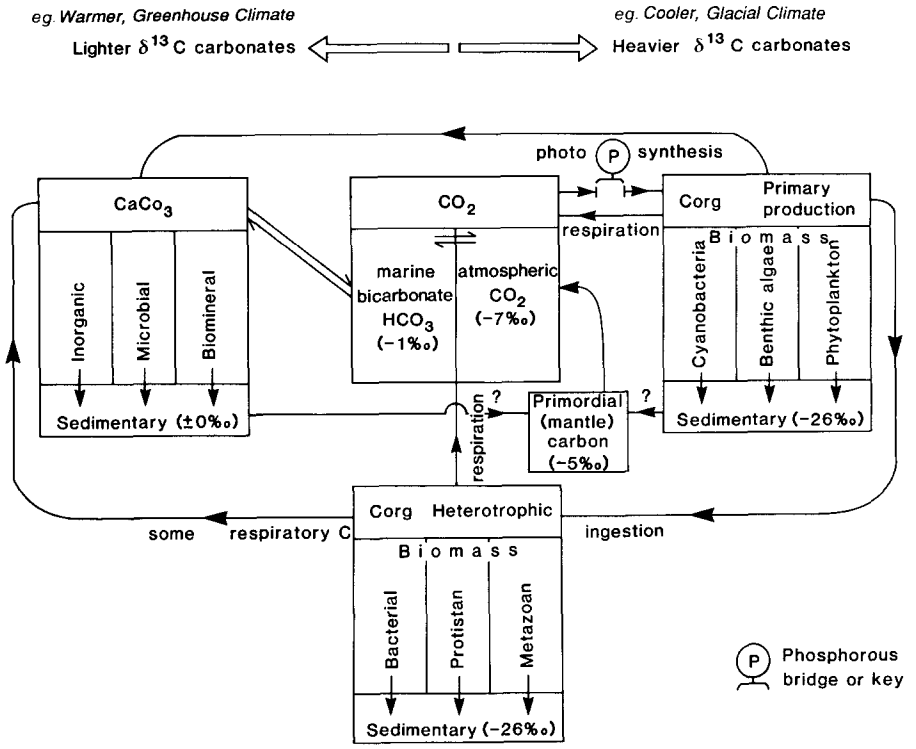

Fig. 1. Box model of the biological carbon cycle, adapted to the marine biosphere of the Precambrian–Cambrian boundary interval. Typical present day $\delta^{13}C$ values are shown (based on Schidlowski *et al.* 1983). The strong climatic changes that may result from fluctuations in partial pressures of the 'greenhouse gas' carbon dioxide, require further testing from the rock record.

take place in sea-water unless there is an adequate supply of limiting nutrients. Of these, nitrates are believed to play a major short-term role, related to the balance between microbial nitrate-fixation in surface waters and denitrification associated with fluctuating oxygen minimum zones at depth (e.g. Codispoti 1989). The oxygen minimum zones off the west coasts of California and South America provide modern examples of NO_3-limited ecosystems, where excess phosphate and silica are removed into sediments. These may provide analogies for the nutrient pathways of phosphogenic platform margins of the late Precambrian and Cambrian. Over the longer span of Quaternary glacial cycles, a shortage of iron nutrients may have reduced productivity during interglacial transgressions, owing to the reduction of land-derived dust particles (Martin & Fitzwater 1988).

Three factors are suspected to push a shallow marine ecosystem towards P-limitation: extensive nitrate-fixation by cyanobacteria (so that phosphorus becomes the main limiting nutrient); greater density stratification, especially in epeiric seas (so that phosphorus recycling is restricted both vertically and laterally); and, more speculatively, massive removal of phosphorus into sediments (e.g. Codispoti 1989; Brasier 1990*b*). Reefal communities and those of land-locked epeiric basins such as the Red Sea, Arabian (Persian) Gulf and Mediterranean Sea, provide modern examples of such P-limited ecosystems. These may provide analogies for the nutrient pathways of communities living in restricted shallow carbonate habitats during the late Precambrian and Cambrian.

So strong is the inverse correlation between PO_4 content and $\delta^{13}C$ of seawater that Broecker & Peng (1982) regarded the latter as a proxy record for reconstruction of changes in the PO_4 content of various water masses. Thus light $\delta^{13}C$ indicates a higher dissolved PO_4 content (owing to regeneration and low removal by photosynthesis) while heavy $\delta^{13}C$ indicates the converse. Changing phosphorus levels have been invoked in this way as a driving mechanism for carbon isotope fluctuations associated with major climatic changes in the Quaternary (e.g. Broecker & Peng 1982) and could, of course, have similar implications for the Precambrian and Cambrian climate.

Changing productivity and climatic regime may be brought about by fluctuations in the rate of delivery of 'new P' from the land, in the rate of recycling of P atoms via deep upwelling, or by changes in the amount of biologically 'recycled P' near the ocean surface (e.g. Broecker & Peng 1982; Shackleton & Pisias 1985). As argued below, such changes in the rate and pattern of P cycling may have varied considerably over the Precambrian–Cambrian boundary interval.

Palaeoceanographical changes

Stratigraphical successions across southern Asia provide good case histories for examining the relationships between sea level, phosphate deposition, carbon isotope fluctuations and palaeoproductivity. Of these, the well-known Meishucun section (Fig. 2) lay near the margins of the Yangtze Platform of south China. This small craton was situated in subtropical latitudes along the northern margin of Gondwana (e.g. McKerrow *et al.* this volume) and shared a similar history to the adjacent cratons of Indo-Pak, Tarim, southern Kazakhstan and Iran–Arabia (Brasier 1989*a*). In these areas, sedimentation was nearly continuous throughout the late Proterozoic and early Cambrian, with the latter having faunas belonging to the redlichiid faunal realm. The Chinese stage names of Dengyinxian, Meishucunian and Qionghzusian have been applied to the Precambrian–Cambrian boundary interval here (e.g. Luo *et al.* 1984).

Four related lithofacies are characteristic of this 'Palaeotethyan' margin: (1) peritidal, fine-grained, early

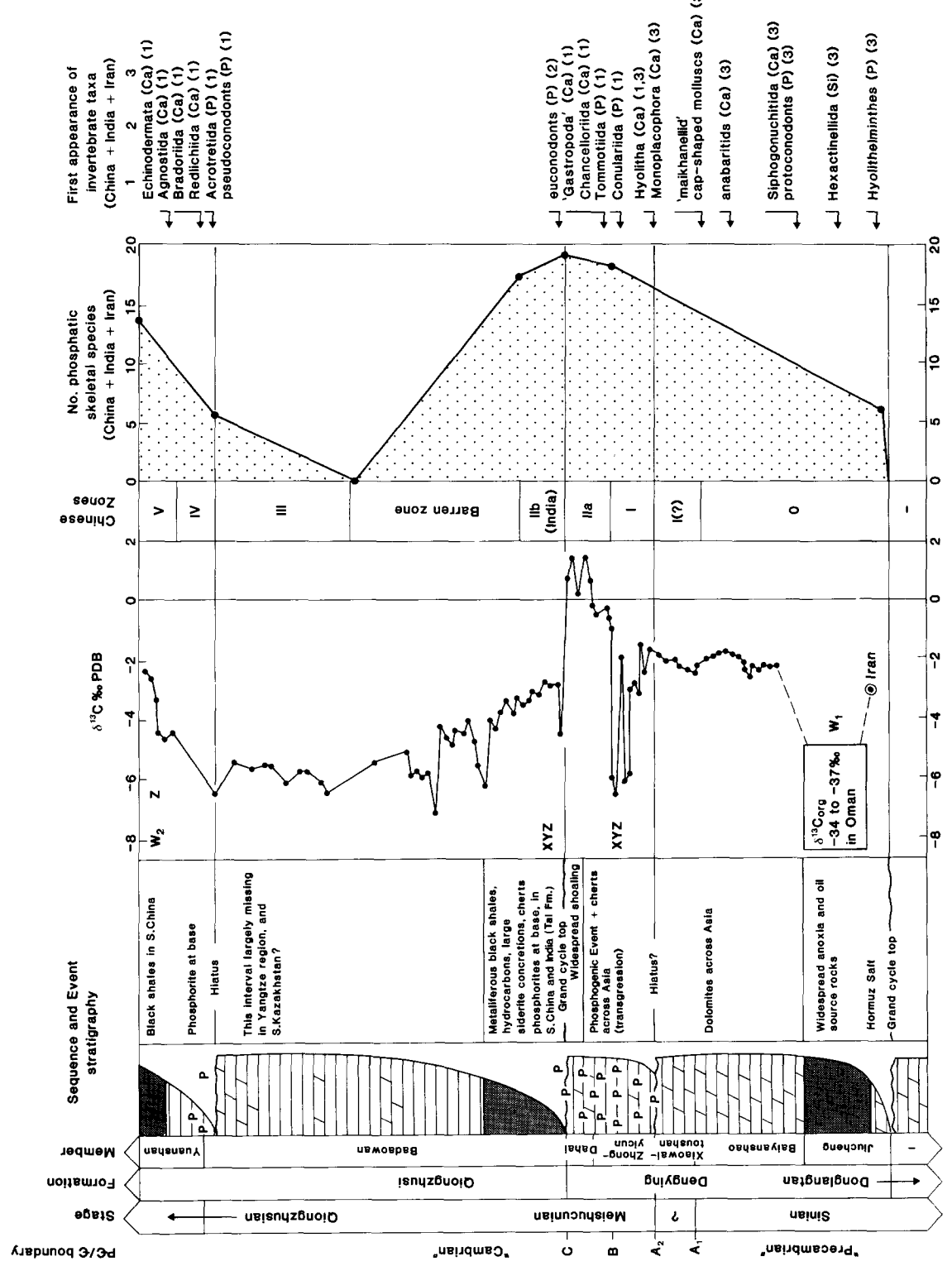

Fig. 2. The carbon isotope record across the Precambrian–Cambrian boundary interval in China, calibrated against the sequence and event stratigraphy for southern Asia. A close relationship is seen between phosphorites, cherts, anoxia and sequence boundaries. The diversity of phosphatic species appears higher at times of rising $\delta^{13}C$. This, like the first appearances of major invertebrate groups (*at right, with biomineral chemistry indicated*), may partly reflect ecological and taphonomic controls. Data from Luo *et al.* (1984), Brasier (1989*a*) and Brasier *et al.* (1990).

Points A, B and C (at left) show levels suggested for the Precambrian–Cambrian boundary in China. The Precambrian–Cambrian boundary point in the Burin Peninsula, Newfoundland, is suggested to lie close to point A2.

Points W to Z show levels with special biota. W, lagerstätten preservation of soft-bodied organisms in black shales (W1, *Chuaria* megaflora of Iran; W2, Chenjiang Fauna of Yunnan); X, sponge spicularites (China, Kazakhstan, India); Y, phosphatized organic matter dominant taphofacies (China, India); Z, appearance of pandemic small shelly fossil fauna that may serve as markers of 'cool' waters rich in nutrients and dissolved organic matter (most regions).

dolostones and limestones; (2) evaporitic facies ranging from peritidal to ?deeper waters; (3) phosphatic dolostones and limestones of restricted lagoons and embayments; (4) laminated black shales of deeper waters (Figs 2, 3). Siliciclastic sandstones and siltstones also occur but red-coloured sediments are lacking, except at the top of the lower Cambrian.

These facies appear to have been related as follows. Dolomites and evaporites formed in restricted basins under an arid climate, at times of relatively low sea level. Early stages of sea-level rise brought oxygen-depleted and phosphorus-enriched waters onto the carbonate platform, leading to phosphorite formation in these restricted embayments. Such surface waters were a distinctive feature of the boundary interval and are here labelled as nutrient-enriched waters (surface 'NEW'). These events were followed in places by deeper, anoxic waters which suppressed carbonate deposition and laid down laminated black shales, rich in organic matter, phosphate, pyrite and trace elements (e.g. molybdenum, uranium and vanadium; Xu *et al.* 1989). Sapropelites ('stone coals') and petroleum hydrocarbons accumulated in these black shales and associated evaporites, and the oils migrated into dolomitic reservoirs, as in the Arabian Gulf region (e.g. Husseini & Husseini 1990). These deeper, nutrient-enriched waters (deeper 'NEW') provided a likely source for the surface NEW described above.

Parts of four sea-level cycles can be traced through the boundary interval of southern Asia, as shown in Fig. 2. Each of these compares with a clearing-upward grand cycle in the sense of Aitken (1966) with a lower unit of siliciclastics and an upper unit of carbonates; detailed studies in the context of sequence stratigraphy have yet to be undertaken. Laminar fenestrae provide evidence for peritidal emergence at the top of the grand cycles (e.g. top Donglangtan and Dengying formations). Organic-rich shales are present in the lower parts of the cycles (e.g. Jiucheng, lower Badaowan and Yuanshan members). The extent of phosphatic and siliceous facies varies across the region, being most extensive in restricted intracratonic lagoons to the southwest (e.g. Li 1986), but they are particularly well developed at two levels across much of Asia (*see* Brasier *et al.* 1990, fig. 1). Comparable events across this region suggest that sea-level changes were intercratonic and may have been in part eustatic.

Carbon isotopes display a similar pattern across the boundary interval along the Palaeotethyan belt, despite facies variations and sedimentary cycles (Brasier *et al.* 1990). These shifts can be related in part to the large scale sea-level changes mentioned above. Lighter $\delta^{13}C$ values in the Dengying Formation coincide with episodes of phosphogenesis and trace-element enrichment, and may indicate the influence of surface NEW. Progressively heavier $\delta^{13}C$ values reached a maximum in the upper, shoaling, part of the Dengying Formation, when restriction may have led to the development of NDW. This peak was followed by a sharp drop in $\delta^{13}C$ values over a regional hiatus that, elsewhere, is known to have spanned strata equivalent to the whole of the Badaowan Member. Much lighter $\delta^{13}C$ values follow, coincident with progressive submergence of the carbonate platform by deeper, oxygen-depleted and trace-element enriched NEW. Extensive carbonate sedimentation was not not re-established until the end of the early Cambrian, when dolomites and evaporites again accompanied a eustatic fall in sea level.

The extent to which $\delta^{13}C$ values obtained from whole-rock carbonates reflect diagenetic, bottom-water or surface-water signals is critical to their interpretation for isotope chronology. Work in progress on the Newfoundland succession (Brasier *et al.* 1992) indicates that micritic calcites invariably carry lighter $\delta^{13}C$ and $\delta^{18}O$ signals than associated biominerals, suggesting that precipitation could have taken place in poorly ventilated pore-waters associated with organic degradation. The problem for many sections, including those of southern Asia, is that biominerals are poorly preserved or lacking, precisely at the point where $\delta^{13}C$ values need to be cross-checked. The organic-rich and ferroan dolomites of the Badaowan Member (Fig. 2) suggest that their light $\delta^{13}C$ value is partly related to organic degradation within anoxic sediments and overlying waters. The light $\delta^{13}C$ value obtained from phosphatic carbonates (Fig. 2) may also reflect diagenesis on the local scale, superimposed upon regional to global signals.

Sea level and ocean-atmosphere chemistry

The model in Fig. 3 attempts to indicate how nutrient-starved waters (NSW) could have developed episodically over the surface of the oceans in the Cambrian. Since this was a broadly transgressive period (Brasier 1980, 1981; Bond *et al.* 1988) the model is focussed on the effects of sea-level rise.

Anoxic water masses (i.e. deeper NEW) were present during the initial early Cambrian transgressions across southern Asia (see above) and were also present by late early Cambrian to middle Cambrian times along the margins of Australia, Laurentia, Baltica, Avalonia and Siberia. Anoxic bottom waters are also inferred from the heavy signatures of late Precambrian and Cambrian sulphur isotopes in evaporites, indicative of a massive biomass of sulphate-reducing bacteria at this time (e.g. Holser 1977). Evaporitic brines are, of course, a possible source for these saline waters.

Figure 3 proposes that extensive precipitation of phosphate minerals took place in the zone of interaction between anoxic water masses and carbonate shelves. It is possible, therefore, that huge amounts of P were being removed from the oceans at this time. The inference of an expansion of the nitrate-reduction zone within the upper layers of these anoxic waters awaits confirmation from further work. Both, however, would imply that nutrient-depletion and reduced primary productivity ultimately took place over large areas of the ocean surface, thereby forming nutrient-starved waters (NSW), much like the 'Strangelove Ocean' conditions envisaged by Hsü *et al.* 1985). Various feedback loops, involving carbon dioxide, weathering, oceanic circulation and climatic change, are contemplated but are less easy to confirm (Fig. 3).

Reductions in the flux of P would limit the photosynthetic removal of carbon dioxide from the atmosphere, and so favour the development of warmer 'greenhouse' conditions. Such a trend is certainly consistent with a variety of phenomena, including the ending of glacial conditions, the global rise in sea-level, the expansion of carbonate, evaporite, phosphorite and reefal facies, changes in microbial precipitation of carbonates, changes in carbonate mineralogy, and the widespread development of nodular carbonates (e.g. Riding 1982; Tucker 1989). More evidence is required, however, including a critical evaluation of oxygen isotope values, which are reputedly suggestive of high ocean temperatures in some Cambrian carbonates (e.g. Hudson & Anderson 1989; Tucker & Wright 1989).

The model presented here implies that sea-level rise, salinity stratification and the burial of P, Si and trace elements eventually had a negative effect upon nutrient recycling, forming nutrient-starved waters in surface layers of the ocean, leading to warmer climatic conditions. Such a model may well

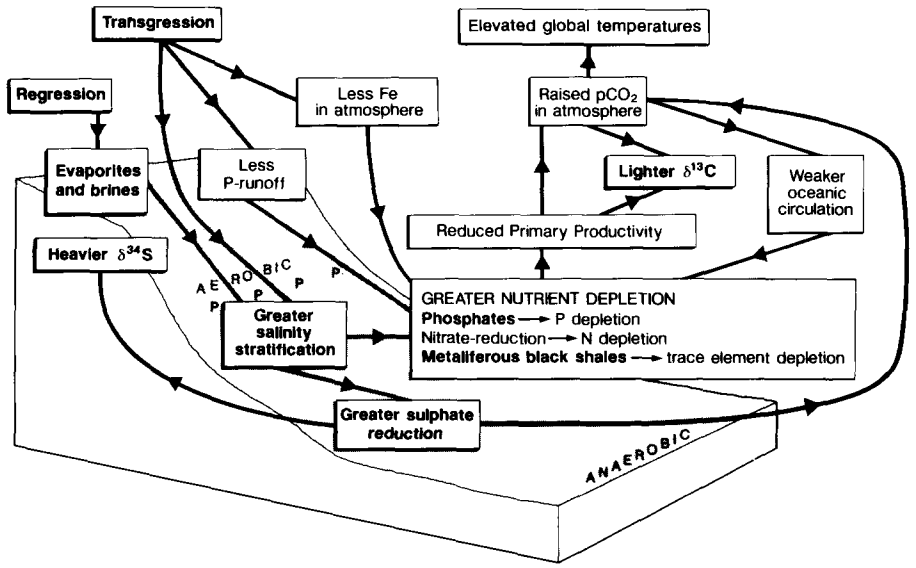

Fig. 3. Flow diagram showing the postulated effects of nutrient-starved surface waters (NSW) during the Cambrian transgressions. Phenomena observed in rocks are shown in bold. Regressive or stillstand conditions would tend to reverse these trends. P, zone of phosphogenesis.

apply to the peak transgressions of the Cambrian. The reverse would be true where stratified water masses were mixed or 'turned over', close to the edges of oceanic gyres and upwelling, or during periods of stillstand, falling sea level and increased terrestrial run-off. Huge concentrations of P, Si and Fe would become available in surface waters (surface NEW), and nitrate-limitation might take over as the main control of ocean fertility. This may have been the case during the positive $\delta^{13}C$ excursions close to the Precambrian–Cambrian boundary in China and Siberia (e.g. Magaritz *et al.* 1986; Brasier 1990*b*) and within the upper Cambrian of the western USA (Brasier 1992).

Palaeobiological evidence for nutrient levels

The nutrient-starved model discussed above resembles that put forward for stratified water masses of the Cretaceous and Silurian, where certain fossil groups provide useful nutrient indicators. Biological opaline silica deposits (mainly formed by diatoms and radiolarians) are associated with high surface productivity, and these were often scarce during Cretaceous oceanic anoxic events (Bralower & Thiersten 1984; Thiersten 1989). At earlier times, the abundance and diversity of phosphatic conodonts have been used. In the Silurian, stratified episodes (S-states) were accompanied by reduced diversity and abundance of conodonts, while mixed episodes (P-states) display increased diversity and abundance (Jeppsson 1990).

Biomineral skeletons appeared and radiated through the Precambrian–Cambrian interval, in groups as diverse as cyanobacteria, sponges, brachiopods and echinoderms (Brasier 1979). The latest evidence on first occurrences and ranges of major biomineralized invertebrate groups is shown in Fig. 4. Several biominerals were utilized for skeletons at this time: calcium carbonate (both aragonite and calcite), calcium phosphate and opaline silica. To these may be added the evidence for agglutinated skeletons, organic-walled skeletons and burrows.

Below, it is shown how the early skeletal fossil record reveals the influence of oxygen-depleted and nutrient-enriched, stratified water masses (both surface and deeper NEW). A spectrum of taphonomic controls can also be detected, from nearshore (where calcium carbonate shells predominated), via various phosphatic and siliceous taphofacies (related to surface NEW), to offshore anoxic environments where special preservation of organic tissues was not uncommon (related to deeper NEW).

Calcium carbonate skeletons

Calcium carbonate skeletons predominate in most skeletal assemblages of late Precambrian–early Cambrian age (e.g. Fig. 4). Many of these are wide ranging, but several distinctive 'core' associations can be distinguished, with distinct ecological preferences: archaeocyathan biofacies, *Anabarites* biofacies and *Coleoloides* biofacies.

As discussed elsewhere (Brasier 1990*b*, 1991*a*), archaeocyathans were adapted to low-latitude, oligotrophic conditions, like modern reef-dwelling sponges and corals (e.g. Hallock & Schlager 1986). They were seldom associated with phosphorites, glauconite, sponge spicule cherts or assemblages of phosphatic shells (e.g. Brasier 1980). As such, they may provide good indicators for nutrient-depleted surface waters (NDW). This contrasts markedly with the distribution of the tubiculous colonies of *Coleoloides* and related forms (e.g. *Anabarites*, *Tiksitheca*) which colonized the phosphogenic margins of Gondwana and Siberia, the cooler waters of Avalonia, Baltica and outer margins of Laurentia. Such *Anabarites* and *Coleoloides* biofacies may therefore mark the occurrence of surface NEW.

The apparent abundance of phosphatic skeletons across the Precambrian–Cambrian boundary owes much to the secondary phosphatization of carbonate skeletons, referred to the phosphatized carbonate-dominant taphofacies by Brasier (1990*a*). The process and timing of this phosphatization varied widely, however, with profound consequences for the start of the skeletal fossil record. On the Siberian Platform, for example, phosphatized Nemakit–Daldynian assemblages appeared diachronously from the platform margins towards the Lena region (Khomentovsky 1986, fig. 12), culminating in a diversity explosion coincident with the extensive glauconite-phosphate facies at the base of the Tommotian. On the Yangtze Platform, the development of phosphatized carbonate-dominant taphofacies likewise governed the appearance of Zone I faunas

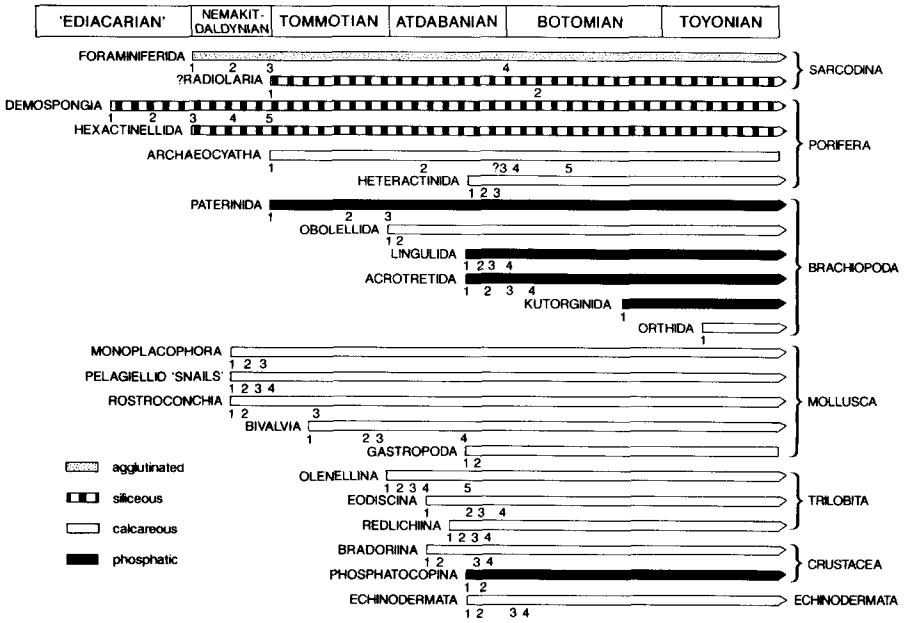

Fig. 4. Fossil evidence for the origin of major invertebrate groups. This is calibrated against the Siberian stratigraphical scale and follows the suggested correlation scheme of Brasier *et al.* (1990). Numbers refer to the earliest occurrences in different sections (data available from the author). The Precambrian–Cambrian boundary point in the Burin Peninsula, Newfoundland, is here suggested to lie at the base of the Nemakit–Daldynian Stage.

in Yunnan and Sichuan. At Fangxian, Hubei, similar dolomites lacked phosphatized carbonate-dominant taphofacies (and fossils) until about Zone III. The appearance of the Nemakit–Daldynian and Tommotian fauna therefore owes much to ecological and taphonomic conditions brought about by the development of nutrient-enriched surface waters.

Calcium phosphate skeletons

Phosphatic skeletons were widespread amongst the earliest assemblages but seldom predominant (*pace* Lowenstam & Margulis 1980). Primarily phosphatic assemblages do occur, however, especially at levels where phosphatized organic matter is the dominant diagenetic fabric (Brasier 1990*a*). These 'phosphatized organic-dominant' taphofacies typically contain phosphatic faecal pellets, phosphatized cyanophytes (e.g. *Spirellus*), sphaeromorphs or globomorphs (e.g. *Olivooides*) and ?conulariids (e.g. *Arthrochites*) as well as abundant primary phosphatic skeletons (e.g. *Hertzina*). This taphofacies is commonly associated with sponge spicule cherts or with Alum Shale lithofacies and is taken to indicate a nearby source of deeper, oxygen-depleted NEW (Fig. 2, marker Y).

Many primarily phosphatic taxa appearing through this interval are 'problematica', barely known beyond the Cambrian. These include (with their first appearance datum, or FAD): *Hyolithellus* and *Rugatotheca* (probable Ediacarian FAD); protoconodonts *Protohertzina* and *Hertzina*, euconodont? *Fomitchella*, various spine-like sclerites and tube *Torellella* (Nemakit–Daldynian FAD); mitrosagophorans *Tommotia*, *Camenella*, *Lapworthella* and *Eccentrotheca* (Nemakit–Daldynian to Tommotian FAD); pseudoconodont *Rhombocorniculum* and button-shaped *Mobergella* (late Tommotian FAD); button-shaped studs of ?annelids *Hadimopanella* and *Cowiella* and net-like caps of problematical uniramian *Microdictyon* (all late Atdabanian FAD); sculptured tubes of *Mongolitubulus* (mid Botomian FAD). To these should be added the first appearances of inarticulate brachiopods (basal Tommotian FAD) and phosphatocopine crustaceans (late Atdabanian FAD). Phosphate as a biomineral was therefore 'introduced' into apparently unmineralized stocks over a considerable time span.

Many phosphatic taxa were geographically wide-ranging, spanning the higher latitude *Coleoloides* biofacies of Avalonia and Baltica to lower latitude archaeocyathan-bearing strata of Siberia and Gondwana (Brasier 1989*b*). Of these, *Hyolithellus*, *Protohertzina*, *Hertzina*, *Rhombocorniculum*, *Lapworthella*, *Hadimopanella* and *Microdictyon* spread between all faunal realms. Their distribution suggests pelagic dispersal of larvae within oceanic currents and they may therefore provide useful markers for the spread of cooler NEW through the course of the early Cambrian (see Fig. 2, marker Z).

The diversity of these phosphatic forms reached an early acme in Siberia and southern Asia, broadly coincident with phosphogenic and carbon isotopic maxima (Fig. 5; Brasier 1990*b*, 1991*a*). In Newfoundland and England, however, these forms peaked later in Atdabanian to Botomian times, associated with glauconite-phosphate facies at Nuneaton and Comley. These diversity peaks may be taken with other evidence to indicate that both surface and deeper NEW had an episodic and diachronous influence on early Cambrian biotas.

Siliceous skeletons

Simkiss & Wilbur (1989) have noted how invertebrate groups (other than protists) that arose after the Cambrian never again utilized silicon as the primary element in forming a mineral skeleton. This may relate to silica-rich coastal waters in the Precambrian–Cambrian boundary interval.

Opaline silica skeletons are relatively soluble and therefore have a patchy fossil record. The silica in sponge spicules is typically replaced by carbonate in limestones and by pyrite or iron oxides in black shales, but occurrences of primarily silica skeletons are also known. Indeed, the early appearance of siliceous demosponge spicules, hexactinellid spicules, and possible radiolarian skeletons (Fig. 4) includes forms preserved in silica at levels broadly coincident with the first development of sponge spicule cherts (Brasier, Hamdi & Azmi, in prep.).

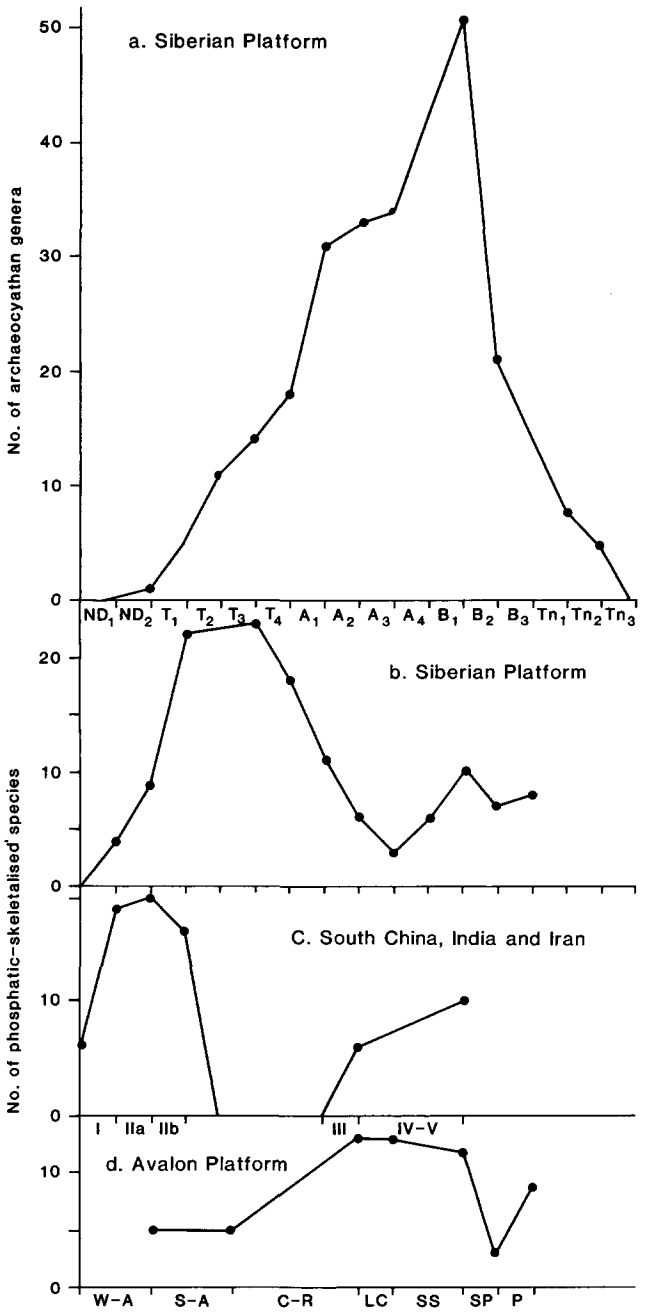

Fig. 5. Taxonomic diversity curves for skeletal faunas through the boundary interval: (**a**) archaeocyathan genera on the Siberian Platform (time divisions at the bottom relate to stages, see Fig. 4); (**b**) phosphatic species on the Siberian Platform; (**c**) phosphatic species on the Palaeotethyan Platforms of South China, India and Iran (roman numerals refer to zones, see Fig. 2); (**d**) phosphatic species on the Avalon Platform (England and Newfoundland). Time divisions refer to: *Watsonella crosbyi* Zone (W–A); *Sunnaginia imbricata* Zone (S–A); *Camenella baltica* Zone (C–R); lower *Callavia broeggeri* Zone (LC); upper *Callavia* Zone (SS); *Serrodiscus speciosus* Zone (SP); *Protolenus* Zone (P). The Precambrian–Cambrian boundary point, as defined in the Burin Peninisula, Newfoundland, is here taken to lie at the left-hand margin of the diagram.

Although the earliest ?radiolarians secreted silica (e.g. *Blastulospongia*, G. Karlova pers. comm. 1990; Conway Morris & Chen 1990), it is doubtful whether the earliest foraminiferids did so. Agglutinated *Ammodiscus* of mid early Cambrian age is the first unequivocal record (Culver in press) but the problematical agglutinated tube *Platysolenites* may also belong here (e.g. Loeblich & Tappan 1988). Suggestions that the cement of the latter was siliceous, however (Rozanov 1983) are rejected by our recent SEM studies.

The association between late Precambrian and Cambrian siliceous sponges, sponge spicularites, phosphatic rocks and metalliferous black shales (e.g. Brasier 1980; Cook & Shergold 1986) clearly suggests a nearby source of NEW. As discussed above, these waters impinged upon carbonate platforms during rising sea-level, coincident with the development of light $\delta^{13}C$ signatures in associated carbonates (Fig. 2, marker X; Brasier *et al.* 1990). Early sponge spicularites may therefore serve as useful markers for surface NEW, developing under the influence of deeper NEW.

Was there a subsequent shift away from silica as a biomineral in the Porifera? The utilization of calcite by archaeocyathan and heteractinidid sponges (Fig. 4) might seem to suggests this. The latter flourished in shallow carbonate habitats (and nutrient-depleted water), remote from the chert-phosphorite-black shale facies (and NEW) in which early Demospongia and Hexactinellida thrived. If correct, this could be viewed as evidence for two stages in poriferan biomineralization: an initial phase, developed around the platform margins in NEW; and a later phase, developed in nutrient-depleted waters as the interiors of major cratons were flooded.

Organic skeletons

The remarkable preservation of soft-bodied skeletons provides further evidence for changing ocean–atmosphere conditions through the boundary interval. As discussed elsewhere (Brasier 1989*c*), taphonomic conditions which preserved the Ediacara fauna in shallow clastic sediments appear to have declined towards the end of the Proterozoic, whereas the incidence of 'black shale' preservation seems to have increased dramatically.

Several intervals of such preservation deserve mention here. Latest Precambrian strata correlative with the Jiucheng Member of South China (Fig. 2, marker W1) preserve carbonaceous ribbons of *Vendotaenia*, *Tyrasotaenia* and large problematical vesicles, including *Chuaria* sp., across a wide part of the globe. Large monaxon demosponge spicules abound at this level in northern Iran (Brasier, Hamdi & Azmi, in prep.), broadly coincident with the Hormuz evaporites and Arabian Gulf hydrocarbons (e.g. Husseini & Husseini 1990). At this level, or slightly higher, occur the organic 'worm tubes' of *Sabellidites*, especially on the Baltic and Avalonian Platforms.

Higher, in the Yuanshan Member of Chenjiang, Yunnan (Fig. 2, marker W2), special conditions preserved a Burgess Shale-type fauna (e.g. Chen *et al.* 1989). Finely-laminated, organic-rich shales in Yunnan and 'stone coal' sapropelites in Hubei bear trace element anomalies (e.g. Xu *et al.* 1989) that attest to the spread of aged, anoxic water masses across the Yangtze Platform in the Qiongzhusian.

Clearly, these lagerstätten horizons record the episodic development of anoxia on a large scale, implying the develop-

ment of NEW. Associated skeletons notably include pandemic soft-bodied taxa (e.g. *Naroia*), pandemic phosphatic taxa (e.g. *Microdictyon*) and siliceous sponge remains.

Conclusions

Nutrient-enriched water masses (NEW) with high levels of dissolved phosphate and silica, and low levels of oxygen, have left a clear imprint on the fossil record of the latest Proterozoic-early Cambrian. At low latitudes, the early skeletal fossil record was enhanced by phosphatization of delicate carbonate shells, leaving 'taphonomic windows' as the NEW impinged diachronously over shallow shelves.

Phosphate and silica nutrients also made an early appearance as biominerals, commonly associated with cherts, phosphorites and metalliferous black shales. Sponge spicule cherts, phosphatized-organic dominant (POD) skeletal assemblages, and selected primary phosphatic taxa all provide potential markers for the spread of NEW.

Diversity patterns of 'phosphatophilic' skeletons and oligotrophic archaeocyathans may also be used to track the history of NEW. The former, together with *Anabarites* biofacies, encroached the Siberian Platform during Nemakit–Daldynian to early Tommotian times, to be replaced by more oligotrophic archaeocyathan biofacies, whose diversification may reflect the formation of more nutrient-depleted waters (NDW). The NEW also had an early influence on biota along the Gondwana margins of southern Asia, which received repeated incursions through the early Cambrian. In Avalonia, however, the acme of phosphatic forms was delayed until late Tommotian–Botomian times, associated with the development of glauconite–phosphate facies.

Further evidence for the spread of oxygen-depleted NEW over the cratons is provided by the remarkable preservation of organic skeletons (*Vendotaenia* flora, *Sabellidites* fauna and Chenjiang fauna) at several horizons through the boundary interval. The increasing incidence of Burgess Shale-type preservation (Conway Morris, pers. comm. 1991) and of Alum Shale facies through middle Cambrian times (e.g. Thickpenny & Leggett 1987) may indicate the continued spread of such water masses.

Various lines of evidence therefore point to the importance of stratified and nutrient-enriched water masses for late Precambrian–early Cambrian palaeobiology and palaeoceanography. It follows that oscillating levels of $\delta^{13}C$ in contemporaneous carbonates may relate to their history. In NEW waters of the Precambrian–Cambrian boundary interval, $\delta^{13}C$ values appear to have been light throughout the watermass. In nutrient-depleted waters, developed in more-restricted shallows, heavier $\delta^{13}C$ values appeared. Oceanic surface waters may ultimately have become nutrient-starved and ^{12}C-enriched, as suggested for middle to late Cambrian times.

Nutrient-starvation of surface waters has great implications for palaeoclimatology, since this is thought to limit photosynthetic extraction of carbon dioxide from the atmosphere, leading to global warming. Such a trend should be recoverable from the oxygen isotopic record. These concepts will need to be tested during the course of IGCP Project 303.

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