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Oceanic anoxia at the Precambrian-Cambrian boundary

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Mistyping Before correction: Ediacarian After correction: Ediacaran

ABSTRACT

The Precambrian-Cambrian (PC-C) boundary separates fossils representing two discrete evolutionary phases: the Neoproterozoic soft-bodied Ediacarian biotas and Cambrian small shelly faunas. The biological discontinuity is suspected to have been a result of mass extinction; however, recent discoveries of the Ediacarian biotas in Cambrian sediments have led to an understanding that the faunal change was gradual through the PC-C transition. Th/U ratios, which are high in oxidizing conditions and low in reducing conditions, show a considerable positive correlation with δ^{13} C values at all studied sites of the PC-C boundary. This correlation indicates that reported δ^{13} C variation across the PC-C boundary from numerous localities corresponds to redox variation in the depositional environment. The negative $\delta^{13}C$ anomaly that occurs worldwide at the PC-C boundary, therefore, corresponds to the widespread development of an oxygen-deficient shallow marine environment. This finding suggests that widespread oceanic oxygen deficiency, which has been interpreted to reflect Phanerozoic mass extinction events, also occurred immediately before the Cambrian explosion.

Keywords: Cambrian, anoxic environments, bioturbation, mass extinctions, Iran.

INTRODUCTION

Stratigraphic separation of two markedly different evolutionary phases at the Precambrian-Cambrian (PC-C) boundary has conventionally been recognized by (1) changes in the visible metazoan assemblages, due to contrasts between the Neoproterozoic soft-bodied Ediacarian biotas and Cambrian small shelly faunas (e.g., Brasier, 1989; Lipps and Signor, 1992); (2) a change in the taphonomic condition, with Ediacarian-type fossil impressions that are unique to the Neoproterozoic (e.g., Gehling, 1999); (3) changes in the trace fossil assemblages, due to the disappearance of distinctive and simple Neoproterozoic trace fossils and the radiation of modern ichnofaunas in the Cambrian (e.g., Crimes, 1994); and (4) increased intensity of overall bioturbation in marine sediments in the earliest Cambrian, due to the onset of extensive colonization of the active infaunal realm (Droser et al., 1999). These biological discontinuities have been attributed to mass extinction (e.g., Brasier, 1989; Brasier, 1995) and/or closure of the taphonomic window for soft-bodied organisms (e.g., Gehling, 1999). Increasing evidence for stratigraphic overlap between the declining Ediacarian biotas and emerging skeletonized invertebrate faunas includes discoveries of Ediacarian biotas in Cambrian sediments (e.g., Conway Morris, 1993; Jensen et al., 1998), which have led to an understanding that no mass extinction occurred before the Cambrian explosion (Jensen et al., 1998). On the other hand, mass extinctions, caused by transgressive upward movement of predicted nutrientenriched anoxic bottom-water masses, have been suggested for the PC-C boundary interval (Brasier, 1989, 1995). Evidence for such a stratified ocean with ¹³C-depleted anoxic deeper waters includes (1)

phosphogenesis and black shale deposition that appear during the initial stages of transgressive events and (2) dramatic fluctuation in δ^{13} C throughout the PC-C boundary interval (Brasier, 1989, 1995). However, it is impossible to determine the degree of anoxia solely on the basis of sedimentological criteria, and little is known about the extent of the anoxia at any specific stratigraphic level. This paper presents evidence for widespread oxygen deficiency in shallow marine environments at the PC-C boundary, just as oxygen deficiency also accompanied some of the Phanerozoic mass extinction events (Erwin, 1993; Wignall and Twitchett, 1996; Hallam and Wignall, 1997).

GEOLOGIC BACKGROUND

The fossiliferous Valiabad and Dalir sections, 60 km north of Tehran in the Elburz Mountains of northern Iran, preserve sedimentary records from the late Proterozoic through the Cambrian (Hamdi et al., 1989; Brasier et al., 1990; Kimura et al., 1997) (Fig. 1). The Soltanieh Formation, containing the PC-C boundary, consists of peritidal flat carbonates and subtidal shales (Fig. 1). The sequence boundary at the top or in the upper part of the Lower Dolomite Member (Fig. 1) is correlated to that at the Neoproterozoic-Manykayan (Nemakit-Daldynian) boundary in Siberia (Brasier et al., 2000) and also to that in member 2 of the Chapel Island Formation at the PC-C stratotype in Newfoundland, approximately 83 m above the PC-C boundary¹.

The $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ values exhibit covariation throughout the successions (Fig. 1) (Kimura et al., 1997), indicating a primary isotopic signature (Knoll et al., 1986). Both of the sections examined here show similar $\delta^{13}C$ curves. A remarkable negative excursion of $\delta^{13}C_{carb}$ reaches a minimum of -7% or -9% in the lower half of the Lower Shale Member, which has been recognized worldwide in shallow water carbonates around the PC-C boundary (see footnote 1), indicating ^{13}C depletion in shallow marine waters worldwide (Kimura et al., 1997).

Th/U VARIATION

Th/U has been used as a proxy for the redox conditions of the depositional environment (Myers and Wignall, 1987; Wignall, 1994; Wignall and Twitchett, 1996). Thorium is unaffected by redox conditions and remains insoluble as Th⁴⁺. Uranium, however, exists as insoluble U⁴⁺ under highly reducing conditions, which leads to U enrichment in sediments, whereas it exists as soluble U⁶⁺ under oxidizing conditions, leading to U loss from sediments. Th/U ratios, therefore, vary from 0–2 in anoxic environments to 8 in a strongly oxidizing environment (Wignall and Twitchett, 1996). In the examined sections, Th/U ratios reach minimum values of 1.0 or 1.5 at the $\delta^{13}C$ minimum, and high Th/U ratios of 6.0 at the $\delta^{13}C_{org}$ maximum (Fig. 1).

V/Sc VARIATION

Vanadium is also a redox-sensitive element that is preferentially concentrated in sediments underlying anoxic or near-anoxic waters (Emerson and Huested, 1991; Wignall, 1994). The degree of V enrichment is most efficiently expressed if the V concentration is normalized by scandium abundance, because both V and Sc are insoluble and V

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¹GSA Data Repository item 2001113, Lithostratigraphy, chronostratigraphy, geochemical and ichnofabric analyses, Figure A (plots of V vs. Al, Ti, Nb, Th, and Sc abundances in examined shales from the Elburz Mountains, northern Iran), and further evidence for widespread oceanic oxygen deficiency at the PC-C boundary, is available on request from Documents Secretary, GSA, PO. Box 9140, Boulder, CO 80301, editing@geosociety.org, or at www.geosociety.org/pubs/ft2001.htm.

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Figure 1. Stratigraphic columns, variations in ichnofabric indices (explained in Fig. 3), $\delta^{13}C_{carb}$, $\delta^{13}C_{org}$, and Th/U ratios in PC-C boundary strata at (A) Valiabad and (B) Dalir sections. Map shows locations of examined sections in Elburz Mountains in Iran, 1—Valiabad; 2—Dalir; 3—Garmab. Data for $\delta^{13}C$ from Kimura et al. (1997), the symbols of which are explained in Kimura et al. (1997) or Data Repository (see text footnote 1). Darker shaded area of 4.7–9.1 in V/Sc shows typical ratios of crustal rocks throughout geologic period (Taylor and McLennan, 1985); dashed line at 7.79 in V/Sc is average measured ratio in examined sections in Iran. Horizontal dotted area represents stratigraphic level where Th/U is ~2 or less. ED—Ediacarian; LD and LDM—Lower Dolomite Member; LSM—Lower Shale Member; MD and MDM—Middle Dolomite Member; NP—Neoproterozoic; T—Tommotian.

varies in proportion to Sc, rather than other insoluble elements such as Al and Ti (Fig. A; see footnote 1). At the negative δ^{13} C anomaly, V/Sc ratios show a threefold increase above the background that is consistent with average crustal values (Taylor and McLennan, 1985) (Fig. 1). In both sections, V/Sc is high (up to 23 at Valiabad and 22 at Dalir) in the lower part of the negative δ^{13} C excursion and decreases toward background values in the upper half of the negative δ^{13} C excursion.

WIDESPREAD OXYGEN-DEFICIENT OCEANS

Both the low Th/U (\leq 2) and the high V/Sc ratios suggest an anoxic depositional environment in northern Iran during the interval of the negative $\delta^{13}C$ excursion. Moreover, the Th/U ratios show a considerable positive correlation with $\delta^{13}C_{org}$, which covaries with $\delta^{13}C_{carb}$ (Fig. 2). This correlation is observed in both northern Iran and southern China throughout the PC-C transition (Fig. 2), suggesting that it represents a paleo-Tethyan or global trend. Therefore, the reported δ^{13} C values from Neoproterozoic-Cambrian strata worldwide appear to correspond broadly to the redox conditions of the depositional environment; high δ^{13} C corresponds to high Th/U and thus to oxidizing conditions, whereas low $\delta^{13}C$ corresponds to low Th/U and thus to reducing conditions. The negative δ^{13} C anomaly at the PC-C boundary, therefore, indicates a widespread oxygen-deficient shallow marine environment. This view is further supported by reported lithological and geochemical evidence at this stratigraphic level worldwide (see footnote 1).

RESPONSE OF BENTHIC ORGANISMS TO OXYGEN DEFICIENCY

An oxygen deficiency lasting much longer than organism life spans is likely to have a significant impact on benthic organisms. However, the response of benthic organisms to this paleoenvironmental change is not particularly well understood, because the coarse chronostratigraphic division and the rarity of invertebrate fossils in the Neoproterozoic have prevented reconstruction of the variation in animal diversity at high stratigraphic resolution (Sepkoski, 1992). Ichnofabric analysis of shales may independently provide information on variations in the intensity of overall bioturbation by benthic organisms throughout any anoxic event. Our analysis, using newly established schemes for fine-grained siliciclastic sediments (Fig. 3), shows that the degree of bioturbation varies in a similar fashion at the microscopic and macroscopic levels at both Valiabad and Dalir (Fig. 1). At Valiabad, at both the microscopic and macroscopic scales, bioturbation decreases during the lower half of anoxic deposition, recovers where V/Sc drops to the background, and starts to decrease again with termination of the anoxia. At Dalir, at both the microscopic and macroscopic scales, bioturbation is sparse during the anoxic deposition and increases in the upper part. In general, the degree of bioturbation tends to be low in the anoxic environment, compared to the post-anoxic interval.

CAUSES OF THE OXYGEN DEFICIENCY AND ITS BIOLOGICAL IMPLICATIONS

The cause of this oceanic oxygen deficiency remains controversial. Similar and different paleoenvironmental observations at the



Figure 2. Relationship between $\delta^{13}C_{org}$ and Th/U ratios. Solid symbols indicate Ediacarian-Manykayan data; open symbols indicate Tommotian-Atdabanian data. Kunyang and Wangjiawan sections in Yunnan, southern China, are described in Luo et al. (1984). Correlation coefficient (R^2) is 0.70 (0.80, if several data out of trend are eliminated from correlation). Shaded area represents $[\delta^{13}C_{org}] = 1.775[Th/U]-36.300 \pm 2.537$.

Permian-Triassic (P-Tr) boundary may provide clues about the paleoceanographic event at the PC-C boundary. The similarities at the P-Tr boundary include a negative $\delta^{13}C$ anomaly (e.g., Jin et al., 2000), a dysoxic shallow ocean (Wignall and Twitchett, 1996), a prolonged period of anoxic deep ocean (Isozaki, 1997), and a regression-transgression couplet (Hallam and Wignall, 1999). A global ocean model suggests that reduced ocean circulation, due to reduced latitudinal temperature gradient, causes anoxia throughout the deep ocean (Hotinski et al., 2001). Such ocean stagnation, also proposed for the PC-C boundary interval (e.g., Brasier, 1995), could have been important for the anoxia and negative $\delta^{13}C$ excursion in the shallow ocean. Introduction of poorly ventilated anoxic deep waters, enriched in ¹²C, into the shallow marine environment would result in a negative $\delta^{13}C$ excursion (Knoll et al., 1996; Kimura et al., 1997). However, mass balance calculations (Kump, 1991) indicate that the estimated duration of the negative δ^{13} C excursion at the PC-C boundary (≈ 1 m.y. or more; Grotzinger et al., 1995; Pelechaty et al., 1996) may be difficult to explain by this interpretation. Sea-level rise, as observed in the Lower Shale Member, could cause an upward movement of the oxygen-minimum zone (e.g., Brasier, 1989; Wignall, 1994; Hallam and Wignall, 1999), resulting in the swing to negative δ^{13} C, coupled with low Th/ U and high V/Sc in shallow environments. This is consistent with the coincidence between transgression and the negative $\delta^{13}C$ shift in Iran and Siberia (Fig. 1; Pelechaty et al., 1996). However, a similar transgressive event in the early Tommotian of the early Cambrian (e.g., Brasier, 1995) does not yield a remarkable negative δ^{13} C excursion such as that observed at the PC-C boundary (e.g., Brasier et al., 1990; Kimura et al., 1997); thus, additional mechanisms are required for one or the other of these episodes. Another strongly ¹³C-depleted C reservoir is methane-hydrate stored in marine sediments, the amount of which is clearly enough to cause a swing to negative δ^{13} C. Massive release and further oxidation of the CH_4 ($^{12}CH_4 + 2O_2 \rightarrow {}^{12}CO_2 +$ 2H₂O) would contribute to the rapid development of a dysoxic shallow ocean and a negative $\delta^{13}C$ shift in dissolved carbonates. Increased atmospheric CH₄ in the early Triassic, indicated by a prominent decrease in $\delta^{13}C_{org}$ of whole paleosol profiles (Krull and Retallack, 2000), supports the idea of mass CH₄-hydrate release at this time (Erwin, 1993). On the other hand, the Antrim Plateau basalts in Australia, previously hypothesized to have erupted at the PC-C boundary (Bartley et al.,



Figure 3. Schematic diagrams of degree of lamination observed at macroscopic and microscopic scales. Macroscopic scale (right side): 1—no bioturbation, all original sedimentary structures are preserved; 2—90%–99% of original structures are preserved; 3— 70%–89%; 4—30%–69%; 5—10%–29%; 6—1%–9%; 7—completely homogenized sediment. Microscopic scale (left side; mm/mm²): 1—total length of visible laminae is >8.5; 2—5.0–8.5; 3—3.5–5.0; 4—2.5–3.5; 5—1.5–2.5; 6—0.7–1.5; 7—<0.7.

1998), in support of the CH₄-hydrate hypothesis (e.g., Katz et al., 1999), has yielded a SHRIMP zircon age of 513 ± 3.3 Ma (Hanley and Wingate, 2000). This age is apparently comparable to the Botomian biotic crisis and coeval oceanic anoxia in the late Early Cambrian (e.g., Zhuravlev and Wood, 1996) but can have no relevance to the much earlier PC-C boundary. An asteroid or comet impact (e.g., Becker et al., 2001) could have been the climax in the environmental catastrophe at the P-Tr boundary, one that has not been reported from the PC-C boundary. An iridium anomaly reported from southern China (e.g., Hsu et al., 1985) is correlated not to the PC-C boundary but to much later, the early Tommotian. Further evidence is, therefore, required to demonstrate an oxygen deficient ocean at the PC-C boundary.

The examined sections in northern Iran do not yield Ediacarian

fossil biotas, unlike some other boundary sections around the world. However, elsewhere, Ediacarian fossils are observed to disappear beneath the PC-C boundary at many localities (e.g., Brasier, 1989), apparently immediately below the negative δ^{13} C excursion (Narbonne et al., 1994). This apparent stratigraphic coincidence between the biological discontinuity and the development of oxygen-limited, shallow marine deposition may imply a cause-effect relationship between them, especially because widespread dysoxia has coincided with some of the Phanerozoic mass extinction events (Hallam and Wignall, 1997).

Ediacarian organisms were immobile, having maximized external surfaces and passive circulatory systems (Seilacher, 1992). As a result, they would have been highly sensitive to environmental changes in the ambient seawater. Persistence of environmental stress, related to oxygendeficient water, for significant periods, could have resulted in the extinction of certain benthic organisms, including some of the Ediacarian biotas (Brasier, 1989, 1995; Kimura et al., 1997; Bartley et al., 1998; Knoll and Carroll, 1999).

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