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Pyrite framboid evidence for oxygen-poor deposition during the Permian–Triassic crisis in Kashmir

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Abstract

The Khunamuh Formation of the Guryul Ravine section in Kashmir provides one of the most detailed deep-water records of the end-Permian mass extinction in Perigondwanan palaeolatitudes. Examination of pyrite framboid size distributions and sediment microfabric reveals a distinct change in the uppermost Permian strata from nonlaminated, pyrite-free silty mudstones to finely laminated, silty shales rich in framboidal pyrite around 1 m above the base of the formation. The size frequency distribution of the framboids is identical to populations from severely oxygen-restricted modern depositional environments. This change to dysoxic benthic conditions coincides with the rapid demise of diverse Permian brachiopod and bryozoan assemblages. Thus, the link between extinction and anoxia is clearly seen at Guryul Ravine and it provides an interesting contrast to other Perigondwanan sections developed in shallower water where both the onset of anoxia and the extinction occurred somewhat later in the earliest Triassic.

Keywords: Mass extinction; Permian; Framboids; Kashmir

1. Introduction

The development of anoxic facies is a widespread feature of Permian–Triassic boundary sections and it is widely regarded as the direct cause of the marine mass extinction (e.g. Wignall and Hallam, 1992; Isozaki, 1997). Only in some shallow-water locations does anoxia appear to be absent in the earliest Triassic (e.g. Lehrmann et al., 2003; Krystyn et al., 2003). It is this severe lack of habitat area that is probably directly responsible for the marine mass extinction. However, the timing of development of anoxia shows some interesting water depth and regional variations. The deep-water facies of Japanese accreted terranes appear to record the start of a long-lasting "superanoxic event" that ranged from base of the Late Permian into the Middle Triassic (Isozaki, 1997). Shelfal and epicontinental sections record a briefer interval of

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anoxia which began abruptly in the latest Permian at a time that precisely coincides with the marine mass extinction (Wignall and Twitchett, 2002). Only in the shelf seas on the southern margin of the Neotethyan Ocean (i.e. the Perigondwanan margin) does there appear to be a somewhat different history to the timing of anoxia. In the Salt Range of Pakistan and in southern Tibet, anoxic facies do not appear until late in the Griesbachian Stage, the oldest stage of the Triassic, and many "Permian" taxa range up to this level (Wignall and Hallam, 1993; Wignall and Newton, 2003). In both these regions the development of anoxia coincides with a deepening event and the development of deep-water facies. Thus, they do not record the redox changes in deeper water settings during the Permo-Triassic transition. The only deep-water record from across the Permo-Triassic boundary in the Perigondwanan region occurs at Guryul Ravine in Kashmir, India. This section thus provides crucial evidence for the redox history of the Neotethyan Ocean during the end-Permian mass extinction.

2. Guryul Ravine facies and stratigraphy

The end-Permian mass extinction and Permo-Triassic boundary is contained within the basal metres of the Khunamuh Formation at Guryul Ravine (Nakazawa et al., 1971, 1975; Nakazawa, 1981). This is a deepening-upward succession of silty shales which contains common shell beds in its lower part (Wignall et al., 1996; Brookfield et al., 2003; Fig. 1). The basal unit of the formation, E1, is dominated by silty shale but it contains within its 2.7 m thickness several paraautochthonous shell beds yielding Permian brachiopods, crinoids and bryozoans. These gradually disappear in the upper part of E1 to be replaced by shell beds with a fauna of Triassic affinity, mainly thin-shelled bivalves and ammonoids, in the overlying unit E2. *Hindeodus parvus*, the conodont used to define the base of the Triassic, first appears in the middle of unit E2, 3 m above the base of the E1/E2 contact whilst the succeeding *Isarcicella isarcica* Zone begins immediately below the base of unit E3 (Wignall et al., 1996; Kapoor, 1992).

The extinction losses at Guryul principally occur in the upper part of E1 and Wignall et al. (1996) have speculated, based on the lithological descriptions of Nakazawa et al. (1975), that the demise of the Permian benthos was due to the development of anoxia. In contrast, Brookfield et al. (2003) suggested that benthic oxygen levels remained normal during the extinction event based on their observation that the rocks were not pyritic. The purported absence of anoxia in the relatively deep water Guryul Ravine section is surprising because it would be the only record of oxygenated deep-water facies in the region. In order to assess the oxygenation history of this section pyrite framboid analysis has been undertaken from samples spanning the mass extinction level and Permian–Triassic boundary.

3. Pyrite framboid analysis

Pyrite framboids are a common diagenetic phase in many shales, and they are especially abundant in strata formed under oxygen-poor depositional conditions (Raiswell and Berner, 1985). The full details of their formation is still debated, but it is clear that they form in the weakly reducing conditions immediately above the sulphidic zone developed within sediments. At this level ferrous iron and hydrogen sulphide react rapidly to produce abundant iron monosulphide microcrysts. These aggregate into spheres (framboids) probably as a result of their conversion to greigite which has magnetic properties. This reaction requires the supply of partially oxidised sulphur species, and it is for this reason that framboid formation appears to be restricted to the vicinity of the redox boundary (Canfied and Thamdrup, 1994; Wilkin and Barnes, 1997). During early diagenesis greigite is converted to pyrite.

Pyrite framboid formation occurs within the surface layers of sediments formed beneath oxygen-poor (dysoxic) bottom waters, where the redox boundary is located close to the sediment surface, and they can occur in a range of sizes typically between 4 and 50 μm diameter (Wilkin et al., 1997). As oxygen-restriction intensifies the redox boundary may move up into the lower water column with the result that framboids are formed syngenetically, as happens in the modern-day Black Sea. Crucially, the time for formation of syngenetic framboids is severely limited because these dense particles rapidly sink out of the water column into the sulfidic conditions below. As a result, syngenetic framboid populations are characteristically