

Mesoproterozoic sulphidic ocean, delayed oxygenation and evolution of early life: sulphur isotope clues from Indian Proterozoic basins

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Abstract – Analyses of sulphur isotope compositions in sedimentary pyrites from the Vindhyan, Chattisgarh and Cuddapah basins show heavy $\delta^{34}\text{S}$ ($> +25\text{‰}$) values during the Mesoproterozoic. The data provide evidence in support of a hypothesized global Proterozoic sulphidic anoxic ocean where very low concentrations of marine sulphate, bacterially reduced in closed systems, produced $\delta^{34}\text{S}$ values in pyrites similar to or even heavier than marine sulphate. The extreme environmental conditions induced by these anoxic oceans could have been responsible for the delayed oxygenation of the biosphere and retarded evolution of multicellular life.

Keywords: sulphur isotope, Mesoproterozoic basin, India, early life.

1. Introduction

The Proterozoic eon (2.5–0.54 Ga) marks the transition from an anoxic Archaean to oxic Phanerozoic ocean–atmosphere system (Holland, 1984; Des Marais *et al.* 1992). Although oxygenation of deep ocean began at *c.* 1.8 Ga (Holland, 1984; Holland & Beukes, 1990), recent studies on biomarkers of sulphur bacteria (Brocks *et al.* 2005), molybdenum and sulphur isotope ($\delta^{34}\text{S}$) compositions in black shales (Arnold *et al.* 2004), and pyrites (Canfield, 1998, 2004; Poulton, Fralick & Canfield, 2004) strongly advocate continuation of the sulphidic–anoxic oceanic state throughout the Mesoproterozoic and parts of the Neoproterozoic period until the $p\text{O}_2$ approached modern levels after *c.* 1 Ga. Bio-limiting trace metals might have been scarce in such a stressed environment, causing a restricted nitrogen cycle and marine primary productivity, or in turn hindering evolution of early life like eukaryotes or triploblastic animals (Hoffman *et al.* 1998; Anbar & Knoll, 2002; Kah, Lyons & Frank, 2004).

In particular, the exact timing of appearance and explosion of triploblastic animals or eukaryotes is an issue of debate. The oldest known records of both triploblastic trace fossils (Seilacher, Bose & Pfluger, 1998; Rasmussen *et al.* 2002) and multicellular eukaryotes (Bengtson *et al.* 2009) have recently been recorded from *c.* 1.6 Ga old rocks of the Vindhyan basin, India. It is peculiar that these metazoans/algae did not evolve and proliferate in the subsequent phases of Vindhyan sedimentation. Also, these purported

traces are not found in any other correlative basinal successions of the world, making them controversial (Jensen, Droser & Gehling, 2005). Understanding the geochemical conditions (e.g. sulphur cycle) of Indian Proterozoic basins, therefore, becomes important, as this can give important insight into the Proterozoic oxygenation and evolution of early life.

The fractionation of sulphur between sulphate (SO_4^-) and sulphide (H_2S) species in oceans is driven by bacterial sulphate reduction (BSR). Sulphide produced by BSR is either recycled back as sulphate or combines with available iron to form pyrite (FeS_2). Burial of sedimentary pyrite (and organic carbon) eventually controls oxygen in an ocean–atmosphere system (Berner, 1984; Bottrell & Newton, 2006). BSR preferentially fractionates ^{32}S in pyrite, making the remaining sulphate enriched in ^{34}S . Since the amount of reduction depends both on the redox state at the sediment–water interface and the supply of sulphate in the water column, the sulphur isotope compositions ($\delta^{34}\text{S}$) of sedimentary sulphides can be used as potential tracers of Proterozoic ocean chemistry.

Here we report preliminary $\delta^{34}\text{S}$ data of sedimentary pyrites from three large Mesoproterozoic basins of India: Vindhyan, Cuddapah and Chattisgarh, which add to the already existing database and suggest that the Mesoproterozoic anoxic sulphidic ocean was indeed global in nature. Our data, although limited, provide additional input to the proposed model of the Proterozoic ‘Canfield ocean’ (Buick, 2007) and suggest that both oxygenation of biosphere and evolution of metazoa or eukaryotes were possibly delayed due to this extreme adverse environmental condition.

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2. Geology

Epeiric seaways were over-represented in the Proterozoic, low-gradient, and much wider and shallower than modern shelves (maximum ~ 100 m deep with no discernible shelf-slope break: Shaw, 1964; Irwin, 1965; Friedman, Sanders & Kopaska-merkel, 1992; Eriksson *et al.* 1998), but exposed to open-ocean tides and waves. However, widespread carbonate deposits and/or phosphate nodules in black shales indicate that depth varied from as low as 30 m to > 100 m, respectively (Friedman, Sanders & Kopaska-Merkel, 1992; Eriksson *et al.* 1998).

Locations, composite stratigraphies and important chronological levels of Vindhyan, Chattisgarh and Cuddapah basins are shown in Figure 1. Palaeocurrent analysis (Bose *et al.* 2001) and basin-scale presence of tidal currents or waves (Banerjee, 1982; Chakraborty & Bose, 1990; Paul & Chakraborty, 2003) suggest the Vindhyan to be an epicratonic sea with an open ocean connection in the northwest (Chanda & Bhattacharya, 1982). Of particular interest in the present study is the Bijaygarh Shale (BS; Fig. 1b). Gradational contact with the underlying shallow marine Lower Kaimur Sandstone, fining-upward sand-free character, absence of current and wave features, occasional phosphatic and strata-bound pyrites indicate the Bijaygarh Shale as the product of maximum flooding (Bose *et al.* 2001) following a transgressive systems tract (TST). The pyritiferous part is interpreted as a condensed zone (Banerjee *et al.* 2006). Within this overall transgressive framework, however, the Bijaygarh Shale registers intermittent storm incursions (e.g. profuse gutter casts: Chakraborty, 2006). Tidal bundles or double mud-layers at its lower and upper parts also suggest occasional oxygenation of the Vindhyan shelf (Bose & Chaudhuri, 1990).

In the Chattisgarh basin, the depositional environments varied from fluvial (Patranabis Deb *et al.* 2007) through estuarine to distal marine shelf below storm wave base (Murti, 1987; Chakraborty & Paul, 2008). A TST across the Rehatikhoh–Saraipali transition in a fan delta-shelf environment is surmised (Chakraborty *et al.* 2009; Fig. 1c). The overlying Charmuria Limestone also shows a retrogradational stacking pattern representing a transgressive event. The limestone is dominantly micritic and pyritiferous. Though rare in the Phanerozoic, such micritic bedded carbonates were abundantly formed in anoxic intertidal conditions in both the Palaeo- and Mesoproterozoic (Sumner & Grotzinger, 1996; Bartley *et al.* 2000). Cyanobacteria is reported at some locations (De, 2007). From its evenly bedded character (0.25 to 1.25 cm thick), the presence of a ‘birds eye’ structure, complete absence of siliciclastic grains and waves or tide, a sub-tidal, low-energy euxinic depositional environment (an isolated platform in a cratonic seaway) has been conceived (Moitra, 1995; Patranabis Deb, 2004).

A coastal to shallow marine depositional environment is proposed for Cuddapah sediments (Nagaraja Rao *et al.* 1987; Basu *et al.* 2007; Fig. 1d). Without any

‘sequence analysis’, based solely on the repeated alternation between quartzite, shale or limestone at the formation scale, recurrent transgressive–regressive cycles and unconformities were suggested (Ramam & Murthy, 1997). In particular, the barite–pyrite-bearing Cumbum shale has been interpreted as a product of transgression in a deep-water cratonic basin (Chaudhuri *et al.* 2002; Mukhopadhyay, Ghosh & Nandi, 2006). All sedimentological evidence indicates absence of any open ocean connectivity for both the Chattisgarh and Cuddapah basins (Patranabis Deb, 2004).

3. Sampling

Sample locations and stratigraphic levels are shown in Figure 1. Strata-bound pyrite from the Amjhore mine, Shahbad district, Bihar, hosted within the Bijaygarh Shale (Vindhyan), was sampled. In the Chattisgarh and Cuddapah basins, pyrites from the Charmuria limestone, Cumbum black shale and Narji limestone were sampled. For assessing the sulphur isotope fractionation between dissolved sulphate and sulphide (Ohmoto & Rye, 1979), barite, hosted in the Cumbum shale (locally known as the Pullampet Formation), was sampled from the Mangampeta mine. The barite is grey, fine-grained and thick-bedded. In addition, selected carbonates were sampled for oxygen ($\delta^{18}\text{O}$) and carbon ($\delta^{13}\text{C}$) isotope analysis from these basins for assessing the extent of burial diagenesis.

4. Chronology of pyrite-bearing strata

Pb–Pb dates of the limestones from the Kajrahat and Rohtas formations are 1721 ± 90 Ma (Fig. 1b; Sarangi, Gopalan & Kumar, 2004; Ray, 2006) and 1601 ± 130 Ma (Ray, Veizer & Davis, 2003) and 1599 ± 48 Ma (Sarangi, Gopalan & Kumar, 2004), respectively. Although the Pb–Pb ages are inherently not very reliable and give a tentative chronology for the lower Vindhyan, the zircon U–Pb dates (both conventional and SHRIMP techniques) of 1630.7 ± 0.4 Ma (Ray *et al.* 2002) and 1628 ± 0.8 Ma (Rasmussen *et al.* 2002) of the Porcellanite Formation occurring between the Kajrahat and Rohtas formations are well consistent with the obtained Pb–Pb dates. Recent palaeomagnetic studies and a LA-ICPMS U–Pb detrital zircon age of 1020 Ma from the Upper Bhandar sandstone (Malone *et al.* 2008) nearly bracket the upper limit of the Upper Vindhyan. The syn-sedimentary pyrites from the Bijaygarh Shale, therefore, suggest an age between 1.6 Ga and 1.0 Ga, that is, Mesoproterozoic (Fig. 1b).

The lower part of the Cuddapah basin provides ages between 1817 ± 24 Ma (Rb–Sr date of the Pulivendla mafic sill emplaced into the Tadpatri shales: Bhaskar Rao *et al.* 1995; Fig. 1d) and 1756 ± 29 Ma (Pb–Pb age of uranium mineralization and stromatolitic dolomite from the Vempalle and Tadpatri formations: Zachariah *et al.* 1999). The ^{40}Ar – ^{39}Ar age of 1418 ± 8 Ma of lamproite dykes emplaced within the Cumbum shale (Chalpathi Rao *et al.* 1999) marks the termination of

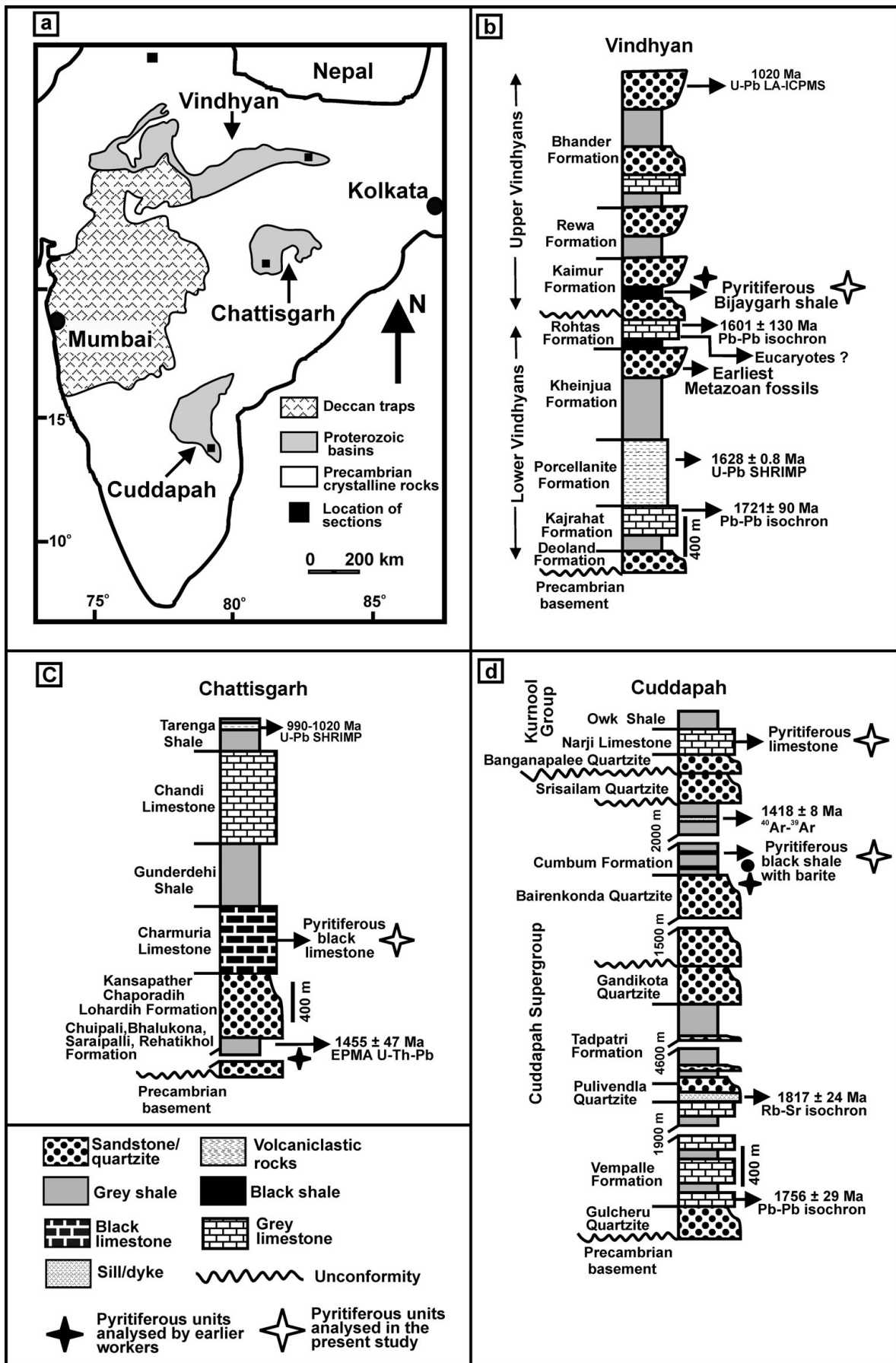


Figure 1. (a) Location map of the three large Proterozoic basins of India: Vindhyan, Chattisgarh and Cuddapah. Composite stratigraphy of (b) Vindhyan, (c) Chattisgarh and (d) Cuddapah basins. Also indicated are chronology (including the dating methods adopted by different workers) of various horizons and positions of the pyritiferous units analysed in the present study (open star); solid star indicates the horizons analysed by earlier workers. Solid circle indicates the barite layer in the Cuddapah basin.

the Cuddapah sedimentation. Although both Rb–Sr and Ar–Ar ages can be easily reset, the ranges suggest that both the pyrite and barite samples of the Cumbum shale, analysed in the present work, have a Mesoproterozoic age between 1.8 Ga and 1.4 Ga. The pyrites of the Narji limestone of the Kurnool Group are younger than 1.4 Ga, but the exact age is difficult to estimate.

Das *et al.* (2009) calculated a *c.* 1455 ± 47 Ma age (EPMA U–Th–Pb dates of monazite grains from bedded tuff) for the basal part of the Chattisgarh succession. The U–Pb SHRIMP date on zircons from the tuff layers in the uppermost Tarenga shale provides an age range of 990–1020 Ma (Fig. 1c; Patranabis Deb *et al.* 2007). Bounded between the two well-dated horizons, the pyritiferous Charmuria Limestone undoubtedly indicates a Mesoproterozoic age. Summarizing, the pyrites studied here were formed during Mesoproterozoic times when regional black shale/limestone deposition was concurrently taking place in all three sedimentary basins of India.

5. Analytical methods

The pyrite samples were polished and examined under a reflected light microscope. For isotopic analysis, powdered (micro-drilled) pyrite and barite samples were packed in tin capsules with a mixture of V₂O₅ to promote full combustion. Samples were combusted in a quartz tube reactor, pre-filled with WO₃ and pure Cu, and kept at a temperature of 1050 °C within a Flash HT 1112 elemental analyser. Purified SO₂ gas was measured in a Delta Plus XP continuous-flow mass spectrometer. Routine precision (monitored by running both NBS-123 and an internal BaSO₄ standard) of ~ ± 0.2 ‰ was obtained for δ³⁴S. The δ³⁴S (‰) values are expressed relative to the Canyon Diablo Troilite standard (CDT). For δ¹⁸O and δ¹³C analyses, powdered carbonates were reacted with orthophosphoric acid and purified CO₂ measured in the same mass spectrometer. The system was calibrated by the NBS-19 standard. Analytical precision was ~ ± 0.1 ‰ for both δ¹⁸O and δ¹³C.

6. Results and interpretation

6.a. Mode of occurrence and petrography of pyrites

Mesoscopically the pyrites occur as massive, bedded (~ 0.8 m thick) cryptocrystalline variety (e.g. at Amjhore, Vindhyan), microclots (maximum size being ~ 0.3 cm; e.g. in Charmuria Limestone), disseminated and large euhedral crystals (e.g. Narji limestone or Cumbum shale). Under the microscope, Amjhore pyrite displays both framboidal and euhedral habits. The framboids show a concentration of elliptical to oval (Fig. 2a) or elongated grains that radiate from possible growth nuclei (Fig. 2c). The wavy carbonaceous and pyritiferous laminae in the Bijaygarh Shale have recently been inferred to be microbial mats of cyanobacterial origin (Banerjee *et al.* 2006). From the

growth of quartz cement between the pyrite grains in the form of ‘teeth and socket’ structures, both pyrite and quartz have been interpreted as early diagenetic products (Sur, Schieber & Banerjee, 2006). While this may not be strictly the case, the framboids do indicate a definite early diagenetic origin. The euhedral grains (Fig. 2b, d) could have formed from these original framboids (Sawlowicz, 1993), where variation in grain size possibly suggests different extents of diagenetic recrystallization. Mangampeta pyrites exhibit microscopic-scale banding of small euhedral grains (Fig. 2e). Pyrites from Charmuria and Kurnool are characteristically euhedral in nature (Fig. 2f–h).

6.b. Sulphur isotopes in pyrites

Tables 1 and 2 summarize δ³⁴S and δ¹⁸O/δ¹³C values, respectively, along with the sample details. Our data show moderate to very heavy pyrite δ³⁴S values ranging from minimum 8.1 to maximum 38.8 ‰ in these basins. When compared and put together with the published data, the δ³⁴S values of the Chattisgarh and Vindhyan show means of 26.3 ± 0.9 ‰ (n = 12) and 25.5 ± 8.7 ‰ (n = 42), respectively (Sinha *et al.* 2001; Guha, 1971; Table 1). It is important to note that the earlier work on the Vindhyan pyrites reported a mean value of ~ 9.3 ‰, much lower than the maximum enriched value, up to 31.8 ‰, obtained in the present work. This indicates distinct geochemical differences (namely, the amount of sulphate reduction) that operated during the precipitation of these two sets of pyrite samples, as evident from the sedimentological signature of alternating depositional environments in the Bijaygarh Shale (see Section 2). No published record of syn-sedimentary Cuddapah pyrite is available, and the limited data show a mean δ³⁴S of 28.3 ± 11.8 ‰ (n = 6). When all available data are considered, the δ³⁴S of Indian pyrites range from 4.5 ‰ to 40.7 ‰.

Frequency distributions of all δ³⁴S data from the three basins are shown in Figure 3a–c. No facies-dependent variation in the δ³⁴S values (see Table 1 for facies types), as reported by Shen, Canfield & Knoll (2002), is observed. All Indian pyrites show high ³⁴S enrichment, irrespective of the nature of the pyrite (framboidal, euhedral or laminated), and none shows moderate to extreme negative δ³⁴S values as observed in most sedimentary pyrites of Phanerozoic age (Strauss, 1999; Canfield & Raiswell, 1999; Canfield, 2004 and references therein). The δ³⁴S values as high as ~ 40 ‰ are closer to or even higher than the known δ³⁴S value of Proterozoic marine sulphates (Strauss, 1997; Kah, Lyons & Chesley, 2001; Gellatly & Lyons, 2005; Canfield, 2004) and require discussion.

7. Discussion

7.a. Diagenetic effect on sulphur isotopes composition

In modern environments, authigenic pyrite is formed by BSR; the magnitude of reduction depends on specific

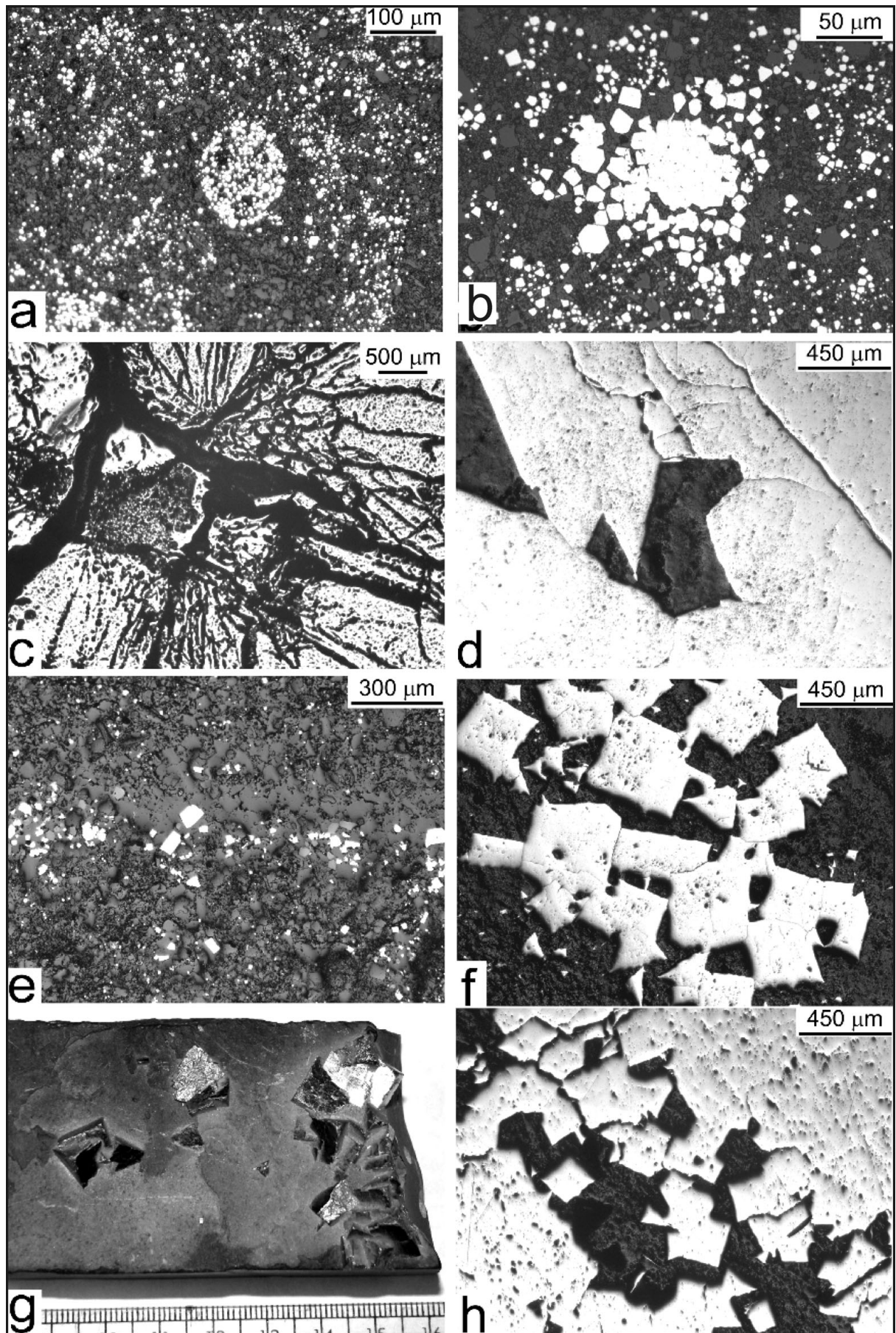


Figure 2. (a–c) Reflected light photomicrographs of pyrite showing framboidal texture from Amjhore; (d) euhedral grains with more diagenetic recrystallization from Amjhore; (e, f, h) laminated bands of small euhedral grains from Mangampeta, Charmuria and Kurnool, respectively; (g) euhedral pyrite crystals in a hand specimen of Kurnool limestone.

Table 1. Sulphur isotope composition of Indian pyrites

Sample number/ Location	Basin	Formation/unit	Age	Rock type/mineral	Facies	$\delta^{34}\text{S}$ ‰ CDT	Data source
A-7, Amjhore	Vindhyan	Kaimur, Bijaygarh shale	Mesoproterozoic, < 1.6 Ga, > 1.02 Ga	Laminated black shale, pyrite	Distal deep water	+10.6	Present work
A-1, Amjhore	"	"	"	"	"	+25.1	"
A-4, Amjhore	"	"	"	"	"	+37.7	"
1, Amjhore	"	"	"	"	"	+25.5	"
2, Amjhore	"	"	"	"	"	+28.3	"
A-3, Amjhore	"	"	"	"	"	+19.4	"
A-2, Amjhore	"	"	"	"	"	+31.8	"
Amjhore	"	"	"	"	"	+4.52 – +19.9 (36)	Guha (1971)
C-5, Charmuria	Chattisgarh	Charmuria limestone	Mesoproterozoic, < 1.45 Ga, > 0.99 Ga	Bedded black limestone, pyrite	"	+25.4	Present work
C-2, Charmuria	"	"	"	"	"	+26.4	"
C-1, Charmuria	"	"	"	"	"	+27.6	"
C-3, Charmuria	"	"	"	"	"	+25.9	"
Rehatikhoh	"	Rehatikhoh	"	Feldspathic arenite, pyrite	Proximal fan delta	+27 – +40.7 (6)	Sinha <i>et al.</i> (2001)
Saraipali	"	Saraipali	"	Black shale, pyrite	Distal deep water	+27 (1)	"
Rehatikhoh	"	Rehatikhoh	"	Quartz arenite, pyrite	Proximal fan delta	+23.7 (1)	"
CB-1, Mangampeta	Cuddapah	Cumbum shale	Mesoproterozoic, < 1.8 Ga, > 1.4 Ga	Laminated black shale, Barite	Distal deep water	+42.3	Present work
Mangampeta	"	"	"	"	"	+41.8 – +45.5 (7)	Clark, Pooleb & Wang, 2004
"	"	"	"	Laminated black shale, pyrite	"	+8.1	Present work
CSB-1, Mangampeta	"	"	"	"	"	+38.3	"
CSB-1/1, Mangampeta	"	"	"	"	"	+38.8	"
CSB-1/2, Mangampeta	"	"	"	"	"	+25.3	"
K-36, Kurnool	"	Narji limestone	< 1.4 Ga	Bedded limestone, pyrite	"	+25.7	"
KN-1, Kurnool	"	"	"	"	"	+35.6	"

The $\delta^{34}\text{S}$ (‰) values are expressed relative to the Canyon Diablo Troilite standard (CDT).

geochemical conditions (Goldhaber & Kaplan, 1974; Berner, 1984; Canfield, 2004). Normally BSR is completed within a few metres of the sediment–water interface (Riciputi, Cole & Machel, 1996). Large amounts of H_2S are produced by this mechanism, provided the diagenetic environment is anaerobic ($E_h < -100$ mV), has a sufficient supply of dissolved SO_4^{2-} and nutrients for bacterial growth (e.g. high amount of organic matter) and has a lower temperature range of 0–60 °C (Riciputi, Cole & Machel, 1996; Machel, Krouse & Sassen, 1995). At higher temperatures (80–200 °C), abiogenic thermochemical sulphate reduction (TSR; Machel, Krouse & Sassen, 1995) can occur if there is sufficient dissolved sulphate in pore water.

Initial reduction (and consequent rupturing of S–O bonds) in BSR involves a kinetic fractionation of up to 40 ‰, however, formation of intermediate compounds such as thiosulphate can cause an extended range of fractionation, producing H_2S as depleted as –70 ‰ (Rees, 1973; Ohmoto & Rye, 1979; Jørgensen, 1990). The resulting pyrites, thus formed, can be depleted by 15–65 ‰, compared to the parent marine sulphate. The

kinetic fractionation during the $\text{SO}_4^{2-} \rightarrow \text{S}^{2-}$ reduction in TSR progressively decreases from ~20 ‰ at 100 °C to only ~10 ‰ at 200 °C (Kiyosu & Krouse, 1990). In many deep gas reservoirs, insignificant fractionation has been observed between the sulphate and metal sulphide, thereby producing enriched $\delta^{34}\text{S}$ values of pyrites almost similar to that of sedimentary sulphate (Krouse, 1977). The only available marine sulphate, the Cuddapah barite, has a $\delta^{34}\text{S}$ value of +42.3 ‰ and is similar to the earlier reported data (41.8 to 45.5 ‰; Clark, Pooleb & Wang, 2004). The $\delta^{34}\text{S}$ values of the Cuddapah barite are not only enriched by about 10–15 ‰ more than the contemporary (Mesoproterozoic) marine sulphate (Strauss, 1999; Kah, Lyons & Chesley, 2001; Kah, Lyons & Frank, 2004; Gellatly & Lyons, 2005), but also have exceptionally small variation compared to other Proterozoic barite deposits of the world (Clark, Pooleb & Wang, 2004; Strauss, 1999; Kah, Lyons & Chesley, 2001; Kah, Lyons & Frank, 2004; Gellatly & Lyons, 2005). The maximum pyrite value of ~+40 ‰ is not very different from this sulphate value. Hence the distinct possibility exists

Table 2. $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ values of carbonates

Basin	Formation/unit	Rock type/facies	$\delta^{13}\text{C}$ ‰ PDB	$\delta^{18}\text{O}$ ‰ PDB	Data source
Chattisgarh	Charmuria	Plain laminated deep-water black limestone	1.5	-9.48	Present work
"	"	"	1.44	-9.68	"
"	"	"	1.36	-10.64	"
"	"	"	1.3	-11	"
"	"	"	1.46	-10.84	"
"	"	"	1.24	-10.91	"
"	"	"	2.13	-9.33	"
"	"	"	2.14	-9.38	"
"	"	"	3.79	-4.76	Chakraborty <i>et al.</i> 2002
"	"	"	3.66	-5.07	"
"	"	"	2.42	-7.18	"
"	"	"	3.89	-4.07	"
Cuddapah	Narji limestone	"	2.61	-8.65	Present work
"	"	"	2.7	-8.6	"
"	"	"	2.6	-8.6	"
Vindhyan	Bhander limestone	Plain laminated deep-water grey limestone	2.93	-6.66	Chakraborty <i>et al.</i> 2002
"	"	"	3.54	-3.51	"
"	"	"	4.42	-6.11	"
"	"	"	3.54	-4.73	"
"	"	"	3.51	-2.61	"
"	"	"	4.03	-3.2	"
"	"	"	2.42	-4.22	"
"	"	"	4.3	-5.21	"
"	"	"	3.54	-5.82	"
"	"	"	4.53	-4.32	"

that TSR created at least some of the enriched values. A deep burial diagenesis involving TSR will also cause substantial change in both texture and $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ values of basinal carbonates through water–rock interaction. In general, the well-preserved laminations, dominant micritic character and preservation of primary textures, such as stromatolite laminae, pelloidal and intraclastic texture in lime mudstone (Burns & Matter, 1993), suggest early diagenetic character. Although textural preservation is possible even in a post-depositional fluidized diagenetic regime, we consider it to be negligible, based on the ranges of stable isotopes of associated carbonates as discussed below.

Figure 4a shows the cross-plot of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of plane-laminated deep-water pyritiferous limestones of the Chattisgarh and Cuddapah basins. In the Vindhyan basin, although pyrite is hosted in black shale, plain laminated Bhander limestone was also plotted for comparison (Table 2; Fig. 4a; data taken from Chakraborty *et al.* 2002). All data plot within the ellipse representing the $\delta^{18}\text{O}/\delta^{13}\text{C}$ range of global marine carbonates deposited between 1.5 and 0.8 Ga (Kasting *et al.* 2006). Although there is a considerable spread, the mean $\delta^{18}\text{O}$ value of these carbonates (-6.6 ± 2.9 ‰) is considerably depleted compared to modern marine carbonates. This is quite consistent with the observed $\delta^{18}\text{O}$ values of Proterozoic carbonates which are often depleted by as much as 10 ‰ compared to the Late Phanerozoic period (Kasting *et al.* 2006). Such depleted values, earlier thought to be a diagenetic effect, are increasingly considered as products of

depleted ocean water caused by low-temperature water–rock interaction in a hot ocean (Kasting *et al.* 2006). The mean $\delta^{13}\text{C}$ value of these carbonates is $+2.9 \pm 1$ ‰ with all data plotting towards the most enriched end of the global range (Fig. 4a, b). Global compilation of the marine $\delta^{13}\text{C}$ values between 1.5 Ga and 1 Ga also shows enriched values between 0 and 5 ‰ (Brasier & Lindsay, 1998; Kah *et al.* 1999; Bartley & Kah, 2004), consistent with the observed $\delta^{13}\text{C}$ range (Fig. 4b). One possible reason for such enrichment is a reduction in the global dissolved inorganic carbon reservoir and consequent increase in onshore carbonate productivity (Bartley & Kah, 2004; Chakraborty *et al.* 2002). The $\delta^{13}\text{C}$ values of carbonates formed during TSR, on the other hand, are generally depleted, ranging from -20 to -70 ‰, depending on the species of hydrocarbon (e.g. kerogen, crude or bitumen) aiding the sulphate reduction (Machel, Krouse & Sassen, 1995). Further, the Bhander Limestone (Vindhyan) reportedly preserves the original marine Sr isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.705$ to 0.706 ; Ray, Veizer & Davis, 2003). A pervasive diagenesis, however, introduces radiogenic Sr, increasing the Sr ratio to as high as 0.709 (Shields & Veizer, 2002; Ray, Veizer & Davis, 2003). Based on these lines of evidence, we believe that deep burial diagenesis was not a common feature for most carbonates (and associated sediments) in these basins, and hence TSR played an insignificant role in the formation of these pyrites. Instead we consider these pyrites to be the product of BSR in widely varying geochemical conditions, such as redox state and extent of sulphate supply, as discussed below.

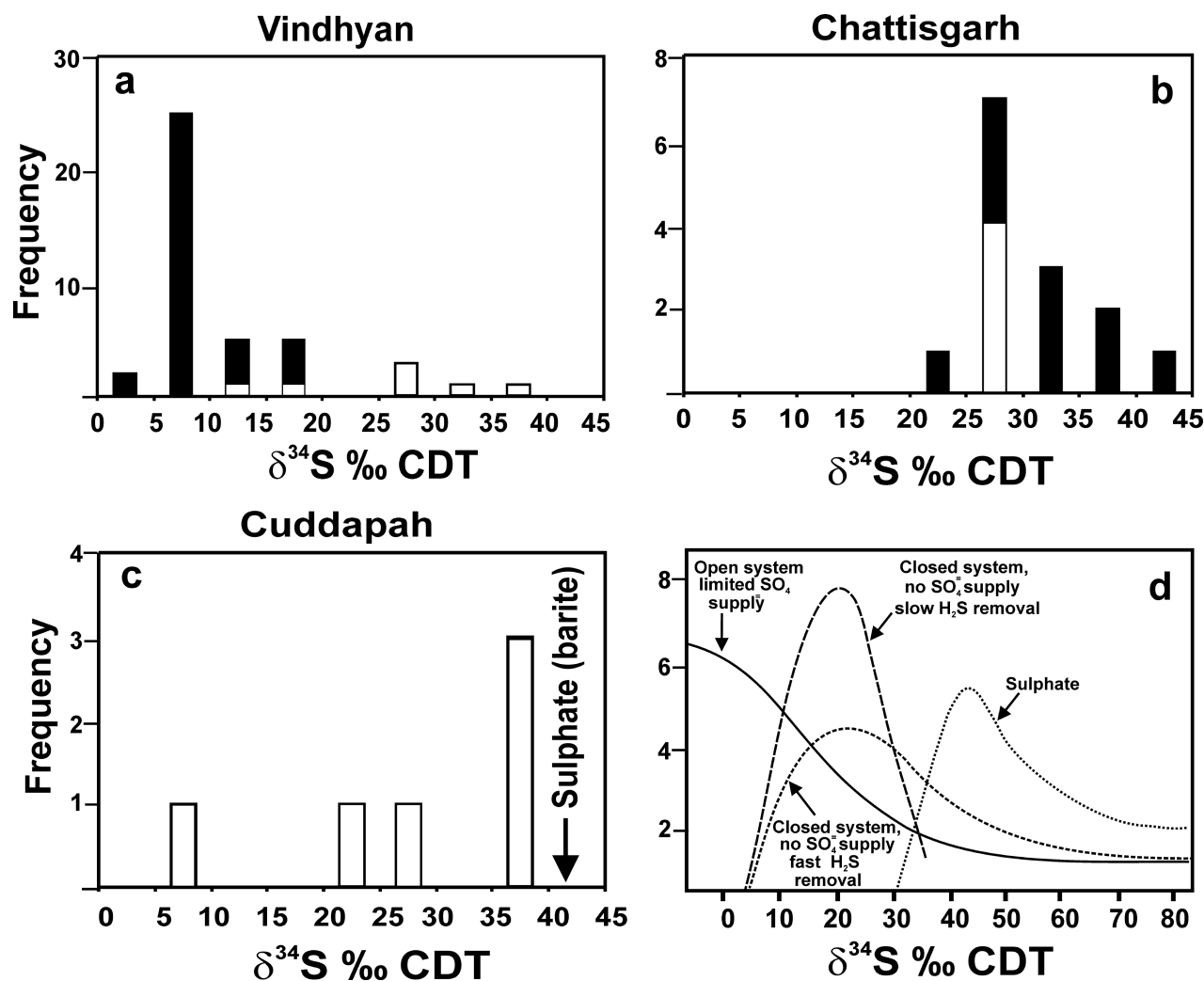


Figure 3. Frequency distribution of $\delta^{34}\text{S}$ values of pyrite from (a) Vindhyan; (b) Chattisgarh; (c) Cuddapah basins. Open bars: data from present work; solid bar: published data. (d) Calculated distribution of sulphide $\delta^{34}\text{S}$ formed from Proterozoic seawater sulphate (+30 ‰) by biogenic sulphate reduction under relatively open (assumed $\text{SO}_4^- - \text{S}^-$ fractionation factor ~ 1.040 , Ohmoto & Rye, 1979) and closed (assumed fractionation factor ~ 1.025) systems. Also shown is the calculated enrichment in sulphate in a closed system capable of producing ~ 42 ‰ value like the Cuddapah barite (c).

7.b. Geochemical modelling

The $\delta^{34}\text{S}$ values of H_2S or metal sulphides, formed during BSR, depend on the kinetic isotope effect (k_1/k_2) during the $\text{SO}_4^- \leftrightarrow \text{S}^-$ reduction and $\text{SO}_4^-/\text{H}_2\text{S}$ ratio of different geochemical systems that are either open or closed with respect to SO_4^- or H_2S (Ohmoto & Rye, 1979). The value of k_1/k_2 varies from 1.025 in a closed system to 1.065 in a relatively open system with high SO_4^- supply, the absolute $\delta^{34}\text{S}$ value of sulphide being dependent on the initial value of marine sulphate and its concentration in the water column. Figure 3d shows the calculated distribution of $\delta^{34}\text{S}$ values of SO_4^- and sulphide in closed systems with no SO_4^- supply, but with fast and slow pyrite removal (Rees, 1973; Schwarcz & Burnie, 1973; Ohmoto & Rye, 1979). Also shown in Figure 3d are the $\delta^{34}\text{S}$ values of sulphides in a relatively open system, where SO_4^- is supplied by slow diffusion from the upper layer of the ocean, a situation often described for the so-called 'euxinic' basin of

the Black Sea. Reported $\delta^{34}\text{S}$ values of barite from the Proterozoic Nagthat Formation of lesser Himalaya, deposited in a continental shelf setting, range from +26.5 to +29.5 ‰ (Sharma, Verma & Law, 2006) and could have been the sea-water sulphate value in this region during the Proterozoic; a range of $\delta^{34}\text{S}$ sulphate values between +25 and +35 ‰ have been obtained from Proterozoic evaporites from different parts of the world (Strauss, 1997, 1999). We assumed an initial sulphate value of +30 ‰ for calculating the change in $\delta^{34}\text{S}$ of either SO_4^- or H_2S . Figure 3d suggests that the highly enriched $\delta^{34}\text{S}$ value (~ 42 ‰) of the Cuddapah barite possibly resulted due to progressive reduction of sulphate in a closed system that enriched the $\delta^{34}\text{S}$ of the remaining dissolved SO_4^- . Our estimation suggests that a ~ 40 ‰ decrease in the initial SO_4^- concentrations can produce the value observed in the Cuddapah barite.

Comparison of calculated values of sulphides with the observed frequency distribution of $\delta^{34}\text{S}$ of the

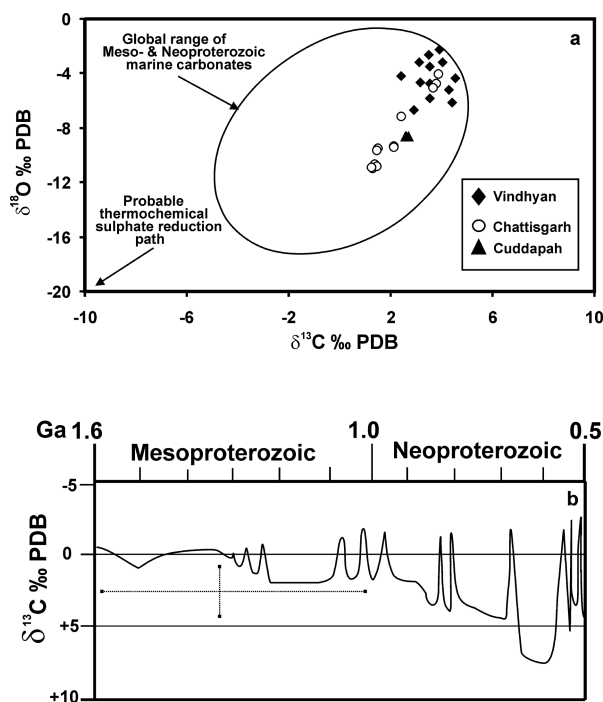


Figure 4. (a) $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ cross-plot of Indian Proterozoic carbonates. Note enriched $\delta^{13}\text{C}$ values and cluster of data away from probable TSR field (for details see text). The ellipse is the global range of marine carbonates between 1.5 and 0.8 Ga (data source: http://www.science.uottawa.ca/geology/isotope_data/; Kasting *et al.* 2006). (b) Secular marine $\delta^{13}\text{C}$ variation through Mesoproterozoic (modified from Brasier & Lindsay, 1998); the range of Indian carbonates shown by dotted line.

Chattisgarh and Cuddapah basins (Fig. 3b, c) is consistent with sulphur derived by BSR in closed systems with no SO_4^- supply. Very high $\delta^{34}\text{S}$ values ($> 35\text{‰}$) in both the basins suggest that pyrite removal or burial was much faster compared to the rate of sulphate reduction (Ohmoto & Rye, 1979; Jørgensen, 1979; Strauss & Schieber, 1990). The higher frequency of lower $\delta^{34}\text{S}$ values in the Vindhyan pyrite (Fig. 3a), on the contrary, suggests a semi-confined marine depositional environment where SO_4^- flux was still higher (though limited) compared to the other two basins. Chemical tracers like U/Th and V/Cr also suggest a fluctuating oxic/anoxic condition during the depositional span of the shale unit (Bijaygarh Shale) that contained these pyrites (Sur, Schieber & Banerjee, 2004). Another possible reason for the variability in $\delta^{34}\text{S}$ of Vindhyan pyrite could be the greater sensitivity of isotopic composition to very low sulphate concentration (Gellatly & Lyons, 2005). It must, however, be mentioned that our dataset is limited, and more extensive sulphur isotope studies in each of these basins are required to assess the Proterozoic ocean chemistry in general.

8. Implications of heavy $\delta^{34}\text{S}$ values

The high enriched mean $\delta^{34}\text{S}$ values of $> 25\text{‰}$ in different types of sedimentary pyrites from various

stratigraphic levels of the Indian Mesoproterozoic basins call for a likely common parameter of low sulphate availability. A large body of data on $\delta^{34}\text{S}$ of pyrite and barite shows a much lower SO_4^- – H_2S fractionation during the Proterozoic and was explained by high rate of pyrite burial with respect to very low concentrations of available sulphate (Canfield & Raiswell, 1999; Canfield, 2004). A rate-dependent model for sulphur isotope change indicates that the marine sulphate concentration was between 1.5 and 4.5 mM (~ 5 – 15% of modern marine value: Kah, Lyons & Frank, 2004), suggesting an anoxic bottom water (Shen, Canfield & Knoll, 2002) throughout the Proterozoic. This prompted the hypothesis of a widespread sulphidic ocean during this period (Logan *et al.* 1995; Canfield, 2004; Hurtgen *et al.* 2002). Based on the Fe speciation data, a classic case for a Mesoproterozoic sulphidic ocean has indeed been demonstrated across the 1.8 Ga old Animikie Group of Canada (Poulton, Fralick & Canfield, 2004). The sedimentary pyrites from Tapley Hill, Australia, showed a range of $\delta^{34}\text{S}$ values ($+10$ to $+55\text{‰}$) that were enriched over the coexisting marine sulphate and strongly suggested a sulphate-poor anoxic ocean during early Neoproterozoic time as well (Canfield, 2004). Total organic carbon (TOC) content in some of the Indian pyrite-bearing shales, such as the Bijaygarh Shale, has been found to be $\sim > 4\%$ (Banerjee *et al.* 2006). This, along with the definite presence of cyanobacterial pyritiferous mat in this shale (Banerjee *et al.* 2006), suggests anoxic stratified bottom water conditions, where the SO_4^- was only being supplied by diffusion from above. The high positive $\delta^{34}\text{S}$ data of sedimentary pyrite, therefore, suggest that even in the intra-cratonic basins a low sulphate–high sulphidic geochemical condition prevailed during Mesoproterozoic time. Our data provide additional evidence that the continued bottom ocean anoxia through much of Proterozoic time was indeed global in nature. The present level of knowledge, however, is insufficient to infer whether these Proterozoic basins were part of an integrated global ocean or not, even though temporal similarity in their geochemical evolution suggests a common driving force, such as low pO_2 –low sulphate of the ocean.

The marine sulphate concentration probably remained low at the ~ 4.5 mM level until about 1.2 Ga and rose to ~ 7 – 10 mM only after 0.8 Ga (Canfield, 1998; Azmy *et al.* 2001; Hurtgen *et al.* 2002; Kah, Lyons & Frank, 2004; Gellatly & Lyons, 2005). Since accumulation of sulphate in the ocean is also controlled by oxidative weathering of the continents, the low sulphate levels possibly implied delayed oxygenation of the earth's ocean–atmosphere system until Neoproterozoic time. Such an inference also has implications for the evolution of early life. The sulphidic ocean might have induced an acute shortage of redox-sensitive bio-limiting trace metals like Cu, Mo, Cd and Zn in the water column by removing them onto sediments (Lewis & Landing, 1992; Helz

et al. 1996; Anbar & Knoll, 2002). Because these metals regulate nitrogen fixation, acute nitrogen stress might have delayed the evolution of eukaryotes, since they need to assimilate fixed nitrogen from ambient water (Anbar & Knoll, 2002). As mentioned before, the oldest evidence of metazoan burrows of ‘wormlike undermat miners’ or possible eukaryotes are recorded from the *c.* 1.6 Ga Vindhyan sediments occurring below the pyritiferous Bijaygarh Shale (Seilacher, Bose & Pfluger, 1998; Bengtson *et al.* 2009; Fig. 1b). Diversification of animal life, however, was very slow until the Early Cambrian, when hard skeletons appeared in an evolutionary explosion (Knoll, 1992). This was coincident with the complete oxygenation of the Ediacaran ocean and a large increase in sulphur isotope fractionation (Canfield & Teske, 1996; Canfield, 2004; Fike *et al.* 2006). It is tempting to speculate that the early metazoans or eukaryotes developed only in the Vindhyan basin due to its limited open ocean connection which locally provided intermittent oxygen supply in an otherwise sulphidic ocean. The pace of the evolution was retarded, however, due to the overall prolonged anoxic sulphidic conditions in the oceans that deposited sedimentary pyrites with heavy $\delta^{34}\text{S}$, as found in the present study and studies of many other contemporary basins of the world.

9. Conclusions

Analysis of sulphur isotope compositions of sedimentary pyrites from the three large Proterozoic basins of India, Vindhyan, Chattisgarh and Cuddapah, gave mean heavy $\delta^{34}\text{S}$ values of $+25.5 \pm 8.7\%$, $26.3 \pm 0.9\%$ and $28.3 \pm 11.8\%$, respectively. The $\delta^{34}\text{S}$ values do not show any relationship either with the mesoscopic/microscopic nature of pyrites or sedimentary facies. The data provide supplementary evidence in support of a hypothesized global Proterozoic sulphidic anoxic ocean, where a very low concentration of marine sulphate, bacterially reduced in closed systems, produced $\delta^{34}\text{S}$ values in pyrites similar to or even heavier than open ocean marine sulphate. The anoxic ocean could have been responsible for the delayed oxygenation of the biosphere and may have retarded evolution of multicellular life.

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