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Pyrite geochemistry and fossil preservation in shales

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As emphasized by Dr Seilacher in his introduction to this symposium, and illustrated in the contribution by Mr Martill, some of the most important examples of fossil Lagersätten occur in marine shales of Mesozoic age. Many of the factors that control the types and preservation of fossils are the same as those that affect the authigenic mineralogy and geochemistry of the shales, notably the degree of aeration or stagnation of the water column and the quantity and quality of the organic matter supplied to the sediment. Perhaps the most important diagenetic reaction in marine shales is sulphate reduction by bacteria that are obligate anaerobes. They can operate in anoxic waters or in 'reducing microenvironments' (such as concentrations of organic matter, or enclosed voids within shells) in sediments whose pore waters are kept generally oxic by the effects of burrowing organisms. Sulphate is reduced to sulphide and in the presence of reduced iron this can be precipitated as iron sulphides, normally found in ancient sediments in the form of pyrite. Pyrite is thus a key mineral in studying shale diagenesis, for its geochemistry as well as for its direct importance in preserving fossils by replacement of soft-parts (see, for example, Stürmer 1984), of aragonitic shells (see, for example, Fisher 1985) and by forming internal moulds of chambered shells (see, for example, Hudson & Palframan 1969; Hudson 1982).

The consequences of sulphate reduction in shales may be many and varied. Complex reactions may lead either to the solution of carbonates (as in some stages of aragonite shell replacement (Fisher 1985)) or their precipitation as carbonate concretions (Raiswell 1976; Hudson 1978). Phosphates liberated from organic matter during sulphate reduction (Krom & Berner 1981) may lead to phosphatization of biological material or phosphatic concretion formation. It is clear that many possible diagenetic reactions can occur and influence one another; not all are well understood.

One obvious, but often overlooked, general point is that sulphate reduction, while not so rapid in its effects as aerobic oxidation, consumes organic matter rather than conserving it. Jørgensen (1978) estimated that 50% of the organic matter deposited or autochthonously produced in the muds he studied was consumed by sulphate reduction. This may be one reason why 'soft bodied' preservation is rare in most shales and why exceptions, such as the Burgess Shale, may represent rapid burial of animal carcasses below the sulphate-reduction zone.

Three factors control the formation of pyrite in shales, the supplies of biodegradable organic matter, of sulphate and of iron. It can be shown (Fisher & Hudson 1985) that δ^{34}S of pyrite, formed either in anoxic water column, or in the zone of bioturbation in more oxic environments, should be low (generally more than 45‰ lighter than the contemporary sea water sulphate). These two environments are, however, generally readily distinguished on other grounds. Pyrite formed within the sediment where access of sea water is only by diffusion will, on the other hand, be isotopically heavier, because it forms from sulphate in pore waters which have already preferentially lost ^{32}S in early diagenesis. This situation usually obtains in organic-rich shales where organic matter is more than sufficient to satisfy sulphate supplied by diffusion.

We can illustrate the effects of some of these factors by means of examples from ammonite-bearing Jurassic shales. These are more fully discussed elsewhere (Hudson 1982; Fisher & Hudson 1985).

(i) Bioturbated shales (for example, Middle and Upper Oxford Clay, S England, Amaltheus Clay, S Germany). Low organic content, dispersed pyrite low in abundance and with low $\delta^{34}S$. Pyrite formation limited by organic supply (after loss of organic matter by aerobic oxidation). Conspicuous occurrence of pyrite in void spaces of fossils, particularly ammonite phragmacones, when it shows complex textures and very variable isotopic composition, but forms faithful compaction-resistant internal moulds. Subsequent solution of aragonite reveals these moulds to the collector. They show beautiful preservation of suture lines, but all information about shell structure is, of course, lost, as is the body chamber and outer phragmacone of all but the smallest ammonites.

(ii) 'Restricted' shales of Morris (1980): Lower Oxford Clay, central England. The significance of the vertebrate fauna is described by Martill in this symposium. The sediment very rapidly became anaerobic, below a relatively thin zone of bioturbation. Pyrite is not generally found in internal moulds, but occurs dispersed in the sediment in greater abundance. $\delta^{34}S$ is relatively heavy, indicating relative importance of pyrite formation in the zone of diffusion due to the limited zone of bioturbation. Aragonite is commonly well preserved but in some beds is replaced by pyrite, generally of heavier isotopic composition than occurs in the host sediment. Replacement appears to have commenced very soon after burial. Ammonites are commonly well preserved including body chambers and apertures, but because they lack pyritic internal moulds are crushed flat.

(iii) Bituminous shales of Morris (1980): Posidonia Shales, S Germany, Dunans Shale (Callovian), Scotland. Lack of benthic fauna leads to preservation of sedimentary lamination, and has generally been attributed to anoxic bottom waters. Because the sediment was totally anoxic, pyrite shows no particular affinity for fossils, but occurs dispersed and as pyritic concretions, many of which post-date compaction. In the Posidonia Shales aragonite solution took place very early, resulting in periostracum-film preservation of collapsed ammonites, which therefore, while complete, lack both shell structure and preserved suture lines (Seilacher *et al.* 1976). $\delta^{34}S$ values are relatively high, indicating that significant sulphate reduction occurred within the sediment rather than mostly in the water column. In the Dunans Shale lower organic content and lighter $\delta^{34}S$ values suggest most pyrite was formed within the anoxic water column. Calcareous fossils are absent from most of the unit, apart from a few calcitic belemnite rostra.

Clearly, many more preservational possibilities exist, and styles of preservation that are good for one type of study may be poor for another. There is everything to be said for collaboration between palaeontologists, sedimentologists and geochemists to extract the maximum possible information from shale-hosted Lagerstätten.

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