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Nature and composition of pyrite frambooids and organic substrate from degraded leaf cuticles of Late Tertiary sediments, Mahuadanr Valley, Palamu, Bihar

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Detailed studies of pyrite frambooids from degraded leaf cuticles have been carried out under scanning electron microscope (SEM) and energy-dispersive X-ray analyser system (EDAX). The investigations indicate that frambooidal pyrites form in the cavities and cell lumen of degraded leaves and other plant entities under reducing conditions. They occur in clusters and as solitary spherules. The elemental analyses indicate that the carbon, nitrogen, oxygen, phosphorus, iron and sulphur are the main constituents of frambooids developed on the organic substrate. The morphological characters of bacterial colonies are generally retained during mineral uptake to form frambooids.

THE pyrite frambooids associated with the biologically degraded organic matter from the carbonaceous shales of Upper Tertiary sediments, Mahuadanr Valley, Bihar (Figure 1) have been observed under scanning electron microscope (SEM). The presence of frambooidal pyrites help in the interpretation of the burial history of the deposits and the diagenesis of organic matter found associated with the sediments.

Frambooidal pyrites occur as solitary spherules or irregular masses on organic matter preserved in shales, carbonaceous shales, coal and other organic deposits. They fill pores or other empty spaces¹. The single frambooidal pyrites are irregularly or heterogeneously distributed, while their clusters are embedded in sheaths or in

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masses of highly degraded leaf tissues (Figure 2) preserved in the sediments. The SEM attached with the energy-dispersive X-ray analyser system (EDAX) provides an opportunity to study the detailed sculpture of framboidal pyrites, elemental composition and fine scale grain-to-grain association and relationship between the substrate organic particles, bacteria and other minerals. The origin of framboidal pyrites has been discussed earlier in a number of papers¹⁻⁶, but none of the authors opined that these bodies have formed initially inside the organic matter and later dispersed over the entire lithotypes. It happens because the bacteria attack first on organic matter (e.g. leaf cuticles, wood fragments, dinoflagellates, microforaminiferal linings, acritarchs, etc.)⁷.

The occurrence of framboidal pyrites in sedimentary sequences indicates the prevalence of reducing environment under euxinic conditions during the deposition^{6,8,9}. Kortenski and Kostova³ opined that the framboidal pyrites form as a result of the activity of bacteria during massive mineralization. In contrast, the purely inorganic pyrites are generated in the sedimentary matrix due to chemical reaction. This results in the formation of crystals, e.g. euhedral and anhedral pyrites. Renton and Bird⁴ postulated that pyritization is the result of crystallization of mineral solutions in organic matter.

The microbial degradation of leaf cuticles and other plant fragments is a specific phenomenon¹⁰. In this process some abscised leaf fragments are quickly degraded,

while others being less susceptible to microbes (fungi and bacteria) remain almost unaltered, probably due to the presence of highly resistant biopolymers (cutin and cutan¹¹). During the degradation of cuticular fragments, bacteria do not cover the entire surface uniformly. They occur in groups or in 'microcolonies' on limited portions, while much of the cuticular surface remain uncolonized^{12,13}. The kind of bacteria involved in the degradation of leaf cuticles may also have phytopathogenic capabilities to act with various minerals available in sediments or present in the plant tissues. These elements (C, O, N, P, K, Ca, S, Mg, Fe, Zn, Bo, Cu, Mo, etc.) which may be the derivatives of various compounds have been absorbed during mineral and nutrient uptake. The bacteria may be cocci, thiobacilli or rod-shaped with rounded ends, having special adoptive features that help in the exploitation of leaf surfaces or other plant fragments. The type of bacteria which thrive over the organic matter are also the sole agents responsible for the conversion of the structured remains into amorphous organic matter and the associated elements to their various inorganic forms¹⁴.

It is known that several elements like iron, sulphur, cobalt, zinc, lead, copper, etc. are involved in the formation of pyrite framboids due to the abiogenic or biogenic activities. The abiogenic activity results in the formation of various morphological types of pyrites, viz. euhedral, anhedral, massive and infilling (infiltration). Such pyrite types form due to chemical reactions, replacement, infilling, etc. which are common in various kinds of coals³. Inorganic pyrites occur in the form of crystals^{3,4} and their outer surface is structureless.

The present investigation was undertaken to understand the nature and composition of pyrite framboids occurring in association with the degraded cuticles. Such studies were also intended to know the genesis of pyrite framboids and their relation with the depositional environments particularly prevailing in continental basins.

The Upper Tertiary sediments of Mahuadanr Valley are exposed along Birha River and its tributaries between Rajdanda and Mahuadanr villages, Palamau, Bihar (lat. 23°23'15"N, long. 84°06'40"E). Here, the total thickness of the sequence is 3.2 m, composed of shales exposed over pyroclastic rocks, conglomerate and sandstone (Figure 1).

Six carbonaceous shale samples were treated in 30% dilute hydrochloric acid and 40% hydrofluoric acid, respectively, for the isolation of organic matter. The extracted organic matter was dehydrated in various strengths of ethanol before mounting on double scotch adhesive tape for placing on an aluminium stub. Then the specimens were sputter-coated with thin layer (60 Å) of gold and palladium alloy. The specimens were examined and photographed on Leo 430 SEM at Birbal Sahnii Institute of Palaeobotany (BSIP), Lucknow.

The percentage frequency of elements present in minerals, organic matter and framboidal pyrites with substrate was

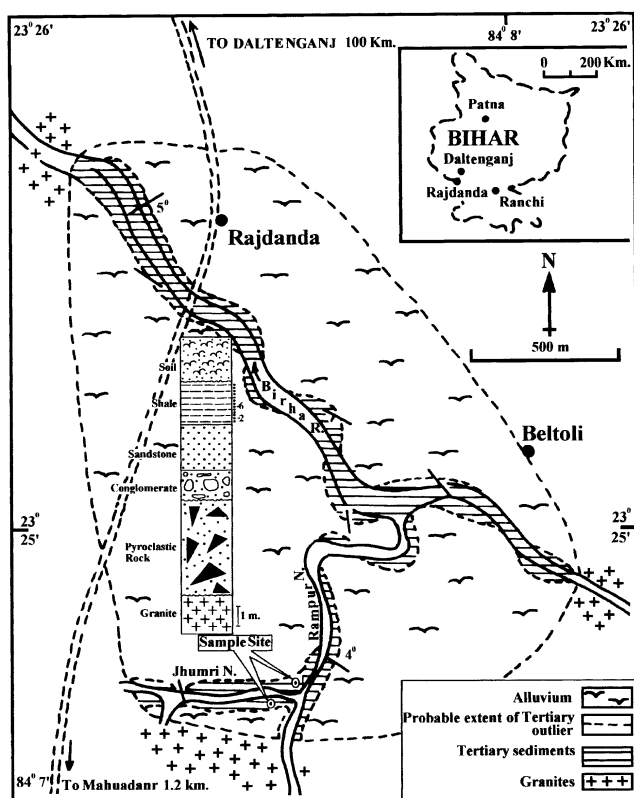


Figure 1. Location of the area with lithocolumn of Mahuadanr, Bihar. (Inset) The state of Bihar (modified after Puri and Mishra).

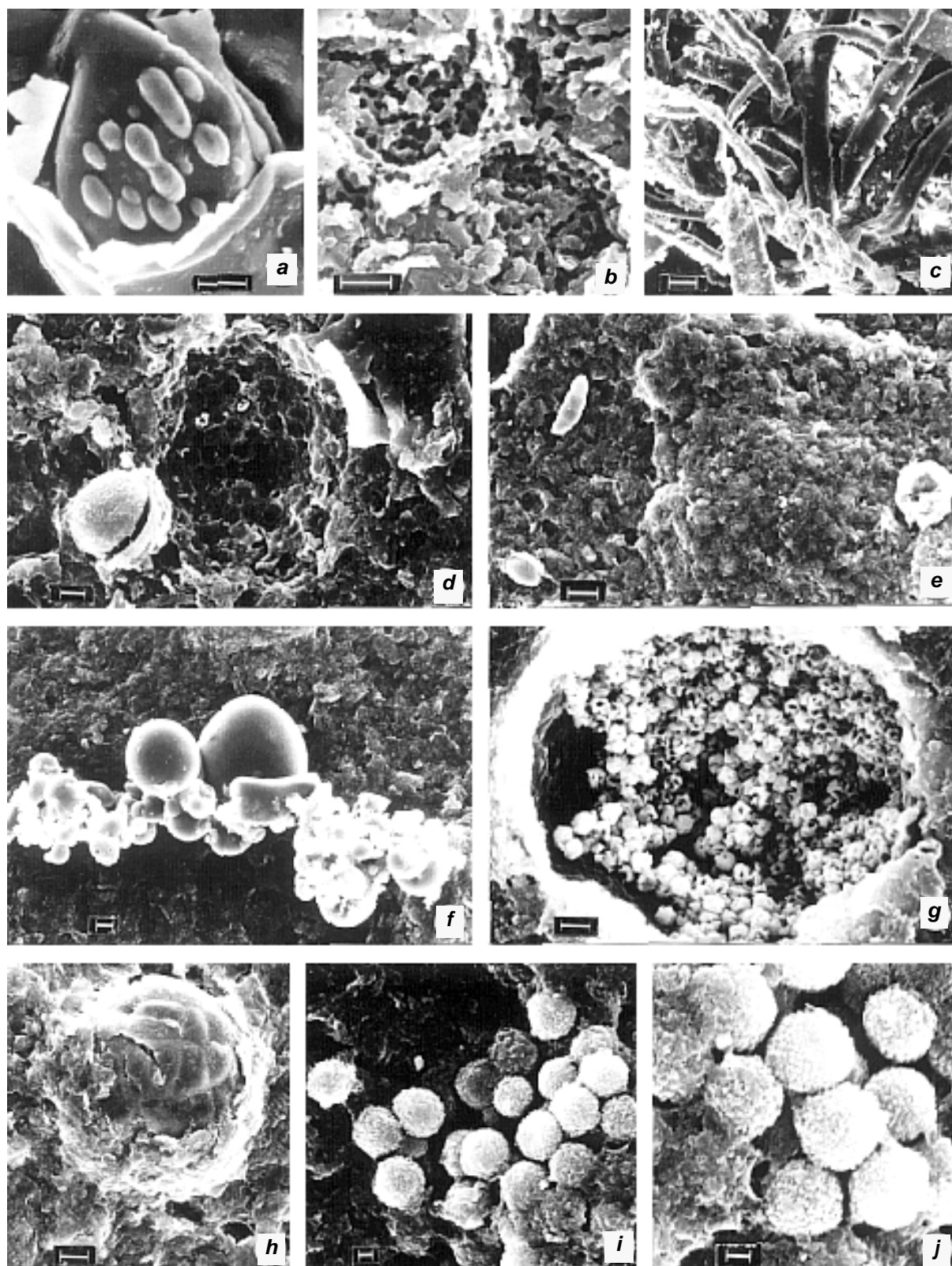


Figure 2. SEM magnification showing bar line of 10 μm in *a*, *c* and *e*; 3 μm in *b*, *d*, *f* and *h* and 1 μm in *g*, *i* and *j*. *a*, Leaf cuticular cells invaded by rod-shaped bacteria; *b*, Biodegraded cuticle showing microbial activity over it; *c*, Cuticle covered by fungal hyphae; *d*, Amorphous organic matter showing a groove with scars of pyrites and a fungal fruiting body (?); *e*, Biodegraded leaf cuticle showing fungal fruiting body *Multicellaesporites* sp.; *f*, Highly biodegraded cuticle showing pyrites of various shapes (2.0 to 10 μm) arranged in a linear pattern. Few silica crystals are also attached; *g*, Cavity at highly biodegraded leaf cuticle filled with clusters of framboidal pyrites; *h*, Framboidal pyrite spherule showing outer coating of various minerals. *i*, Cluster of framboidal pyrites on amorphous organic matter showing ornamented outer surface and *j*, same as *i* but at higher magnification.

determined under computerized energy-dispersive X-ray micro-analyser system, DX4, EDAX (ref. 15). A few pieces of the associated sediments were also analysed for comparison. The EDAX was pointed at various loci separately on different organic matter types (leaf cuticles, pyrite framboids, single pyrite spherule and bacterial remains). The photo-negatives and samples used for the study are housed in the repository of the BSIP, Lucknow.

The framboidal pyrites are the result of the activity of bacteria over plant fragments. Some individual bacterial remains on their colonies may be seen on the pieces of degraded leaf parts. The framboids may occur separately or in aggregates embedded in grooves or pits on the degraded leaf cuticles (Figure 2*f-j*). Sometimes they also ooze out and leave scars (Figure 2*g* and *d*) on the degraded leaf surface. The size of solitary framboids varies between 1.5 and 30 μm , while the maximum size of its aggregate is up to 500 μm . These framboids are ball-like in appearance and their outer surface is characterized by the rugulate, granulate or psilate ornamentation (Figures 2*i, j* and *f*).

The analyses by EDAX on pyrite framboids, single pyrite spherules, bacterial remains and degraded leaf cuticles indicate the involvement of some important elements like carbon, nitrogen, oxygen, iron and sulphur. These elements are comparatively dominant in framboids, followed by bacterial remains and degraded leaf cuticles. Sulphur and iron play a major role during the genesis of pyrite due to the formation of FeS_2 and occur next to these elements in dominance. Sulphur and iron are the only elements that are represented more in the degraded leaf cuticles than in framboids and bacterial remains (Table 1). Magnesium, aluminium and sodium occur in fairly increasing quantity on degraded cuticles, while manganese, cadmium, copper, cobalt, phosphorus and titanium occur in traces without change in their quantity. However, the role of these elements is not well known. The occurrence of carbon in association with sulphur (higher percentage of carbon with low sulphur) indicates freshwater conditions¹⁶. The record of high percentage of carbon during EDAX analysis may be due to its availability in organic matter associated with the pyrite framboids. Besides, the presence of other trace elements, e.g. potassium, molybdenum, nickel, boron, zinc and fluorine in leaf cuticles and associated bacterial remains and their absence in framboids indicate that these elements seem to have been consumed or converted into other compounds during the genesis of pyrite framboids. Molybdenum in considerable amounts indicates that it remains in mineral form in degraded leaves, as it has a major role in nitrogen metabolism in plants¹⁷.

It is known that pyrite framboids develop through one or more precursor iron sulphides at the early stages of peat formation^{1,6}. Further, the morphology of framboids is inherited from the micro-organisms. Several micro-organisms are incorporated during the genesis of

framboids. They have been observed surrounding this structure. These investigations suggest that framboidal pyrites generate in the cavities or cell lumen of degraded leaf cuticles. They occur in clusters, chains or in solitary spherules and balls. The growth of framboids depends on the number of bacteria or their colonies involved in the degradation of cuticles and the availability of major elements during mineral uptake. The coefficient of C, O, N, S and Fe in the organic matter also plays a significant role during this phenomenon.

EDAX analyses of the biologically degraded leaf cuticles and framboidal pyrites indicate significant variation in the quantity of major elements (C, O, N, S and Fe) in their composition. The presence of oxygen indicates the incorporation of carbonaceous substances in the sediments. Increase in CO_2 content and shifting of the oxidation-reduction potential (E_h) at the same time suggest reducing condition¹⁴. The presence of nitrogen indicates enhancement of cellulose breakdown and nitrogen mineralizing activity during catabolism of biopolymers (lipids, proteins, carbohydrates) into monomers (amino acids, fatty acids, sugars, etc.) by the bacteria^{14,18}. Many heterotrophic bacterial species degrade complexes of organically-bound iron and release free iron that reacts with sulphur to form iron sulphide. The iron present in microbial cells may also combine with organic molecules, but these compounds are mineralized with the liberation of the element¹⁴. Involvement of sulphate-reducing bacteria in the early phases of the organic matter diagenesis is considerable. These bacteria may be chemotrophic in nature, and accelerate the activity of the formation and

Table 1. Result of elemental analyses (in per cent) by EDAX on pyrite framboids with substrate, single pyrite spherules, bacterial remains and biodegraded cuticles (based on ZAF analysis of six samples each)

Element	Framboids	Single pyrite spherules	Bacterial remains	Biodegraded cuticle
Carbon	64.34	54.40	33.72	55.41
Nitrogen	–	20.07	11.45	05.86
Oxygen	22.62	18.05	11.56	04.24
Phosphorus	00.05	02.04	00.05	00.32
Sulphur	02.64	01.97	02.94	06.51
Iron	00.62	00.92	00.54	01.00
Cadmium	00.45	00.40	00.19	00.34
Silica	00.18	00.19	00.10	00.27
Magnesium	00.33	00.21	00.09	00.17
Aluminium	00.24	00.07	00.07	00.07
Sodium	00.23	00.15	00.18	00.09
Manganese	00.00	00.16	00.08	00.01
Copper	00.28	00.78	00.35	00.64
Cobalt	00.00	00.12	00.10	00.21
Calcium	00.45	00.40	00.19	00.34
Titanium	–	02.04	00.61	01.76
Fluorine	02.07	–	–	00.24
Zinc	–	–	00.05	00.27
Potassium	–	–	00.04	00.04
Nickel	–	–	00.09	00.21
Molybdenum	–	–	05.19	10.77
Boron	–	–	27.41	–
Chlorine	–	–	00.40	–
Barium	00.60	–	–	–

filling of pyrite in the cell lumen of the plant after their initial biodegradation.

The sulphur is an essential element of the soil, which indicates sufficient water supply in the basin. The bacteria available in the sediments do not react fast till oxygen is present. At this stage, fungi and some aerobic bacteria generally degrade organic matter. After the consumption of available oxygen, the anaerobic bacteria, mostly *Thiobacilli*, considerably replace this phase. These *Thiobacilli* are involved in the transformation of sulphate into sulphide during the change-over from oxidizing to reducing conditions. Under anaerobiosis, the sulphide formed from sulphate and organic sulphur compounds may remove iron ions to iron sulphides^{14,19}, but rarely degrade carbohydrates²⁰. The substrate of organic matter provides energy for microbial proliferation during the decomposition of carbonaceous substances and iron is released, which precipitates as insoluble ferric salts. The precipitation thus induces direct action on the organic portion of the compounds, rather than the iron. The high percentage of carbon in degraded leaf cuticles and pyrites indicates the availability of carbon in form of carbohydrates (C₆H₁₂O₆), sugars, etc. It serves a dual function in nutrient supply for both the plants and microorganisms. The biopolymers are transformed through bacterial activity into monomers and other inorganic geopolymers¹⁸. When the degradation of organic matter starts, some compounds quickly disappear, while others (trace elements) which are less susceptible to microbial enzymes persist in the sediments.

Critical observations on the nature and composition of pyrite framboids in freshwater (Mahuadanr) deposits indicate that the framboids were formed in euxinic conditions. Their formation is related mainly to the presence of sulphate-reducing bacteria under the prevalence of reducing conditions in the basin of deposition. The main requisite for the formation of pyrite framboids is a reducing condition and not the location of depositional site under continental or marine realm.

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A new approach to the analysis of transverse river valley profiles and implications for morphotectonics: A case study in Rajasthan

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Study of river profiles provides significant information on both hydrodynamic factors and geomorphic features of drainage basins. Longitudinal river profiles have been extensively studied and different parameters have been proposed by various authors for these profiles, but transverse river valley profiles (TRPs) have not received similar attention. A new approach to the TRP analysis has been proposed here. It identifies several TRP parameters that are easily quantifiable. These quantified parameters are useful for inter-TRP and as well as inter-drainage basin comparisons. These are also useful to derive drainage basin attributes such as valley symmetry and the state of valley erosion, identify and correlate geomorphic features such as plantation surfaces, and importantly, to draw morphotectonic inferences. The procedure has been successfully tested in a case study of the Banas drainage basin, Rajasthan.

GEOMORPHOLOGISTS study two types of river valley profiles to assess drainage basin evolution and to draw inferences on geologic controls as well as on morphotectonics.

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