An Example of Systems Heirarchy in the Aggregation of Pyritic Framboids in Natural Aquatic Environment – Ranen Sen¹ and Sharadindra Chakrabarti*², ¹Formerly at Department of Metallurgical Engineering, Colorado School of Mines, USA. ²Department of Geology, Sister Nibedita Government College, Hastings House, Kolkata, India (*E: sharad_presi@rediffmail.com)

Aggregation or clustering or agglomeration characterizes the nanoparticles in nature. Aggregates/ clusters of fine grained siderite concretions and of pyrite frambooids reported (Ravi Shankar et al., 2001; Pal et al., 2002) from the reducing environment of the arsenic bearing shallow aquifer sediments at Baruipur of the Bengal Delta on a re-appraisal are observed to belong to a range of nanoparticles. They are, in fact, nanoclusters. In the Subarnarekha river, Jharkhand, where the geological setting is different, aggregation of iron oxide nanoparticles is a common feature (Fig.1a and b) with scaling characteristics.

Ravi Shankar et al. (2001) have suggested that both siderite concretions and pyrite frambooids in the aquifer sediments are probably of biogenic origin. In fact, the biogenic influence is also borne out by their organic association. The frambooids may occur in close spatial relationships with organic matter which influence their formation and growth. However, in reality, the frambooidal nanoparticles interact with microbes where size, shape, chemical composition and state of agglomeration may change the effects upon bacterial activity. And the frambooids may accordingly attain a sensitized form as we find one in the aquifer sediments (Fig.1c). More quantitative work in this field needs to be performed. The topic of nanoparticle-bacteria interactions is still in its infancy and is wide open for further investigations.

On the other hand, the aggregates of the iron oxide nanoparticles in the Subarnarekha river require a detailed examination before suggesting the exact mode of origin. The nanoparticles in the Subarnarekha sediments are found to be mostly located in the network spaces of the river channel system (Dayasagar and Chokalingam, 2004, Chokalingam and Dayasagar, 2005). In such a drainage configuration pattern, energy expenditure is minimized (Rodriguez-Iturbe and Rinaldo, 2001). Natural nanoparticles in such a scenario evolve towards their own geometric characteristics through least energy expenditure requirements. This harmonious systemic linkage of locations of two such states of minimum energy dissipation reflects self organization necessitating an induction of fractal geometric attributes which explains the textural pattern of the nanoparticles in the river sediments.

It has been mentioned earlier that both the siderite concretions and the pyrite frambooids exist in a clustered form in the Baruipur aquifer sediments of the Bengal basin and that their state of aggregation shows a pattern arising out of their microbial interactions. Z. Sawlowicz in his quantitative work (Sawlowicz, 2000) reports that frambooidal forms are often structured hierarchically over three size scales with complexities ranging from microframboids to frambooids and to polyframboids.

In the pyritic frambooids as referred to from the Bengal basin, the hierarchy is borne out by their pattern of growth. In these pyritic frambooids, the constituent finer near spherical equant pyrite particles (Set A) aggregate to form a coarse spherical unit (Set B) without any distinct grain boundary. The latter, i.e. the coarse spherical units do again aggregate and form a bigger cluster patch (Set C), (Fig.1c). Both the frambooids and the concretions are examples of hierarchical self-assembly (self-organized cluster) of nanoscale building blocks. In terms of pyritic frambooids which have been studied here in detail, aggregated spherical clusters (patches) occasionally of the size of a few micrometers show as a whole a fractal dimension, $D_f = 1.67-1.69$ (Set C), (Fig.1c). The pattern may be described as diffusion limited cluster-cluster aggregation, a process of percolation (Christenson and Molony, 2005). The spherical individual nanoparticles vary in size from 3-5 nm (Set A) and build up the spherical coarser mass (Set B). The fractal dimensions of individual nanoparticles (Set A) present a $D_f$ range of 1.54-1.56 while $D_f$ of the individual cluster unit (Set B) exhibits 1.60-1.65. The fractal dimension pattern thus demonstrates a hierarchy and expresses the manifestation of a systemic form.

There is a fractal face to the geometry of nature (Mandelbrot 1977; 1983). The fractal character of a system has many implications for its properties. Particularly, a fractal set tends to fill the whole space in which is embedded and has a highly irregular structure. It possesses a
certain degree of self-similarity. This character is captured by the so-called fractal dimension. Fractal in fact is a complex geometrical shape and is relevant to describe systemic patterns and growth processes in earth and ecological sciences, behavioral processes, organism distribution, turbulent processes, species diversity, evolution and many more. Though a degree of self-similarity in the framboids structure can be discerned, the range of variation of fractal dimensions among Sets - A, B and C may probably be explained as a manifestation of stages of spatial and temporal interaction between microbes and pyrite grains.

It is pertinent to point out that each spherical nanoparticle in the cluster has a discrete identity. No neighbourly particles display the same fractal dimension, that is, discreteness is borne out by individual fractal dimensions of each nanoparticle. They, however, form clusters at different scales probably resembling the “Typed Sets” resulting in a web of characters embodying a Boolean signature (Garnier and Taylor, 2010).

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References

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In the article on “Numerical Simulation of Groundwater Flow and Vulnerability in Wadi El-Natrum Depression and Vicinities, West Nile Delta, Egypt by M. El. Osta, H. Hussein and K. Tomas, published in the August 2018 issue of the Journal (v.92, pp.235-247). On page 236, Figure 1 should be replaced by the figure given below.

Fig.1. Location map of Wadi El - Natrun area.