ENVIRONMENTAL PURSUITS IN NANOMATERIAL SYSTEMS SCIENCE WITH INDIAN EXEMPLARS

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ABSTRACT:

The behavior and pattern of NPs of minerals in the evolutionary history of the earth vis – a –vis the environmental context are inquired into, with a riverine system as a model. The study of fractal dimensions of NPs of interest serves as an aid to obtain a comprehensive view of natural NPs in the model system. The present study combines inputs from work done on nanoparticles, derived from Subanarekha River System and products of base metal mine effluents that are rich in NPs of minerals. The authors believe this study would help to establish certain universalities about NPs and provide an updated framework for understanding the current state of nanomineral science.

PROLOGUE :

Nanominerals are minerals that are found only in the size range of around one to a few tens of nanometers in at least one dimension, e.g. Clay minerals and metallic oxide minerals. Mineral nanoparticles, on the other hand exist in nano dimensions but their existence is possible in larger sizes too. Amorphous nanoparticles are similar in all aspects to NPs of minerals but are conspicuous by the absence of atomic structural order.

The behavior of nanoparticles (NP) of minerals in the natural earth systems are still to be universally comprehended. An insufficient database is the main reason for this lack of comprehension. Serious research in this area began only in the last years of the 20th century.

Mineral nanoparticles and nanomineral particles are most abundantly distributed in the atmosphere, oceans, earth's surface, soil surface, surface waters, underground waters,. Their presence is commonest in all living systems. Most of the major components of a living cell are in the nanodimension .In fact such a wide occurrence is expected as the development of Earth as a life bearing planet is based on the dynamic interaction of geological and biological evolution.

Our concern centers around the delineation of potential impact of nanoparticles on the environment. NP of minerals form a part of the critical environmental chain and thus their interaction with microbes are a key aspect of the resulting impact.

Although many aspects -bacteria interactions remain to be understood, these have the potential to effectively impact bacterial life and their activities. The attachment of toxic metals to NP of minerals through chemisorptions, their subsequent transportation and relocation as contaminant sediments are yet to be evaluated vis-à-vis bioavailability in the environmental pollution context on the ecosystem.

Reflections on microbe-mineral interactions as observed in Cu-sulphide leaching operations are reported here as an important illustration of our thesis. During bioleaching of chalcopyrite mine wastes at Malanjkhand Copper Complex near Kanha Reserve Forest, M.P., India, nanaojarosites were observed to nucleate and adsorb heavy metals. These nanojarosites, a microbe-mineral interaction product in the waste chalcopyrite heap were precipitated by *Acidothiobacillus ferrooxidans* and *A.thiooxidans*. No elemental sulphur was detected. It indicates that the role of bacteria was limited to rapid oxidation of iron in solution. The resultant cation Fe^{+3} set to work on chalcopyrite mineral and ferric iron were precipitated as nanojarosite. These nanojarosites with adsorbed heavy metals are making an impact on the surrounding agricultural fields.

It is not certain how the NP of minerals grow, are deposited and why they are ubiquitous in nature. Neither can their exact source be deciphered. Hydrated oxides of iron, particularly ferrihydrite, oxyhydrites like schwaratmannite,vernadites and Mn-Fe hydrates tend to adsorb toxic metals ,almost universally. Hematite and goethite in this respect do not follow the rule universally. The sorption behavior of NP not only depends on the surface area but also on its size. Attributes like degrees of metastability in terms of growth and variations in surface topology are manifested by some iron hydroxide nanoparticles (Waychunas et.al. 2005). These variations are characteristically reflected in the variant fractal dimensions that the said NPs demonstrate. (Sen et al.2011)The present workers on the other hand observe that NP of minerals with occasional higher fractal dimension of 1.90 in the Subarnarekha River, India may trap more toxic metal contaminants as adsorbed species. It is relevant however to note here that the NP of minerals in the Subarnarekha river system shows a lower regime of fractal dimensions, a little above 1.0. [Fractal analyses included box counting are-perimeter methods (Seuront 2010)].

Nature is the creator of the NPs and acts also as a sink. Probably, since the beginning of creation, nature has continually produced its Fe-Oxide nanoparticles which act as carriers of different elements and compounds in rivers and ground water and are transported over long distances. Among other NPS, metal sulfides, carbonates, oxides and silicates are common. Cadmium is observed in the Sagar Isles in Bay of Bengal. It is transported by nanomineral courier (ferrihydrites and nanogoethites) for more than 150 kms from Ghatsila (south of $86^0$2'E, $22^0$7'N) into the Bay of Bengal near Balasore ($86^0$6'E, $20^0$1'N) and then a further 50 kms north-east to the Sagar Islands ($88^0$2'E, $20^0$5'N), by the northerly ocean currents. Radionuclides can similarly move through great distances though thermodynamically they are known to be essentially immobile. In the Mayak Region in Russia, Plutonium (70% <5nm size) has been found to travel for long distances in local aquifers, carried by ferric iron oxide nanoparticles for a long distance. Duran (2008) holds the view that nano materials are highly mobile, and have a greater potential for exposure, as they are dispersed over greater distances. In a way NPs are a vehicle for contaminant transport.The final result is that their persistence in the environment increases, Wiesner et.al (2006), suggests that nanoparticles are probably not very mobile, since their larger affinity to diffusion processes would enable them to produce more frequent contacts with the surfaces of porus media in nature. Such contradictory claims show that we still have a long way to go in getting a clear perspective on nanomineral systems.

GEOLOGICAL ATTRIBUTES

The nano phenomenological events may perhaps be explained by their geological attributes. Geologically speaking the interior of the Earth is a cauldron where intensive high temperature reactions are taking place continuously. From time to time, the Earth ejects, volcanic exhalations, to balance the temperature of the earth giving a boost to the existing life forms and generating new life forms. The gaseous component spewed, balances the carbon dioxide in the atmosphere. The interior of the earth thus works like a thermostat. In nature, nanomaterials, mostly nanomineral particles and / or mineral nanoparticles are a part of this reaction and contain huge inherent thermal energy rendering instability in their attributes. This latter character tends to make them clump together and regain stability. Thus their potential for reactivity is reduced. The effect of water chemistry in the local environment may lead to aggregation and the spherical build up of aggregated grains is probably due to topological transformation of pentagons and hexagons. As an example, simple topology arguments suggest that twelve pentagons have to be present to form a spherical shape. The erosion and weathering activities may disintegrate the minerals into their nanoforms with high free energy on their surface making them unstable. To attain stability they may again clump together and if single may become capped.

While speaking of geological attributes, it may be appropriate to point out that since the magma rises along the junction of the non collisional plates, the process of formation of nano-size particles appears to have very little to do with the rising of magma.

Common natural NPs of minerals have been known to exhibit enhanced chemical reactivity relative to bulk mineral surfaces but the origin of the above characteristic is not yet well established.

In addition to the processes of growth and weathering, nanoparticles of minerals may be generated from mechanical grinding. One of the most interesting places in nature where this happens is along the faults which generate the earthquakes where nanoparticles show a size range of 10-20 nm. (Wilson et.al 2005). It has also been observed during the investigation of a rock phosphate beneficiation plant at Jhamarkotra rock phosphate mine in Rajasthan, India that nanoparticles are generated in the crushing and grinding circuit due to mechanical stress and these nanoparticles (10 nm to 50 nm) cannot be removed in the flotation circuit but are again encountered in the tail. (Whether nanoparticles *are produced in* the mines after blasting is not known and remains to be examined). In this context, it may be mentioned that any violent reaction where tremendous energy is expended, nanoparticles are generated. That is why, an earthquake produces nanoparticles in the surrounding zone, say within a radius of about 500 meters. Similarly, fly ash, a waste product of the thermal power generating plant, contains nanoparticles.

CHARACTERISTICS

All characterstics NPs) of minerals vary significantly vis-à-vis their exact size, shape, state of aggregation and the specific environment they are in. In the NP range, (of minerals) surface energies (Interfacial energies) can dominate and be stable. In a riverine system, because of grain transport, the basic energy transformation is represented by lowering of the surface energy of the nano grains. However, the consequential effect of such energy transformation has not yet been studied. For some the ability of an atom or molecule to absorb or emit energy in quanta influences the NP behavior. A metastable nanophase may be generated by a kinetic effect. It difficulties possible to assess in experimental studies if any observed nanophase is thermodynamically stable or metastable but how far it may be applicable to Nature may not be known.. (Gilbert et.al 2005) propound that nanoparticle surface interactions with water can be strong, and decisive in stabilizing particular mineral structures.

Every mineral evolves through a nanophase as it begins to grow. Why and how the growth is inhibited to allow minerals such that their growth is restricted to nanophase is not clearly understood. There are some interesting examples, the present workers have come across while studying sulphosalts in the Khetri Copper Belt, Rajasthan, India (A.D.Mukherjee, pers.com, 2010), Dariba-Rajpura Complex Sulphides, Rajasthan, India (Pillay et.al 1984), and in the North Norwegian Caledonian base metal deposit (Sen et.al 1972, 1973a, 1973b) – all characterized by polyphase metamorphic crystallization. Sulphosalts like Bournonite, Boulangerite, Jamesonite and Macknawite have been noted to often restrict their growth to a size, less than 1 micrometer on the periphery of the major associated mineral(s), from which in the later stages of metamorphism, their major elements are probably derived. For example Bournonite, Boulangerite, Jamesonite is seen mostly on the periphery of chalcopyrite, galena and geochronite assemblages. Polybasite is dominant on the fahlertz grain boundary. Mackinawite tends to occupy the periphery of pyrrohotite grains. Most of these sulphosalts are metamorphically recrystallized during the closing phases of metamorphism. At that point, the chemical element did not perhaps retain enough mobility to grow further and the minerals remained as nanosized particles.

Crystalline mineral nanonparticles in the natural environment are associated with variable surface geochemical phenomena like adsorption, precipitation, mineral growth and ion mobility. The surface reactivity of these nanoparticles is uniquely different from their equivalent macro forms because of modification of thermodynamic properties of the surface influenced by nanosized anatomy.

Moreover, no related reports or data are available on particulate interface. The behavior of interfacial region between heavy metal and aferrihydrite surface is not well understood. Though the phenomenon of attachment of heavy toxic metal grains to mostly nanoferrihydrite surface is confirmed as chemisorptions, there is a lack of knowledge about the electrochemical characteristics of this system. There is also an incomplete understanding of the surface states (particularly lying in the electronic band gap) of controlling impurity atoms incorporation. In fact, environmental nanoparticles and synthetic analogs are poorly studied. However, it is now postulated (Waychunas et.al 2005) that nanogoethite, akaganeite, hematite, ferrihydrite and schwartmannite have high sorption capabilities for metal anionic As, Cr, Pb, Hg, and Se – the sorption is found to be mainly chemical, accomplished by surface complexation. Whether the phenomenon is universal in nature still remains to be confirmed. Hochella and his group (1990, 1999, 2005, 2005a, 2005b) discovered toxic heavy metals as components of several nanocrystalline phases on the Clark Fork River bed and floodplain sediments. They also observed metal bearing nanonparticles in water samples. The generation of these metal bearing nano particles in relation to transport/transformation as well as their preferential adsorption of a particular type of toxic metal element, if any, has not been studied in detail.

INDIAN EXEMPLARS

Sediments from Indian rivers, flowing close by the base-metal terrains, like the Subarnarekha,in Jharkhand,(beside the Singhbhum Copper complex,) and the Tidi,in Rajasthan, (around the Zawar Pb-Zinc) near Udaipur(24^{0} 04 ' N,74^{0} E) mines have been examined in terms of NP of mineral systems. The most detailed study was undertaken in the Subarnarekha river (Fig 1) around Ghatsila (South of 86^{0}2'E, 2207'N) where copper smelter is fed by Mosaboni, Rakha, Surda group of mines of the Singhbhum Copper Complex into the river. The nanomaterials (nanogoethites and ferrihydrites,Fig .2) in the river sediments reflect the following distinguishable behavior patterns.

1) NP assemblages commonly occupy the network places of the river channels. This is true for all the three rivers studied.
2) NPs are often characterized by the formation of clumps by aggregation. DLS results show a higher size distribution curve (>100 nm)
3) NPs show quantum characteristics (common in all rivers). NPs in the Subarnarekha are conspicuous by the absence of variation of electron density.
4) NP sizes in the Subarnarekha particularly when aggregation takes place vary within very short distances.
5) 5NPs tend more to aggregate (due to high surface affinity) in the Subanarekha. Evidence of partial disaggregation is also observed. It may be due to variation in the water chemistry (Hochella 2009). In the Subarnarekha both the aggregation and partial disaggregation phenomena are characterized by an assembly of near-spherical finer NPs, (around 3nm -5nm in size) forming a coarser spherical patch. This aggregation to a coarser sphere or ellipsoid points to a diffusion limited aggregation was also confirmed by lower fractal dimensions (1.3-1.6) of the coarse aggregated patch. The latter may or may not be of nanodimension. The finer iron hydroxide NPs in the Subarnarekha, aggregate to form spherical coarser patches. Thus there are two sets of aggregations. These constituent smaller NPs (~3nm ~5 nm), show a fractal dimension of 1.80.It agrees well with the fractal dimensions of natural fern leaves D_F1.826). It suggests that the NPs are self assembled and self similar. Do the two sets of aggregations with two fractal dimensions in two self similar

domains point to a mixed fractal structure? Such a possibility exists in a natural fractal environment.

The Subarnarekha River with its advective and turbulent flow system is further complicated by the continuous inflow of the mine - smelter effluent, and their variant attributes. A biological input into the system by the flora and fauna present in the said ecology, cannot be ignored. The scenario is of a non-linear nature and the pollution pattern of heavy metals represents a Hopf bifurcation with jumps in amplitude of period doubling cascades. It suggests instabilities in flow systems (Drazin and Reid 1992). The non-equilibrium conditions play a dominant role in the formation of fractal clusters and produce self assembled NPs (of metallic minerals) in non-equilibrium conditions.

The nanoparticles ferrihydrites in the Tidi River System, Udaipur, Rajasthan exhibit a similar geometric pattern to that of Subarnarekha. From the above exposition it may be remarked that the shape of NPs and their aggregation re a function of particle geometry. It appears from the evidence presented by SEM images, that the pattern of aggregation of NP is a function of particle geometry. The pentagons, hexagons or 7-sided structures of crystallized nano particles of minerals will topologically transform to spherical shapes due to changes in stress factors related to flow system dynamics of the river and the finer spheres will tend to aggregate to form spherical coarser entities. Fractal dimension is inversely related to the number of 7-sided structures.The fractal dimensions usually varying from 1 to 2 in the present exemplar is thus well in accord with the topological theories.

We would like to point out that the geometric pattern of NPs of minerals present in the two fluvial systems around base metal mining belts is surprisingly similar.

Further investigations of different river systems around metal mining belts is warranted to establish, if the pattern is consistent. The question then arises, is there a particular pattern in natural manifestations? And does Nature maintain a similar behavior pattern? Nowadays engineered nanoparticles are disposed off in natural ecosystems. Their interactive behavior vis-a- vis the naturally ocuuring NPs of minerals is yet to be understood.

A THEORETICAL MODEL - A CHANGE IN THE SYSTEM CONFIGURATION

In search for the hidden order of the temporal and spatial variability in the Subarnarekha river basin, some fractal features and the role of the role of self organization are considered. The main theme is the dispersion- distribution of nanoparticles of minerals and the evolved river channel network.

It is known (Rodriquez-Iturbe et.al 2001), that natural fractal structures like river networks may evolve as a coupled consequence of optimality and randomness.

Nanoparticles of minerals are observed to assemble in the network space of the Subarnarekha. The network space has a higher fractal dimension. (D_F ~2) and concentrates the nanomaterials (coarse spheres) with lower fractal dimensions (D_F normally ~ 1.3 – 1.6). Natural fractal structures like the channel network space are dynamic optimal states (op.cit), where evolution has achieved stability.

It induces the nanoparticles to settle in the network space. Thus from the standpoint of signature of the above fractal dimensions, the scenario is compatible.

The optimal channel networks (inclusive of network spaces) in the river basins are evolved by long periods of stasis punctuated by explosions of activities in high entropy conditions. Such a temporal behavior of dynamics is accompanied by spatial activities on all scales as in SOC (Self organized criticality) phenomena. Adiabatic thermodynamic conditions prevailing in the subsequent phase conserve the evolved network space, while entropy becomes zero. The alignment of nanoparticles of minerals in the network space is probably activated self-organizingly during the explosive period. Subsequently they are conserved in the adiabatic phase. Thus there is a continuity of change, of systems configuration in the whole process as the channel network evolves.

Models in this kind of studies thus reflect the likelihood of changes in the systems form under thermodynamic framework.