

Hydrothermal from – Geology to Nanotechnology and Nanogeoscience (Part - II)

K. Namratha¹, M.B. Nayan^{2,3}, M.D. Pandareesh⁴, H.T. Basavarajappa¹ and K. Byrappa^{4*}

¹Department of Studies in Earth Science, Center for Advanced Studies in Pre-Cambrian Geology, University of Mysore, Manasagangothri, Mysuru - 570 006, India

²Center for Materials Science and Technology, University of Mysore, Vijnan Bhavan, Manasagangothri, Mysuru - 570 006, India

³Department of Studies in Environmental Science, University of Mysore, Manasagangothri, Mysuru - 570 006, India

⁴Center for Research and Innovations, Adichunchanagiri University, BGSIT, N.H.-75, B.G. Nagara - 571 448, India

*E-mail: kbyrappa@gmail.com

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ABSTRACT

Hydrothermal process from a pure geologic science has now become one of the fast-emerging processing technologies to synthesize nanomaterials in the laboratory. Today it is an advanced technological tool, which facilitates to obtain nanomaterials and nanoparticles with desired size, shape, quality and functionality. In fact, hydrothermal technique has its bearing on the nature-inspired or geo-mimetic processes that are being employed extensively in the laboratory. The natural hydrothermal processes are acting ever since earth came into existence, and leading to the formation of a large variety of minerals, rocks and ores. Earth is a blue planet of the universe, where water is a major component which plays an important role in the formation of geological materials and hydrothermal circulation has always assisted by bacteria, photochemical and other related activities. The synthesis of advanced technological materials often occurs in the presence of biomolecules, proteins, organic ligands, DNA and amino acids. An understanding of nanogeoscience is becoming very relevant in the current context and is crossing into almost all the branches of geology including palaeoecology, mineralogy, environmental geology, energy geology, geochemistry, etc. Similarly, the hydrothermal processes in nature cover several branches of geology whether it is the origin of ores, minerals, rocks, but also life on the earth. In the present review, the authors discuss all the above aspects in detail with a future perspective of the field. Also, the authors have described the evolution of hydrothermal process from pure geology to the nanotechnology, nanogeoscience, nano-geopolymers, etc., with specific examples and depicted its relevance to the geologic science.

INTRODUCTION

There is a great difference between the hydrothermal research before 21st century and the present. For example, hydrothermal technology was in its peak during mid-20th century and focused mainly on high temperature and pressure synthesis, especially to synthesize natural mineral analogues. The lack of knowledge on the hydrothermal solution chemistry was distinct. But the First International Hydrothermal Reaction Symposium (1982) organized at the Tokyo institute of Technology, Japan brought together specialists from inter-

disciplinary science including earth scientists, especially to acknowledge the role of physical chemistry, thermochemical computation, use of organic solvents also as mineralizers (Somiya, 1982). The addition of biomolecules, external energy like microwave, sonar, mechano-chemical, electrical, magnetic, and so on has greatly contributed to take forward the hydrothermal technology towards green technology and has opened up a new chapter in hydrothermal technology (Yoshimura and Byrappa, 2008; Byrappa and Yoshimura, 2013). Similarly, a systematic understanding of the above concepts has led to the instant hydrothermal reactions to obtain nanoparticles in a shortest possible time that leads to the concept of chemistry at the speed of light and the instant hydrothermal vending machine.

As mentioned earlier, the discovery of hydrothermal activity in the deep sea during 1980s has resulted in the emergence of marine biology and geochemistry. It is strongly believed that the routes of life on the earth can be found in the hydrothermal ecosystem (Abott and Hoffman, 1984; Baross and Hoffman, 1985; Shock, 1992; Fornari and Embley, 1995; Hanley, 1996). It is well known that the earth is blue planet of the universe, where water is a major component, which plays an important role in the formation of geological materials and hydrothermal circulation has always been assisted by bacteria, photochemical and other related activities. Naturally occurring nanoparticles are geogenic or biogenic or aerogenic, and accordingly nanoparticles especially inorganic nanoparticles are present everywhere in the geologic systems (Banfield, and Zhang, 2001; Waychunas et al., 2005). In the last one decade, several reports have appeared on the nanocrystalline minerals like cassiterite (SnO₂), geikielite (MgTiO₃), clays, osbornite, etc., associated with a variety of rocks and at different levels of the earth's sub-surface (Kvasnytsya and Wirth, 2009; Parthasarathy and Sreedhar, 2011a,b). There are several other natural nanoparticles produced unintentionally through automotive catalytic converters. Such unintentionally produced nanoparticles usually contain Pt and Ru. In the present review, the authors discuss the natural nanoparticles and other nano-geological features and their contribution to understand geology more explicitly.

HYDROTHERMAL TECHNOLOGY FOR NANOPARTICLES SYNTHESIS

The hydrothermal processes in nature play a prominent role in

nanogeoscience whether it is nanominerals, or nanogeopolymers, or nanofossils or the origin of life, and so on. The natural processes have been systematically adopted in the laboratory for the experimental synthesis of these nanominerals or nanomaterials. The nanomineralogy is an emerging field of science, which has brought in a revolutionary breakthrough during the 21st century leading the geologists to understand ultra-, micro- and nanoscale minerals. They not only have the resource value, but also geoenvironmental attributes (Ju et al., 2020)

Table 1 gives some representative bio-assisted materials of natural origin. This can be taken as a model for the synthesis of advanced technological materials using nature inspired processes that often occur with the assistance of biomolecules, proteins, organic ligand, DNA and amino acids. A great variety of biomaterials can be fabricated under near ambient conditions by employing nature inspired processes. This is an important development in the field of hydrothermal technology from geology to modern technology.

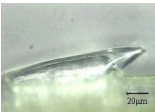

It is to be noted that the discovery of fullerene in geological samples like shugunite from Russia has generated various thoughts among geologists (Busek et al., 1992; Parthasarathy et al., 1998)). Similarly, fullerenes have also been reported from pillow lavas, coal, fossil dinosaurs' egg, interstellar dust, etc., (Busek, 2002). Also, there are several reports on the Indian occurrences of natural fullerene (C₆₀) in iridium rich Cretaceous-Tertiary boundary layers of Deccan intertrappean deposits, at Anjar, Kutch, Gujarath. Here, fullerene occurs in the carbonaceous matter extracted from the intertrappean sediments (Parthasarathy, 2008). Besides, fullerene bearing shungite suite rock is found in Mangampeta area of Cuddapah region of

Andhra Pradesh, wherein the shungite suite of rocks occur with carbonaceous slates (Misra et al., 2007). However, scientists failed to report fullerenes from meteorites. Therefore, there are various contradicting approaches explaining the formation of this technologically important nanoparticles - fullerenes in nature. In this context, the natural nanomaterials formed by hydrothermal processes are better understood and contribute greatly to the enrichment of knowledge on the geologic processes. Today hydrothermal technique is popularly being used in the synthesis of a great range of nanominerals like native metals, nanoparticles (Au, Ag, and Pt), magnetic metals (Co, Ni, and Fe), a variety of oxides, silicates, carbonates, perovskites, garnets, hydroxides, phosphates, chalcogenides, tungstates, molybdates, nanotubes and so on for various technological applications.

Zhu et al., (2003) have reported the synthesis of silver dendrite nanostructures using anisotropic nickel nanotubes via hydrothermal reactions. Here nickel acts as both reducing agent and strong catalyst under hydrothermal conditions. Figure 1 shows the characteristic TEM images of Ag dendrites. The addition of PVP surfactant, these Ag nanoparticles transformed into bulk or compact particles under hydrothermal conditions.

In recent years supercritical conditions have provided reactions for synthesizing nanoparticles of Ag, Au, Pd, In, Pt, Si, Ge, Cu, etc, and are becoming very popular as a consequence of fast kinetics and rapid particles production with the shortest residence time. Similarly, the coating of nanocrystalline films of Cu, Ni, Ag, Au, Pt, Pd, Rh, etc., on silicon wafers for microelectronics, data storage, etc., has been reported (Blackburn et al., 2001). Such an approach has been extended

Table 1. Bio-processed materials (after S. Mann and modified by M. Yoshimura, 2008)

Metallurgical Materials	None (except for Au peromicrobium)		
Organic Materials	Plenty and Versatile		
Inorganic Materials	Evolutionally Limited and Selected		
1. Silica (Opal)	Diatoms, Radiolaria Plants	Skeleton Leaves, Cell wall	Silica blade of Pampas grass 
2. Iron oxides	Bacteria, Tuna, Salmon Chitons, Limpets Beaver, Rat, Fish	Sensors Teeth Teeth surface	
3. Iron sulfides	Gastropod	Dermal sclerite	Gastropod with iron sulfide armor 
4. Ca carbonates	Mollusks, Gastropod Corals Coccolithophoridae Aves	Shells Cell wall Cell wall scales Egg shells	
5. Ca phosphates	Fish Vertebrates Mammals Chitons	Scales Bones Teeth Teeth	
6. Ca sulfate	Jellyfish	Gravity receptor	
7. Ba sulfates	Loxodes, Xenophyophora	Gravity receptor	
8. Sr sulfates	Acantharea	Skeleton	

Other Minerals (<100) are formed outside the bodies by bacterial process.

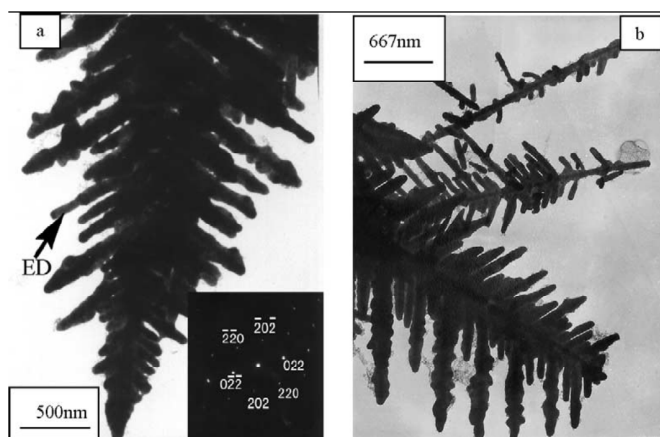


Fig. 1. Characteristic TEM images of Ag dendrites (Photos courtesy Prof. Y.T. Qian).

to several other materials like the coating of nanocrystalline carbon on Si wafers and so on.

Green synthesis of gold nanoparticles (GNPs) has gained great interest as an eco-friendly, cost effective and a simple alternative to conventional physical and chemical methods. The gold nanoparticles have been employed to determine the anticancer activity of biogenic gold nanoparticles against leukemic cell lines along their biocompatibility with red blood cells (RBC). Recently, a rapid eco-friendly approach for the preparation of GNPs using novel isolate for the *Bacillus oceanisediminis* isolated first time from the Indian gold mines has been reported (Srinath et al., 2018). GNPs were prepared using gold salt as the precursor and extracellular material from bacteria as a reducing and stabilizing agent. Similarly, biomineralization process is popularly employed in the synthesis of a great variety of nanominerals of carbonates, sulphides, oxides of various metals, and also a series of native elements like Cu, Pt, Li, Zn, etc. (Rezz et al., 1997; Parthasarathy et al., 2003; Rawlings et al., 2003; Sreedhar et al., 2009; 2011; Dhimi et al., 2013; Reichel et al., 2017).

The rich metal deposits are formed in nature under submarine hydrothermal processes at the ocean bottoms. These metals deposits may be Mn, Fe, Ni, etc., formed by the action of bacteria even at temperature much above the ambient conditions leading to fine, or ultrafine and nano-size particles (Namratha et al., 2022). For nanoscale science, prokaryotes during the geologic past synthesized fully functional nanoscale structures and utilizing properties that exist only at nanoscale. Today most of the 1030 prokaryotic cells on earth exist in close association with mineralogical components in soil and subsurface environments (Whitman et al., 1998). It is here that within the geologic womb of nature, the prebiotic molecules are formed on the mineral surfaces and subsequently developed into single cell organisms. Since that time bacterial life and evolution are closely coupled with mineralogical processes as the minerals provide the raw materials for life (Lower et al., 2000; 2001; Berkeley, 2002).

NANOGEOSCIENCE

Nanogeoscience originated from the colloids science which is about 200 years old. The term is gaining prominence in the last two decades. The term nano- has essentially derived from the ancient Greek word. It refers to the size range 0.1 nm -100 nm (10^{-9} m). The term nanotechnology was first used by a Japanese researcher, Norio Taniguchi in 1974 to define the miniaturization of electronic devices. Since then it has entered into all the fields of science and technology with the prefix nano- like nanochemistry, nanoscience, nanogeoscience, nanomineralogy, nanofossils, nanostructures, nanobiotechnology, etc. The International Mineral Association (IMA) has reported more than 5780 official mineral species. Each year about 120 new mineral species

are added to the list. A vast number of phase diagrams are available describing the stability of mineral phases under vivid physico-chemical conditions. However, in the present context one should look into different types of phase diagrams involving phase variables by considering the mineral size, shape and surface parameters (composition and structures) of nanominerals. This obviously makes the study of nanophase stability and thermodynamics more complex. Therefore, it is predicted that the next few decades will decide a new trend in geoscience with an emphasis on nanogeoscience and its entry into all other branches of geoscience. Accordingly, the nanogeoscience is showing a revolutionary leap in the 21st century crossing into almost all branches of geology like petrology, mineralogy, energy geology, environmental geology, geological hazards, structural geology, and so on. Accordingly, the nanogeoscience can be classified into nano-mineralogy, nano-petrology, nano-geochemistry, nano-structural geology, nano-paleontology, nano-energy geology, nano-oregeology, nano-earthquake, nano-environmental geology, nano-atmospheric science, nano-marine science, nano-marine geochemistry, nano-palaeo-geochemistry, paleo-ecology, paleo-oceanography, paleo-climate geology, etc. The nanominerals exist in nature ever since the earth came into existence some 4.5 Ba. The common ones are from the one-, two-dimensional and layered group challoysite, carbon family (CNTs), etc. In fact, they fall into four categories: (1) clay structures, (2) quasi crystal nanostructures, (3) nanostructures in colloids, and (4) nanostructures in crystalline rocks.

The nanominerals give information on the early stage of nucleation. In recent years, energy geology is gaining prominence as the structure and composition of nanominerals of shale and clay with a wide range of pore diameter and pore volume, size, shape, and connectivity can reveal information on the possibility of oil and natural gas reservoirs. Clay minerals mostly control the development of mesopores and macropores (Chen, et al., 2019; Zhu, et al., 2019; Li, et al., 2019; Jia et al., 2020). These pores characteristics also indicate the good hydrocarbon storage capacity. In recent years, shale gas development technology and horizontal well volume fracturing have made a great revolution and are directly related to the micro- and nano-pores for gas storage and production (Xia et al., 2021).

With the development of knowledge on hydrothermal solution chemistry, the mild or soft hydrothermal synthesis is becoming more popular especially in nanoscience and technology. Nanogeoscience is a fast-emerging branch in earth science. Although it started from 1980s especially after the development of High-Resolution Scanning Tunneling Microscope (HRSTM). Nanogeoscience has a great bearing on nanomineralogy, nanogeochemistry, nanofossils, nano-paleoecology, paleoenvironment, geopolymers, etc. The nanominerals can form in nature through both top down and bottom up routes. The hydrothermal fluids can play a major role in the bottom up origin. Whereas the nanominerals in the shear and fault zones can form through top down route. Natural nanomaterials or nanominerals of technological importance can occur in the lithosphere, atmosphere, hydrosphere, and in and/or on several living organic species as shown in Table 1, and also within some proteins like ferritin. Hochella et al., (2008) have described in detail such occurrences of nanominerals and nanoparticles in earth systems. Similarly, Hochella (2008) has discussed in detail the importance of nanogeoscience from origins to cutting-edge applications. Today nanomaterials in technology play a prominent role and the money involved is over several trillion dollars.

Before the invention of the X-rays, HRSTM and other sophisticated spectroscopic methods, most of the fine particles of the natural systems such as in air, water, and earth were regarded either as amorphous or glassy or dust. Now with the emergence of nanoscience in geology, it has changed the mindset of geologists. In nature nanomaterials can form by physical, chemical or biological processes. Man imitates all

three processes to synthesize nanominerals of technological importance.

Similarly, nanosize clay minerals formed due to the stress-induced scaly exfoliation can enhance the entry of rare earth elements (Zhang, et al., 2019). Such studies have been carried out in several other metal ore deposits areas, and it is generally believed that the ore forming elements in soils can come from deep-seated ore bodies, and show an obvious relationship between metal nanoparticles in fault gouges and soils. In spite of a considerable progress achieved in nanogeoscience, our understanding in terms of the formation mechanism of mineral elements, the migration process, structural form, and disaster-related and environmental effects of nanoparticles and the mineralization of nanopores is still in the infant stage. Similarly, high pressure silicates like ringwoodite and wadleyite nanominerals indicate the role of deep focus earth quakes at ~300 to 700 km depths in earth's mantle (Green and Burnley, 1989).

Nanobiomineralization occurs through biotic processes through bacterially driven redox reactions of aqueous species in the presence of some cell function. This has revolutionized the nanomaterials synthesis using biomimetic techniques. One of the best examples is the magnetotactic bacteria synthesizing magnetite nanoparticles, which are aligned along the long axis of the bacterium and these magnetite nanocrystals act like a magnetic compass, which facilitates the bacteria

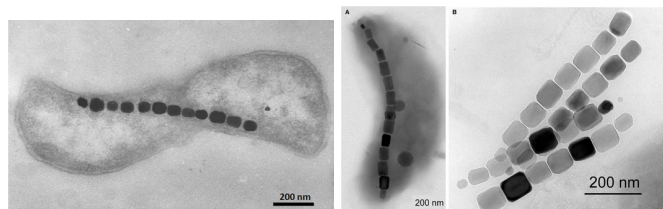


Fig.2. Magnetotactic bacterium synthesizing nanoparticles of magnetite (Fe_3O_4) aligning along the longer axis of the bacterium and acting as a tiny compass by using the earth's magnetic field for the navigation of the bacterium (Chen et al., 2012; Posfai et al., 2013).

to navigate using the earth's magnetic field. Figure 2 shows TEM image of a magnetotactic bacterium synthesizing a chain of 12 magnetite (Fe_3O_4) nanoparticles that are arranged along the longer axis of the cell. These magnetite nanoparticles function as a tiny compass that allows the microbes to navigate using earth's geomagnetic field (Chen et al, 2012; Posfai et al., 2013). Similarly, metal carbonate like SrCO_3 has been synthesized using gum acacia containing carbohydrates, amino acids, glucuronic acid and glycoprotein complex. The presence of proteinaceous core with amino acids stabilize the metal carbonates in mimicking the biomineralization process and it is becoming one of the green synthesis approaches for mineral synthesis (Sreedhar et al., 2011).

Similarly, lotus leaves have a coating of a nanofilm, which makes the lotus leaves hydrophobic as seen in Fig.3 (Darmonin and Guittard, 2015). Such a natural phenomenon is being used extensively

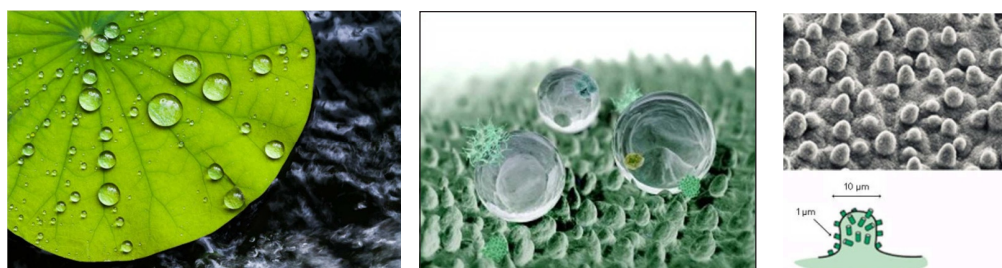


Fig. 3. Natural lotus leaves having thin nanomaterials coating giving hydrophobic property (Darmonin and Guittard, 2015).

to prepare nanomaterials for technology. For example, the use of hydrophobic nanofilm coating of anatase phase TiO_2 on the bathroom mirrors to prevent moisture on the mirror surfaces, and also in the automobile wind shields to prevent the water particles on the wind shields during rainy weather. Therefore, the nanoscience and technology are the next revolution in earth science. In the preparation of these technologically important nanomaterials or nanominerals, the hydrothermal technology is one of the most popularly used ones because of its advantages in getting nanoparticles with desired shape, size, surface chemistry and functional characteristics. It is well-known that the properties of nanosized mineral materials are different from their bulk counterparts because of the quantization effect. Earth scientists play an important role in earth's sustainability issues in future through the nanotechnology. Also, researchers have reported the pre-solar dust which is likely to be attributed to the super novae, and often this dust comprises of nanodiamond based on the spectroscopic studies involved in the space exploration (Bell, et al., 2000; Dai, et al., 2002). Even chondritic meteorites and interplanetary dust particles show such nanomineral phases of higher pressure and temperature conditions (Saikia et al., 2017). Similarly, the occurrence of nanominerals like geikielite associated with kimberlites indicate the deep mantle conditions (Parthasarathy 2011).

The most important aspect of such atmospheric nanophases or nanomineralization is just in the infant stage and needs a trans-disciplinary approach to understand the formation of halite (NaCl), and hydrous sulfate evaporates from the sea can act as water droplet nucleation and growth centres, which even helps in the cloud formation when the size of these droplets reach ~40nm. In the atmospheric nanomineralization process the size and density of these nanomineral particles control the different scattering of solar radiation like Rayleigh scattering, Mie Scattering, and non-selective scattering of the solar radiation. In the atmospheric nanominerals, usually the size ranges from 1.5 nm to around 40 nm. The smallest nanomineral reported so far is that of sphalerite (ZnS) showing the size of 1.5 nm (Banfield and Zhang 2000).

The other unexplored area of nanogeoscience is the role of placer deposits of nanophases and heavy metals, which have a strong bearing on the nanogeochemistry including biogeochemistry, palaeoecology and nanotoxicology. The occurrence of nanomineral particles away from the source defying the thermodynamic relationships with the place of their present occurrence clearly indicates the transportation. It has been well demonstrated that the field, microscopic and spectroscopic studies showing that radionuclides, and heavy metals can be transported by both surface groundwaters over several kms within a short span of time are some of the best examples for such nanomineral placer deposits as observed in the nuclear waste processing plant near Mayak, Russia, where 70 to 90% of the plutonium transport in groundwater is by way of ferric oxides less than 15 nm in size, as well as via a few other nanophases (Novikov et al., 2006). Similarly, in the western Montana state (USA) the heavy metals like copper, zinc, arsenic, lead, and cadmium are highly toxic due to the mining activities started about 160 years ago. These metals have been

carried to several 100s of kms owing to the action of primary carriers like nanominerals, nanoparticles of manganese and iron, oxyhydroxides (Hochella et al., 2005). In Karrighatta region of Mandya district, Karnataka, India, the heavy metals from the minerals present in the pegmatite dyke cutting across the river Cauvery basin near KRS dam at Katteri area have been moved to several kms away by the action of river Cauvery. These heavy metal phases and nanominerals occur in the eastern part of Karrighatta, Karnataka (Malini et al., 1995).

Leaching of silica rich minerals can lead to the formation of 1d-2d-3d-nanomaterials in nature as both amorphous, and crystalline minerals, the cationic exchange properties of these nanominerals in the presence of aqueous or biological and organic media with variation in *pH* also contribute to the geochemistry of the area. In environmental geology, the nanomineral particles in the environment irrespective of their origin such as biotic or abiotic or natural or anthropogenic, geographic distribution influence the environment significantly. For example, mining dust, volcanic dust, and asbestos dust in the nanosize can cause environmental damage and can be highly toxic. Therefore, an understanding of nanotoxicology with respect to the environmental human activities is very important. In fact, environmental processes record at nanoscale through the mineral coatings which preserve products of past biotic, and abiotic soil process (Schindler, and Hochella, 2015). The focused ion beam microscopy (FIB) and HRTEM can reflect on such surface mineral coatings which can decipher a memory of the past environmental processes. Such studies on paleosols, relict soil, buried soil of any age are becoming very popular in understanding the weathering in geo-environment and the composition of the medium. For example, focused ion beam microscopy has yielded different layers of soil coating under varying *pH* and also Si:Fe ratio. The occurrence of adsorbed phosphate species and layers of illite and chlorite crystals within the Fe (hydro)oxide matrix of layer, and clearly indicate the influx of pressure and an increase in soil *pH* during the reclamation period.

Here the authors discuss briefly the hydrothermal synthesis of a few selected nanominerals and their significance in modern technology. The nanoparticles of zincite, anatase/rutile, corundum (α-alumina), hydroxyapatite (HAP), chalcogenides, etc., play a most prominent role in technology. In fact, hydrothermal technique has facilitated the synthesis of exceptionally high-quality nanoparticles of these minerals which are totally unagglomerated having desired size, morphology and surface chemistry. This is possible because hydrothermal method facilitates a highly controlled diffusion, and the growth under isothermal conditions, which provide almost defect-free high quality nanoparticulates. The nanoparticles of zincite, rutile, anatase, corundum, magnetite, perovskite, HAP, etc. are the most potential technological materials. In this context hydrothermal technology is a key to processing of technological materials with desired properties. The significant reduction in the particle size of these mineral analogues has resulted in several newer applications such as quantum dots, bioimaging, drug delivery, food packaging and storage, and so on. In this context, hydrothermal method has several advantages over other synthesis methods. However, intentional introduction of defects like oxygen defects in ZnO, TiO₂, nanoparticles, enhance the catalytic properties of ZnO, TiO₂, and better biological properties for HAP. Similar tuning of properties can be carried out for a wide range of other nanominerals like magnetite, spinel, perovskite, garnet, and so on. One of the greatest advantages of hydrothermal technique is the *in situ* surface modification using an appropriate surface modifier as seen in Fig. 4 (Byrappa, 2009). More recently, bio-surfactants are being used to synthesize nanomineral particles for biomedical applications with zero-toxicity. Such an approach has been developed in the laboratory taking the clue from the natural processes. This can be even termed as biohydrothermal process (Zare et al., 2018).

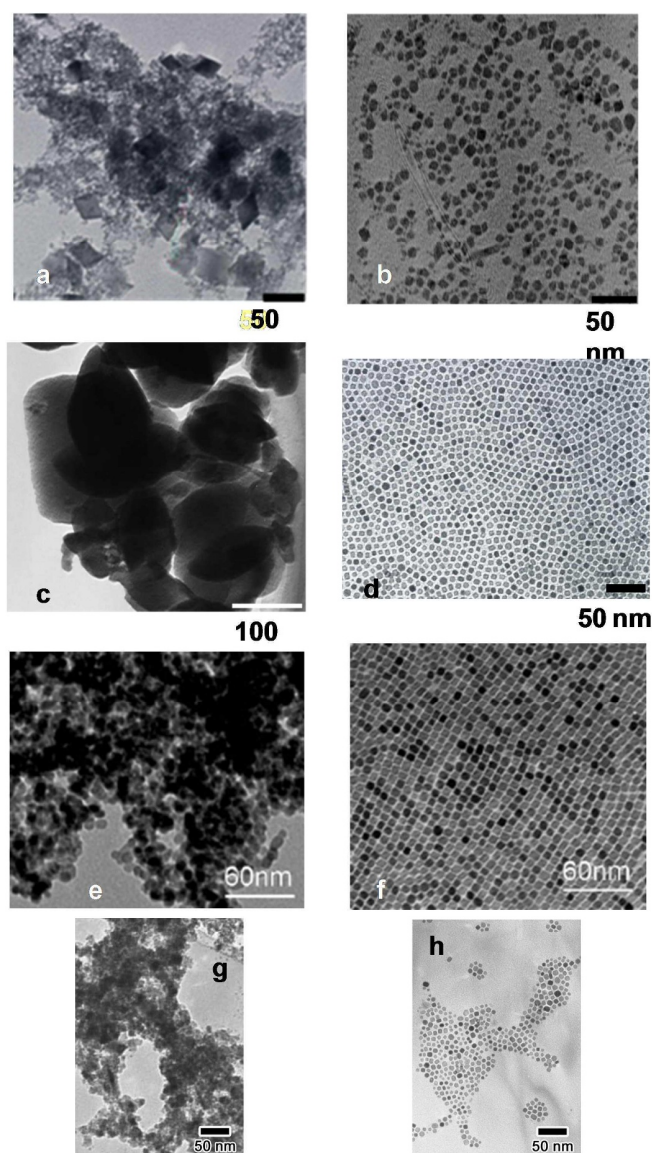


Fig.4. TEM images of nanocrystals synthesized under supercritical hydrothermal conditions. (a) Fe₂O₃ (without modifier); (b) Fe₂O₃ (with modifier); (c) Co₃O₄ (without modifier); (d) Co₃O₄ (with modifier); (e) CeO₂ (without modifier); (f) CeO₂ (with modifier); (g) TiO₂ (without modifier); (h) TiO₂ (with modifier); (from the works of Adschiri, T. and Byrappa, K.)

HYDROTHERMAL SYNTHESIS OF SOME SELECTED TECHNOLOGICALLY IMPORTANT NANOMINERALS

Zincite

Zincite, (ZnO) is the mineral form of zinc oxide. It's bulk or large size crystals formation is rare in nature; a notable exception to this is at the Franklin and Sterling Hill Mines in New Jersey, an area also famed for its many fluorescent minerals (Dunn, 1979). It has a hexagonal crystal structure and a color that depends on the presence of impurities.

The experimental studies on the hydrothermal synthesis of ZnO nanoparticles are usually carried out using General Purpose autoclaves of 30 ml. capacity within the temperature range 150 to 250 °C and with an autogeneous pressure. The Teflon lined autoclaves are extremely handy for the synthesis of nanoparticles of zincite under severe chemical environment in a closed system.

Hydrothermal and supercritical hydrothermal methods are used popularly in the synthesis of ZnO nanoparticles. Usually chemical

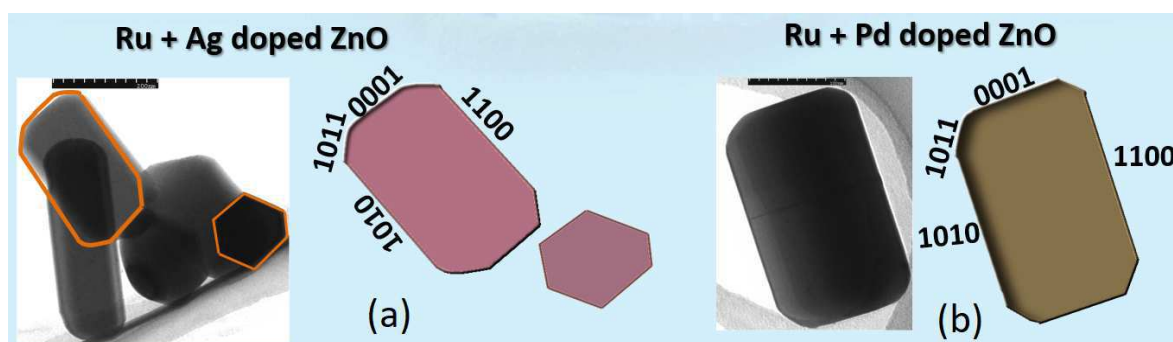


Fig. 5. HRSEM images of zincite. (a) HRSEM of zincite using 3.5 M caprylic acid as surfactant. (b) HRSEM images of zincite using 5 M *n*-butylamine as surfactant (Namratha and Byrappa, 2012).

reagent grade ZnO is taken as the raw material, and several variety of both aqueous and non-aqueous mineralizers are used in the synthesis along with a suitable surface modifier for *in situ* surface modification to alter the surface chemistry. The surface modifiers can alter the surface chemistry of ZnO nanoparticles either into hydrophilic or hydrophobic without any agglomeration and can yield desired size and controlled morphology. ZnO nanoparticles have tremendous multi-functional application potential such as piezoelectric, UV-detectors, photocatalysts, antibacterial, varistors, which are used to prevent voltage surges in devices like mobile phones, pigments in paints, etc., (Namratha and Byrappa, 2012).

A thin coating of ZnO nanoparticles on Ca-aluminium silicate beads as supports under hydrothermal conditions has been reported and this helps to recover the beads without losing any nanoparticles during photocatalysis applications (Shivaraju et al., 2010).

Fig.5a & 5b show the surface modified ZnO nanocrystals synthesized under hydrothermal conditions with pressure-autogenous, temperature-180 °C and in the presence of caprylic acid, or *n*-butylamine (Namratha and Byrappa, 2012). Similarly, ZnO nanoflowers have been prepared under hydrothermal conditions at 190 °C for 1 h using an organic additive like 1 ml of diethyl amine. The field emission scanning electron microscope (FESEM) image shows the presence of five well-defined morphologies in a single sample: (i) a ZnO flower consisting of nanorods with tapering features and pointed ends; (ii) a ZnO flower with a mixture of hexagonal nanorods and quasi-triangular petals (Fig. 6); (iii) a beautiful ZnO flower with a tower-like pistil and quasitriangular petals; (iv) a ZnO flower consisting of hexagonal prisms with planar and hexagonal pyramid tips and (v) bundles of hexagonal nanorods (Hezam et al., 2017).

Jiang et al., (2020) have reported that ZnO-nanoparticles are

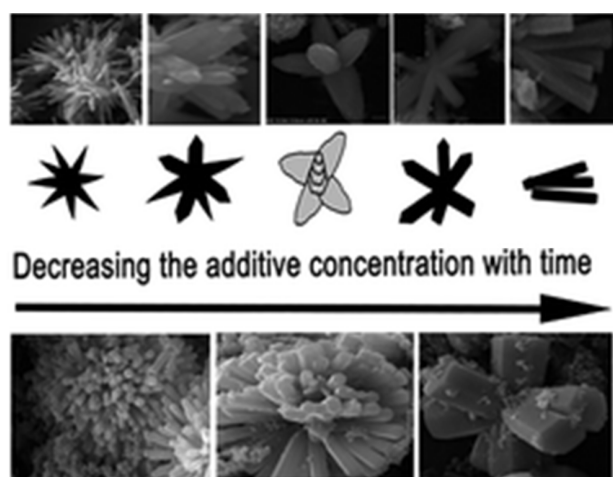


Fig. 6. FE-SEM images of the sample ZnO nanoflowers at two magnifications (Hezam et al., 2017).

considered as relatively safe metal oxide with the inherent ability to induce reactive oxygen species production and lead to apoptosis, and possesses antibacterial, antifungal, and wound healing activities. Similarly, Cruzl et al., (2020) have reported the biomedical application of ZnO in detail. Mustapha et al., (2020) have reported anchored ZnO on clay found to be a good promising sequesters and have been explored for wastewater remediation via nanotechnology. This water treatment method includes adsorption/absorption, photocatalysis, and microbial disinfection. These nanocomposites provide more active surface sites and reduce the agglomeration of the nanoparticles, but leaching has been their shortcomings. To overcome this, the filtration technique may become significant for the removal and avoidance of fouling of wastewater. This can be achieved through the fabrication of nano-based filters using the nanocomposites. Reinprecht et al., (2018) have reported that nano-ZnO-treated particles board had a better biological resistance against bacterial, mold, and decay attacks compared to the control untreated particle boards. Positive effect of ZnO nanoparticles reducing the growth activity of the molds *Aspergillus niger* and *Penicillium brevicompactum* on the top surfaces of particle boards was unambiguous. Srivastava et al., (2013) have reported zinc oxide (*n*-ZnO) nanoparticles synthesis by simple solution-based approaches. *n*-ZnO nanoparticles were used for the removal of Cd(II) from aqueous solutions. A high (92%) removal of Cd(I) from its aqueous solutions with initial concentration of 200 mg/L by *n*-ZnO particles was achieved. The deep-sea floors are rich in the sulfide deposits of polymetals, especially copper, iron, manganese, along with other metals like gold, lead, barium, zinc, and silver even in the comparatively shallow waters at a depth of <2000 meters (Hein et al., 2013).

Titanium Dioxide

Rutile, (TiO₂) is an oxide group of minerals. It often appears as pale golden, needle like crystals inside quartz. When not enclosed in quartz, it is usually yellowish or reddish brown, dark brown, or black. Crystals are generally prismatic, but can also be slender and needle like. Multiple twinning is common and is either knee-shaped, net- or lattice like, or radiating, forming wheel-like twins. Rutile may also radiate in star-like sprays from hematite crystals. Rutile often occurs as a minor constituent of granites, gneisses, schists, and also in hydrothermal veins and in some clastic sediments. It commonly forms microscopic, oriented inclusions in other minerals, producing an asterism effect (Dunn, 1979).

The synthesis of either rutile or anatase phase TiO₂ is usually carried out in small autoclaves of the Morey type provided with Teflon liners. The conditions selected for the synthesis of TiO₂ particles are: T = < 200 °C, P < 100 bars. Such pressure temperature conditions facilitate the use of autoclaves of simple design provided with Teflon liners. The use of Teflon liners helps to obtain pure and homogeneous TiO₂ particles. Though the experimental temperature is low ~ 150 °C,

TiO₂ particles with a high degree of crystallinity and desired size and shape could be achieved through a systematic understanding of the hydrothermal chemistry of the media (Parvin et al., 2012; Pasang et al., 2014). Similarly, Behzad et al., (2015) have reported iron doped TiO₂ (Fe:TiO₂) hybrid nanoparticles synthesized under mild hydrothermal conditions (T = 100 °C, P = autogenous, t = 16 h) by varying the dopant percentage and amount of surface modifier in a simple General-Purpose autoclave.

Ziental et al., (2020) have reported that a recent rise in scientific interest in TiO₂ is linked to its exceptional photoactivity. After the illumination in aqueous media with UV light, TiO₂ produces an array of reactive oxygen species. The capability to produce reactive oxygen species and thus induce cell death has found application in the photodynamic therapy (PDT) for the treatment of a wide range of maladies, from psoriasis to cancer. Titanium dioxide nanoparticles were studied as photosensitizing agents in the treatment of malignant tumors as well as in photodynamic inactivation of antibiotic-resistant bacteria. Both TiO₂ nanoparticles themselves, as well as their composites and combinations with other molecules or biomolecules can be successfully used as photosensitizers in photodynamic therapy. Gohari et al., (2020) have discussed the role of titanium dioxide nanoparticles in plant growth and especially in plant tolerance against abiotic stress, a greenhouse experiment was carried out to evaluate TiO₂ nanoparticles' effects (0, 50, 100 and 200 mg L⁻¹) on agronomic traits of Moldavian balm (*Dracocephalum moldavica* L.) plants grown under different salinity levels (0, 50 and 100 mM NaCl). Results demonstrated that all agronomic traits were negatively affected under all salinity levels, but application of 100 mg L⁻¹ TiO₂ nanoparticles mitigated these negative effects. TiO₂ nanoparticles application on Moldavian balm grown under salt stress conditions improved all agronomic traits and increased antioxidant enzyme activity compared with plants grown under salinity without TiO₂ nanoparticles treatment.

Hydroxyapatite

Hydroxyapatite (*HAp*), with the chemical formula Ca₁₀(PO₄)₆(OH)₂ has been extensively used in medicine for implant fabrication and is one of the most biocompatible materials owing to its similarity with mineral constituents found in hard tissue (i.e. teeth and bones) (Aoki, 1991). It is commonly the material of choice for the fabrication of dense and porous *HAp* bioceramics. Its general uses include biocompatible reinforcement in composites, coatings on metal implants, and granular fill for direct incorporation into human tissues. Hydrothermal experimental conditions are planned based on the calculated phase boundaries in the system CaO-P₂O₅-NH₄NO₃-H₂O at 25-200 °C. Also, *HAp* powders are hydrothermally synthesized in stirred autoclaves at 50-200 °C and by hydrothermal or mechanochemical-hydrothermal methods (Suchanek and Yoshimura, 1998). FESEM photographs of selected batches of *HAp* crystals synthesized at 200 °C in 1 wt.% KCl (aq) and 50 vol.% 2-propanol (aq) are shown in Fig. 7. *HAp* crystals synthesized in 50 vol.% 2-propanol (aq) had low aspect ratios ranging between 2 and 3 and diameters between 20 and 40 nm (Fig. 7a). Conversely, uniform nanosized needles (dimensions of about 20 x 100-160 nm, aspect ratio of 5-8) (Fig.7b) were formed when 1 wt.% KCl additive was used (Riman et al., 2002). Magnesium-substituted hydroxyapatite (*Mg-HAp*) powders with different crystallinity levels were prepared at room temperature via a heterogeneous reaction between Mg(OH)₂/Ca(OH)₂ powders and an (NH₄)₂HPO₄ solution using the mechanochemical-hydrothermal route shell may be useful for bone-related applications (Suchanek et al., 2004).

Magnetite

Magnetite, Fe₃O₄ is an important iron ore mineral occurring widely distributed throughout the world (Dunn, 1979). Wan et al., (2005)

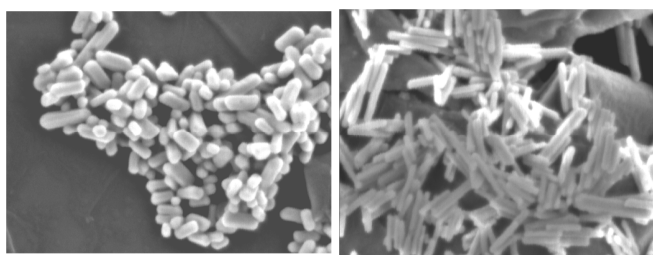


Fig. 7. *HAp* crystals prepared hydrothermally at 200 °C for 24 h using moderate stirring. Room temperature *pH* of precursor slurries was 10. (a) Powders crystallized in 50 vol% 2-propanol in H₂O (aq); (b) Powders crystallized with 1 wt.% KCl (aq.) (Riman et al., 2002).

have proposed a soft-template-assisted hydrothermal route to prepare single crystal Fe₃O₄ nanorods with an average diameter of 25 nm and length of 200 nm at 120 °C in 20 h. The formation of these Fe₃O₄ nanorods has been ascribed to the presence of an organic additive-ethylene diamine, which plays a crucial role not only as a base source but also as a soft template to form single crystal Fe₃O₄ nanorods. Fig. 8 shows the Fe₃O₄ nanorods obtained through a soft-template-assisted hydrothermal route.

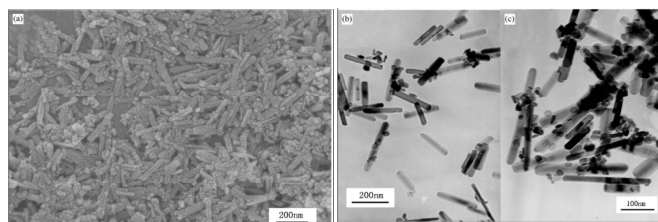


Fig. 8. FESEM and TEM images of Fe₃O₄ nanorods (Photos courtesy Prof.Y.T. Qian).

Several workers have prepared the α-Fe₂O₃ (hematite) phase as nanoparticles under hydrothermal conditions (using both aqueous and non-aqueous solvents) with or without surfactants (Zheng et al., 2005). These hematite particles find extensive applications as catalysts, pigments, recording medium, sensors, etc. Hydrophilic magnetite particles for biological applications have been synthesized by hydrothermal method in the presence of D-Glucose as both reducing and capping agent in a facile, one-step, low energy and environmentally friendly route. The role of D-Glucose as a reducing agent in the formation of magnetite particles under mild hydrothermal conditions has been investigated. The absence of D-Glucose results in the formation of hematite (Keerthana et al., 2015). Similar reduced geological environment can be found in nature also for the large-scale formation of magnetite and hematite.

Corundum

Aluminium oxide (Al₂O₃), is a chemical compound of aluminium and oxygen with the chemical formula Al₂O₃. It is the most commonly occurring mineral of aluminium oxides family (Dunn, 1979). It is popularly called as alumina and may also be called aloxide, aloxite, or alundum depending on its particular forms or applications. It occurs naturally in its crystalline polymorphic phase.

α-Al₂O₃ as the mineral corundum has several varieties like precious gemstones - ruby and sapphire. α- alumina is one of the most widely used ceramic materials owing to its high mechanical strength and hardness, good wear resistance, low electric conductivity, high refractoriness, high corrosion resistance (Richards, 1986). Corundum powders can be synthesized at 400 °C to 700 °C and high pressure less than 15MPa under hydrothermal conditions.

Figure 9 shows pure and Mn-doped α-alumina particles. The

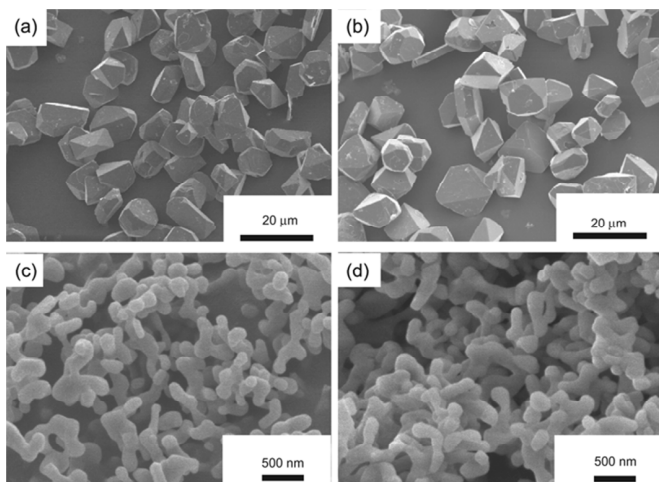


Fig. 9. Scanning electron microscope photographs of hydrothermally synthesized phase pure α - Al_2O_3 powders: (a) undoped 10 μm ; (b) Mn doped 10 μm ; (c) undoped 250 nm; (d) Mn doped 250 nm. All powders were in as-synthesized form. Note the same magnifications in (a)–(b) and (c)–(d) (Photo courtesy : W. L. Suchanek)

synthesis of ultrafine α -alumina has a great technological potential especially as high temperature ceramics, catalytic supports, refractories, abrasives, and most importantly in the manufacturing of scratch proof paints for automobiles.

Halloysite

Halloysite, $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ is a two-layered aluminosilicate clay mineral belonging to kaoline group (Joussein et al., 2005). Halloysite shows typical tubular, spheroidal, and slaty morphologies which is controlled by the crystallization conditions. This is one of the most common minerals occurring in nature. Halloysite nanotubes (HNTs) are found abundantly in soils, in weathered and hydrothermally altered rocks. HNTs are found in nature abundantly and not only ecofriendly but in the near future could replace a more expensive CNTs which are more expensive, less abundant, and also less biocompatible. Until the end of 20th century HNTs and halloysite clay attracted the attention of researchers only from the geological, and mineralogical significance. But today halloysite is more widely studied for its application potential in the field of biomedical applications, drug delivery, in addition to the conventional ceramic and refractory applications. Hence, halloysite, clay nanotubes, halloysite based nanocomposites and nanopowders, are now emerging as trend-setters in green nanotechnology. The recent developments in biomedical field involve the use of inorganic HNTs for the encapsulation and subsequent release of tetracycline chlorohydrate, khellin and nicotinamide adenine dinucleotide. Similarly, HNTs can be used as a key material in cosmetic applications for example, controlled and extended release of glycerol, as moisturizing agent (Vergaro et al., 2010). Similarly, there are so many other important applications for halloysite with respect to its functionalization with a variety of other materials for catalysis, environmental applications, drug carriers, and so on. Hydrothermal technology is used as functionalization of HNT's. Fig. 10 shows the SEM and TEM images of halloysite nanotubes (Vergaro et al., 2010).

Hydrothermal Synthesis of Carbon Nanoforms

High quality carbon nanoforms such as graphite, diamond, amorphous carbon, diamond like carbon fullerenes, carbon nanotubes, graphene oxide, graphene, etc., are obtained popularly by hydrothermal method, although there are other methods more popular for the large scale production of these carbon nanostructures. In nature the stabilities of diamond and graphite are mostly controlled by pressure-temperature-

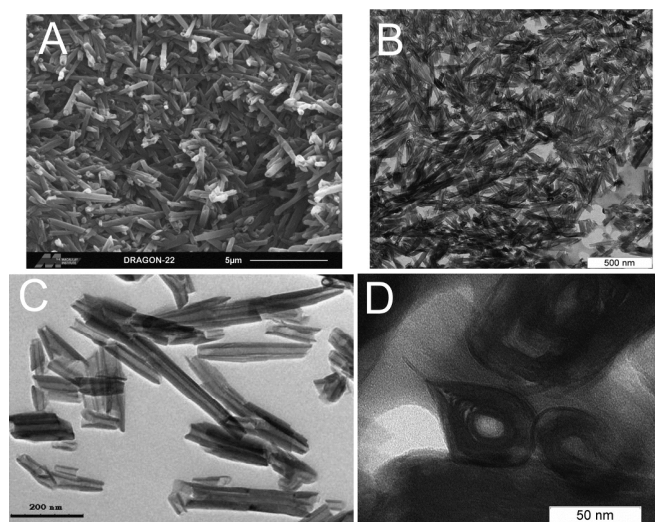


Fig. 10. (a) SEM image of halloysite nanotubes powder, as supplied from Dragon Mine, Applied Minerals, Inc. TEM images of halloysite clay nanotubes: (b,c) longitude and (d) cross-section (Vergaro et al., 2010).

oxygen-fugacity in the C-CO-H-system (Melton and Giardin, 1974). Hydrothermal synthesis of nanodiamond under sub-natural conditions ($P=200$ - 300 MPa and $T=600$ - 800 °C) has been reported (Basavalingu et al., 2001).

Figure 11 shows SEM images of diamond particles showing well developed octahedral facets adhered to the inner walls of the broken spherical particles. The discovery of CNTs in 1991 made a revolution in nanotechnology research because CNT shows outstanding electrical and mechanical properties. The interesting electronic and photonic properties coupled with their unusual molecular symmetries have made CNTs very attractive for many potential applications including single molecular transistors, scanning probe microscope tips, gas and electrochemical energy storage, catalyst, protein/DNA supports, molecular-filtration membranes and artificial muscles (Frank et al., 1998; Dai et al., 1996). Fig. 12 shows TEM an image of CNTs prepared through hydrothermal pyrolysis at temperature 550 °C with oxides of Co, Ni as catalyst (Zhang et al., 2004).

Chalcogenides Nanomineral Particles

A chalcogenide is a chemical compound consisting of at least one chalcogen anion and one more electropositive element. Transition metal chalcogenides occur with many stoichiometries and crystal structures. Most common and most important technologically, however, are the chalcogenides of simple stoichiometries, such as 1:1 and 1:2. Extreme cases include metal-rich phases (e.g. Ta_2S), which exhibit extensive metal-metal bonding, and chalcogenide-rich materials such as Re_2S_7 , which features extensive chalcogen-chalcogen bonding (Hughbanks, 1995).

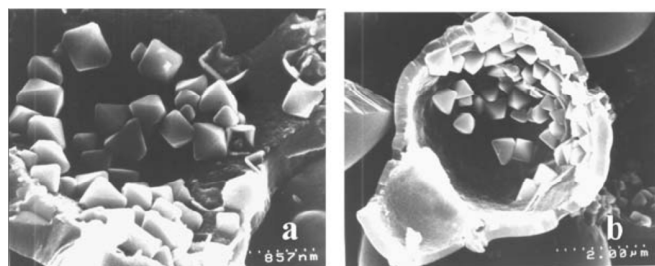


Fig. 11. SEM images of diamond particles showing well developed octahedral facets adhered to the inner walls of the broken spherical particles (Courtesy: B. Basavalingu).

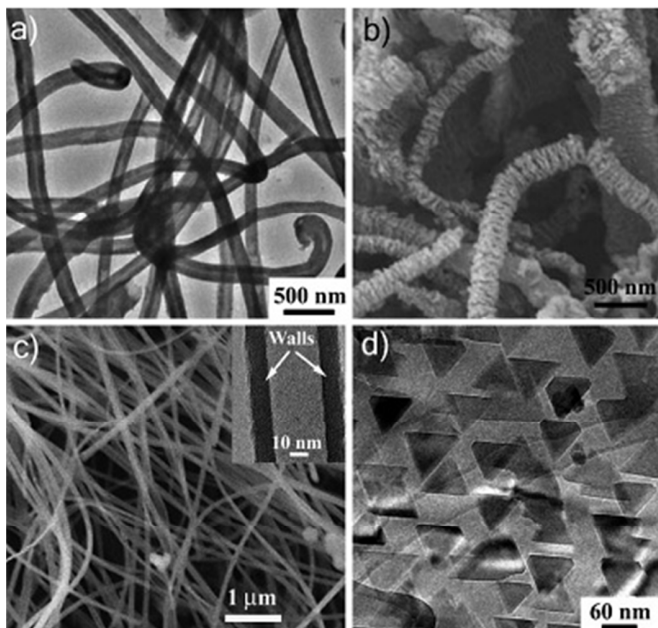


Fig. 12. TEM images of CNTs prepared through solvothermal pyrolysis of: (a) polypropylene and maleated polypropylene with Ni catalyst at 700 °C; (b) tetrahydrofuran in the presence of Ni powders at 600 °C; (c) ferrocene in the presence of sulfur at 200 °C, the inset is a HRTEM image of individual amorphous CNTs; (d) Fe₂O₃ nanoplates between two carbon films synthesized by pyrolyzing ferrocene and sodium oxalate at 600 °C (Photos courtesy: Prof. Y.T. Qian).

For the purpose of classifying these materials, the chalcogenide is often viewed as a dianion, i.e., S²⁻, Se²⁻, Te²⁻, and PO²⁻. In fact, transition metal chalcogenides are highly covalent, not ionic, as indicated by their semiconducting properties. Sulphides of various divalent, trivalent, and pentavalent metals form an important group of minerals for a variety of technological applications. They popularly form II-VI, III-VI, V-VI, group of semiconductor minerals. Several hundreds of reports on the hydrothermal synthesis of chalcogenide groups are found in the literature and the most important ones are CdS, PbS, ZnS, CuS, FeS₂, and so on. Among the sulphides II-VI group of chalcogenides, AX (A=Cd, Pb, Zn; X=S, Se, Te) form an important group of semiconductor minerals with applications in solar cells, light emitting diode, nonlinear optical applications, optoelectronic, electronic devices, biological labeling thermoelectric coolers. (Schur et al., 1998; Zhang et al., 2005; Liu et al., 2006). Figs. 13 & 14 show the characteristic SEM and TEM images of some selected chalcogenides nanoparticles synthesized using hydrothermal method.

Nannofossils

During 70 and 80s micropaleontology was one of the most leading subjects not only to understand the stratigraphic significance, but also to understand the distribution of oil and natural gas (Foraminifera, Pecten, Ostracod, etc.), paleoecology, paleo-oceanography, and so on. However, with the emergence of nanoscience and technology the interest among the earth scientists and paleontologists started looking into nannofossils which were thought to be nonexistent because of the lack of high resolution SEM. Starting from 1980s calcareous nannofossils are being studied more and more as they are extremely useful paleo-ecological proxies, which give information on paleoecology, paleoclimate, paleo-oceanography (Roth, 1981; Mutterlose, 1987; Williams and Bralower, 1995; Herrle, 2003). This study also results in the understanding of surface water temperature, nutrient availability, detrital input, surface water salinity and primary

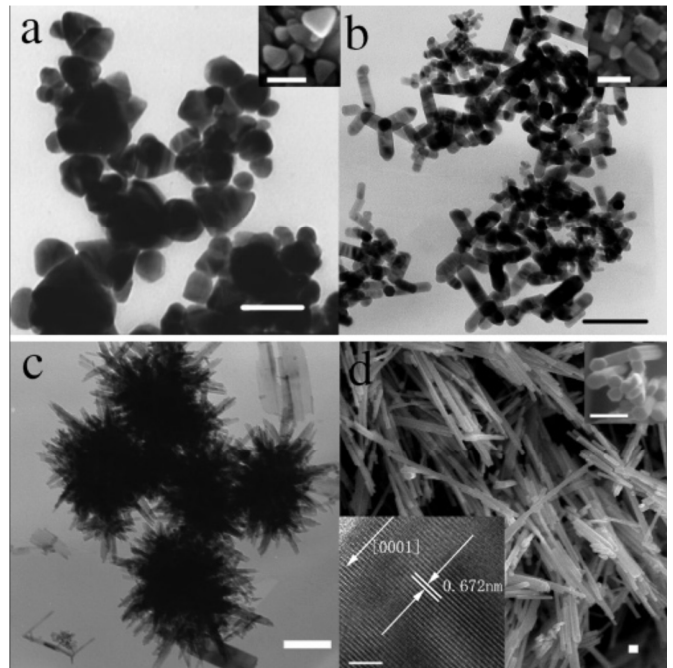


Fig. 13. TEM and SEM images of CdS products obtained at 180 °C for 5 h in mixed solvents with different volume ratios: (a) 5% of en, TEM image with SEM image as inset; (b) 15%, TEM image with SEM image as inset; (c) 65%, TEM image; (d) 100%, SEM image with the upper right inset showing a magnified picture of the hexagonal ends of the long rods, and the lower left inset showing the HRTEM image of a nanorod. The scale bars in the TEM and SEM images all represent 100 nm. The scale bar in the HRTEM image is 5 nm (Photos: Courtesy: Prof. Yan Li).

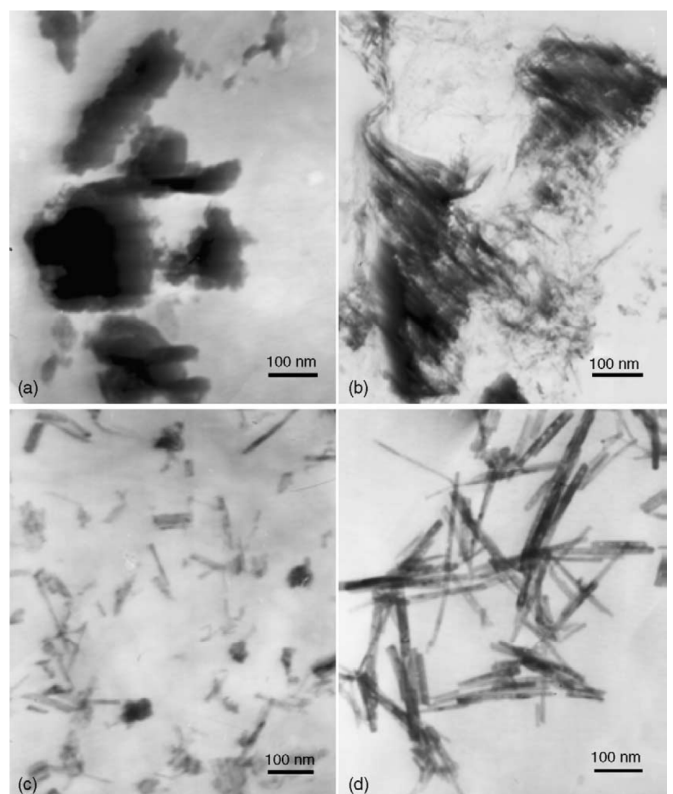


Fig.14. TEM images of CdS_xSe_{1-x} products with different reaction time: (a) 1 h; (b) 2 h; (c) 3 h and (d) 4 h. (Photos: Courtesy: Prof. Yong Liu)

productivity. A wide range of nanofossils have been reported from different continents and most of these nanofossils are calcareous nanofossils which are mostly confined to the shallow depths and also mostly occur in the upper tertiary and quaternary periods like Pliocene, Miocene, cretaceous and carboniferous periods and most of the nanofossils are carbonaceous, or calcareous and found in more recent sediments. It is interesting to note the history of these calcareous nanofossils. It first goes back to Ehrenberg (1836, 1840, 1854), who first described these small elliptical discs from the Cretaceous formations, and believed them to be inorganic origin. Later Huxley (1857) coined the term “coccolith” for these elliptical discs found abundantly in the Atlantic floors (in Dayman, 1958). Subsequently Wallich (1861) found coccoliths forming a minute sphere, which he named “coccosphere” and believed them to be larvae of planktic foraminifera (Ustinova, 2015). It is noted that Fig. 15 shows the calcareous nanofossils from middle Volgian deposits (ammonite *panderi* zone). O’Regan et al., (2020) have reported the calcareous nanofossils anchoring chronologies for Arctic ocean sediments back to 5050 ka. Similarly, Kameo et al., (2020) have reported the calcareous nanofossil biostratigraphy of the lower-middle pleistocene boundary of the GSSP, Chiba composite section in the Kokumoto formation of central Japan. The role of hydrothermal vents in the ocean floors giving warmer temperature conditions and the presence of these nanofossils are yet to be studied systematically to understand the paleo-ecology.

It is to be noted that these calcareous nanofossils/coccoliths have high extinction and speciation rates. All these nanofossils were species in very large number during late Jurassic (Tithonian period). These nanofossils form an important and most reliable tool for the biostartigraphic dating of both Mesozoic and Cenozoic sediments. Researchers have found index species of these nanofossils common to the Pacific, the Indian ocean and the Atlantic ocean providing very

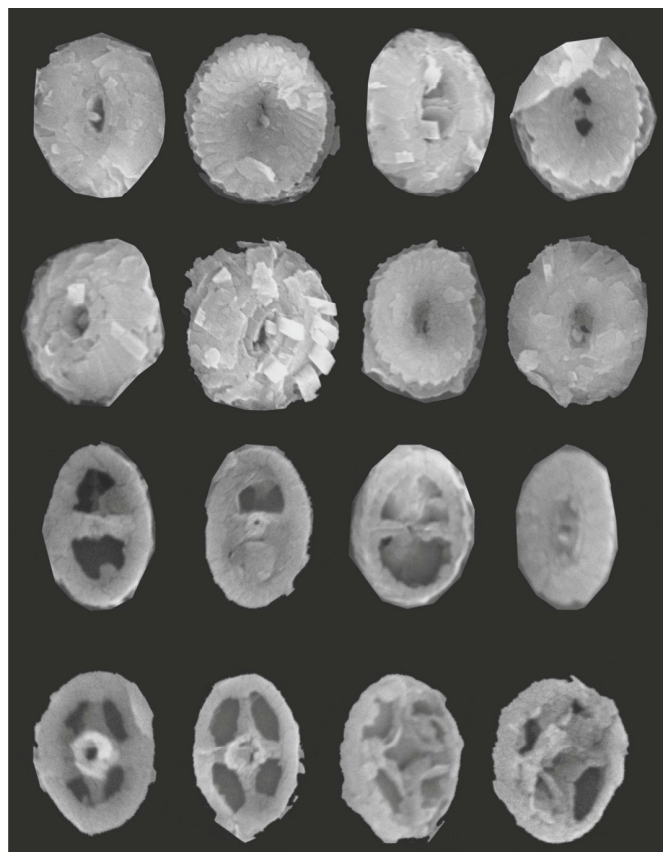


Fig. 15. Calcareous nanofossils from middle Volgian deposits (ammonite *panderi* Zone) of the Loino section (Reprinted with Permission from Elsevier Sci. Publ.)

powerful biostartigraphic zonation, thereby indicating the water mass boundaries defined by distinct differences in temperature, salinity (*pH*) and nutrient levels.

Geopolymers

The term geopolymers was coined by ‘Joseph Davidovits’ in 1978 and established a non-profit French scientific institution (Geopolymer Institute). The term refers to the material originated by inorganic polycondensation or geopolymerization which is nothing but alkali activation of aluminosilicate materials. A more broader term which describes such an alkali activated aluminosilicate is “inorganic polymers” (Skvara, 2007). When once the aluminosilicate powder is mixed with alkaline solutions a viscous, paste is formed that quickly hardens into a geopolymer. If this paste or the gel is allowed to crystallize slowly it will form zeolite mineral framework. The most important aspect of this geopolymer is lower water content with lower calcium content. Geopolymers can be alkali activated, or silicate polymers or inorganic polymers, with Ca-free binding material, which in turn a replacement for the conventional Portland cement, wherein the water intake is very essential for hardening. In contrary, alkali activated aluminosilicate need addition of an alkaline component in the aqueous form. Therefore, hydroxides and concentrated alkali metal silicates are used. Sometimes alkali metal carbonates or sulfates are used rarely. The alkali activation of aluminosilicate materials depends on the mix compositions and reactions conditions like such as Al_2O_3 : SiO_2 , alkali metal curing temperature, curing time, water-solid ratio, *pH*, and other dopant metals used for enhancing the modular properties. These geopolymers are the future of low weight and high strength construction materials for skyscrapers. The greatest environmental problem being faced by man is the waste disposal, recycling of waste, mitigation of CO_2 emission, well organized and structured, safe disposal of effluent, sludge, byproducts like rice husk, blast furnace slag, calcined clay (metakioline) nuclear waste, concrete waste material, construction debris and so on. There is an urgent need for a technology to process and recycle these large quantities of waste materials and by-products into more advanced technological materials as an alternative to ordinary conventional Portland cement. In this context hydrothermal technology is the key to resolve these issues. Therefore, the present authors have briefly discussed the geosynthesis of alkali activated aluminosilicates. The driving force for such a technology is the reaction of silicon, aluminium atoms, in the presence of various of alkali metals forming molecules that are chemically, and structurally matching with those responsible for natural rocks (Komnitsas and Zaharaki, 2007). The greatest advantages of geopolymers are the low creep and very little drying shrinkage.

Fig. 16 shows a simple structural model of the geopolymer designed for a poly-sialate-silox type formed by alkali activation of metakioline. Geopolymers also exhibit fire resistance property. When a 10 mm thick panel of geopolymer is exposed to 1100 °C flame, the measured reverse-side temperature reached 240-283 °C after 35 min. Similarly, geopolymers show a great stability for microbial activity which is a

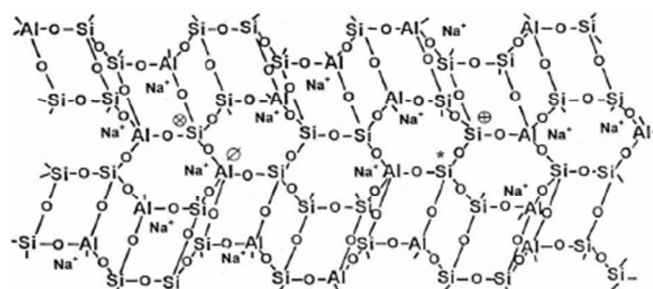


Fig.16. Davidovits model of geopolymer structure (Davidovits, 1978).



Fig. 17. Recycled concrete waste (calcium silicate by hydrothermal method) as fire resistant light weight material (Courtesy: Konoshima Chemicals, Japan)

boon to the modern construction material because even after several months in the microbes containing solutions remain unaffected and there is no significant or noticeable change in the compressive strength and leachability (Hermann et al., 1999). Geopolymerization has become a fast-emerging technology for the immobilization of toxic and hazardous metals including nuclear waste materials. Davitovtis reported the effective immobilization of uranium waste and other nuclear waste in the geopolymeric matrix. It has been well studied geopolymeric matrices are the ideal ones for the effective immobilization and minimizing leaching of iron, cobalt, cadmium, nickel, zinc, lead, arsenic, radium, and uranium. Fig.17 shows recycled concrete waste material processed using hydrothermal technique. This material shows light weight, high mechanical strength, high temperature resistance and also fire resistant, with antimicrobial characteristics. Therefore, such a recycled material can be called as green material of the future.

The future of hydrothermal technology will be definitely of both geological and technological importance.

SUMMARY

In spite of a considerable progress achieved in nanogeoscience, our understanding in terms of the formation mechanism of mineral elements, the migration process, structural form, and disaster-related and environmental effects of nanoparticles and the mineralization of nanopores is still in the infant stage. Geological processes at the nanoscale need a transdisciplinary approach to understand the formation of various minerals, rocks, ores, structures, and organic life. Especially geopolymers are going to be the futuristic construction materials and toxic waste disposal materials, because of their technological significance. Similarly, the study of nanofossils contributes to the understanding of palaeoecology and also palaeoceanography. Besides, the distribution of various nanominerals deposits, the nanostructures will throw light upon the geochemistry and open up new avenues related to the role of organics, biomolecules, some specific volatiles and fluids in the mineral genesis. Quantum dots formation and existence in nature have not been explored at all, although such materials do present in nature.

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