

# Hydrothermal – From Geology to Technology (Part 1)

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## ABSTRACT

The term hydrothermal is of geological origin. A great variety of crystals, minerals, ores and rocks have hydrothermal origin and occur as bulk, fine, ultrafine, and nanosized geologic materials. Hydrothermal refers to the action of water and other solvents at elevated temperature and pressure conditions in bringing about changes in the earth crust leading to the formation of rocks, minerals, crystals and ores. It also refers to the post-magmatic and pre-metamorphic stages. In the hydrothermal processes, a variety of volatiles also play an important role in the chemistry and geochemistry of hydrothermal solutions. The origin of a variety of metal deposits in deep-seated submarine hydrothermal ecosystems link with the origin of life on the earth. Today, hydrothermal has become one of the most important experimental methods of understanding the natural systems leading to the crystallization of rocks, minerals and ore deposits. Similarly, it has become one of the environmentally most benign techniques to synthesize a great variety of technological materials with desired functional properties. The technique has advanced so much that under laboratory conditions a wide range of pressure-temperature conditions can be created using specially designed hydrothermal autoclaves, PT sensors and controllers. In the present review, the authors discuss the evolution of hydrothermal process from geology to technology to develop technological materials in different sizes with specific functional properties. Also, the review describes some characteristic natural systems under hydrothermal conditions leading to the formation of some important geologic materials, the influence of different volatiles in the formation of various rocks and mineral deposits. Also the current trends in hydrothermal technology has been discussed with reference to the lowering of temperature and pressure conditions for the synthesis of high melting compounds like alkali rare earth tungstates, vanadates, diamond, etc. in this article.

## INTRODUCTION

The largest known single crystal of natural origin (beryl crystal weighing >1000kg) and the largest quantities of single crystals produced by man in the laboratory (quartz crystals weighing over 5000 kg in a single hydrothermal experimental run) are both of hydrothermal origin. The term 'hydrothermal' was first used by Sir Roderick Murchison, a British geologist in mid 1840s, and this term was referred

to the action of water at elevated temperature and pressure in bringing about changes in the earth's crust leading to the formation of rocks, minerals and ore deposits. Hence hydrothermal is considered as purely of geological origin (Byrappa, 1990). Today crystals and minerals either bulk or fine or ultrafine or nanosize are the unacknowledged pillars of modern technology owing to their ever increasing demand from the fields of electronics, piezoelectric, nonlinear optics, magnetic, catalytic, opto-electronics, thermo-optic, photonics, spintronics, ceramics, biomedical, nanotechnology, etc (Byrappa and Yoshimura, 2001). Man started synthesizing minerals and crystals in the laboratory only in the 19<sup>th</sup> century. Whereas the natural crystals and minerals are found in nature ever since the earth came into existence some 4.5 billion years ago. As far as the crystal quality, purity, morphology and rarity are concerned the hydrothermal method plays an important role both under natural and laboratory conditions.

The discovery of deep-seated hydrothermal activity in the ocean beds like Galapagos spreading center in 1977 has led to the discovery of a large number of other spectacular sub-marine hydrothermal systems of global significance, which have contributed to the general acceptance of plate tectonics theory and hydrothermal ecosystems (Corliss, 1979). Such studies have also led to the new thinking in marine biology, geochemistry, and in economic geology. Similarly, researchers are looking for such submarine hydrothermal conditions to understand the primitive forms of life. Hence it is strongly believed that the roots of life on earth can be found in hydrothermal ecosystems.

In nature most of the minerals formed in the post-magmatic and metamorphic stages in the presence of water at elevated pressure and temperature conditions are said to be hydrothermal origin (Jensen and Bateman, 1979). The term hydrothermal is defined as any heterogeneous reactions in the presence of aqueous solvents popularly known as mineralizers under high pressure and temperature conditions to dissolve and recrystallize (recover) minerals that are relatively insoluble under ordinary conditions (Ballman and Laudise, 1963). The high pressure and temperature usually refer to the supercritical conditions.

## EARLY EXPERIMENTS IN HYDROTHERMAL SYNTHESIS

Most of the early experiments on hydrothermal synthesis of minerals confined to the imitation of natural conditions in the laboratory and hence a large variety of minerals were synthesized in the 19<sup>th</sup> century. By the end of 19<sup>th</sup> century over 130 mineral species were

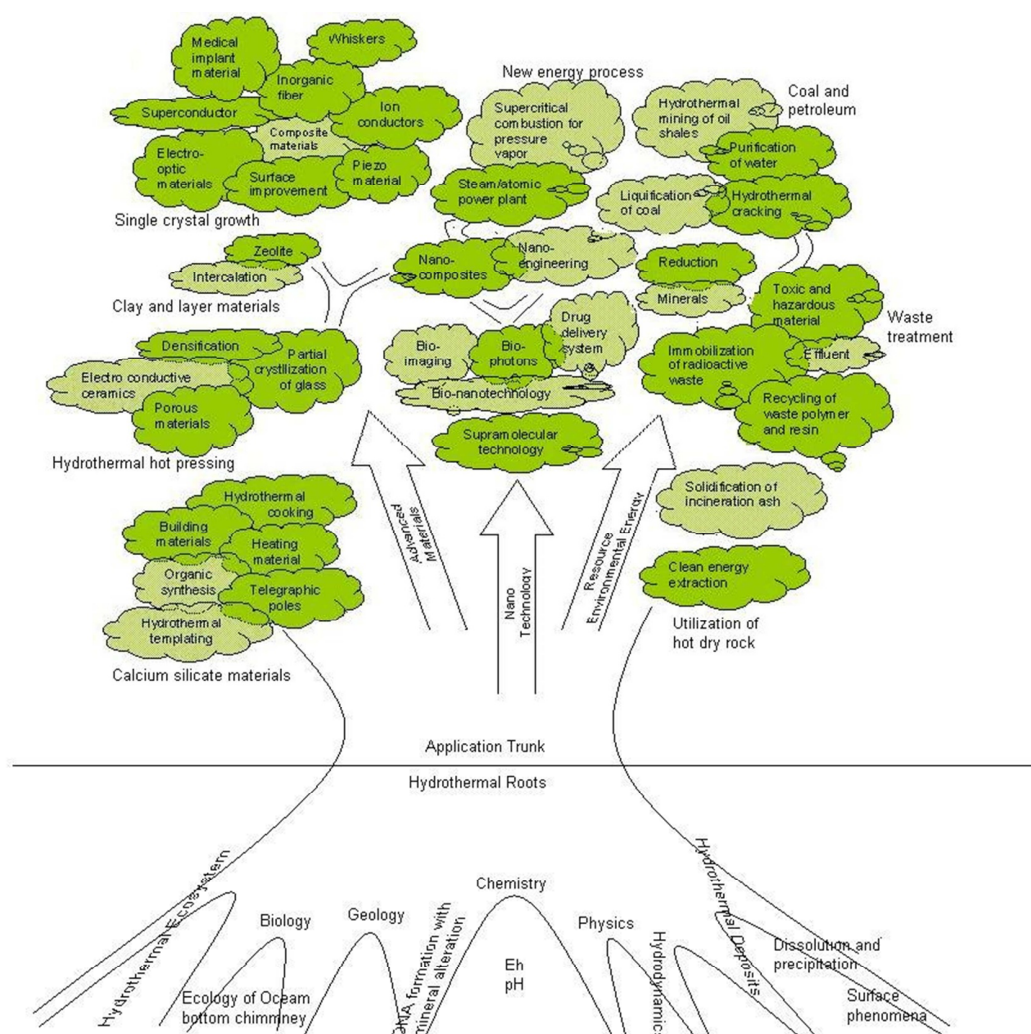
synthesized. These experiments were carried out under hydrothermal conditions to investigate various geological phenomena ranging from the origin of ore deposits to the origin of meteorites. Similar studies are being carried out today extensively by Earth Scientists to understand several problems in Petrology, Geochemistry, Mineralogy, Ore Genesis, and Paleontology. Thus, the earlier works provided a basis to explain geological problems and also contributed to the design and fabrication of high pressure and temperature equipment for advanced geological studies leading to the unraveling of hitherto unknown natural geological processes of rocks and mineral formation. All these experiments on the synthesis of mineral species from the family of oxides, chalcogenides, sulphides, silicates, hydroxides, carbonates, were carried out using water as solvent. However, the high melting temperature, and ultra-low solubility of several oxides species did not prove to be successful with pure water as a mineralizer that led to the use of alkaline mineralizers which significantly increase the solubility of these high melting compounds under hydrothermal conditions. The authors quote a classical example that early hydrothermal experiments used to be tedious since experiments sometimes lasted for 3 to 6 months without any bearing on the petrogenesis and phase equilibria, and ended up with nanosize products whose status were not clear (Morey, 1953) during that time due to lack of sophisticated analytical tools. The majority of the early experiments carried out during the 1840s to early 1900s were simply discarded as failure due to the lack of sophisticated electron imaging technology (Hautefeuille and Perrey, 1888; Byrappa et al., 2015). These early failures could be attributed

to the lack of knowledge on the hydrothermal solution chemistry. With the availability of scanning tunneling microscope (STM), high resolution scanning electron microscope (HR-SEM) and high-resolution transmission electron microscope (HRTEM) from 1980 onwards hydrothermal researchers started observing such fine products which were earlier discarded as failures, now provide most useful information.

Recently, computer simulation work has shown that life if it ever originated on Mars may have followed liquid water progressive at greater depth, where life could have been sustained by hydrothermal (heating) activity and rock abundant liquid water in the Noachian era. Similar geological conditions noticed on Earth, geothermal heat form sub-glacial lakes in areas of the west Antarctic ice sheet, Greenland and Canadian Arctic (Ojha, et al., 2019).

### Recent Developments in Hydrothermal Research

With a further development in the hydrothermal research, an emphasis was made on the search for an effective solvent which led to the use of other volatiles like  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ , and even some organics in the second quarter of 20<sup>th</sup> century. Accordingly, the hydrothermal was named as carbonothermal, ammonothermal, glycothermal, solvothermal, etc. Such studies have laid a firm foundation for understanding the origin of life. Today hydrothermal has advanced so much especially with early contribution by the geologists who had a solid bearing on hydrothermal technology by designing high temperature and high pressure reactors, search for a new mineralizers,



**Fig.1.** Hydrothermal tree covering different branches of science and technology (Byrappa and Yoshimura, 2013).



understanding the phase equilibria, construction of phase diagrams for a large number of natural systems have further transformed hydrothermal from geology to technology. The application of hydrothermal technique on the whole plays a great role in modern day preparative chemistry and nanotechnology. The present authors have reviewed the evolution of hydrothermal research from a pure geology perspective to the technological modern day advancement such as nanogeoscience, nanostructures, nanofossils, geopolymers, palaeoecology, palaeobotany, etc. The nature inspired processes or geomimetic processes have greatly contributed in the synthesis of a variety of natural mineral analogues including diamond, corundum, pervoskite, garnets, etc., under sub-natural conditions (Lobachev, 1971). Perhaps the perovskite family ( $ABO_3$ ) of species have the largest number of polytypes (over 260), which can be synthesized in the laboratory under vivid conditions by imitating various geological environment. Therefore, hydrothermal technique although started by geologists occupies a unique place owing to its advantages and becoming a more inter-disciplinary subject popularly being used by physicists, chemists, ceramists, hydrometallurgists, materials scientists, engineers, biologists, technologists and so on (Fig. 1).

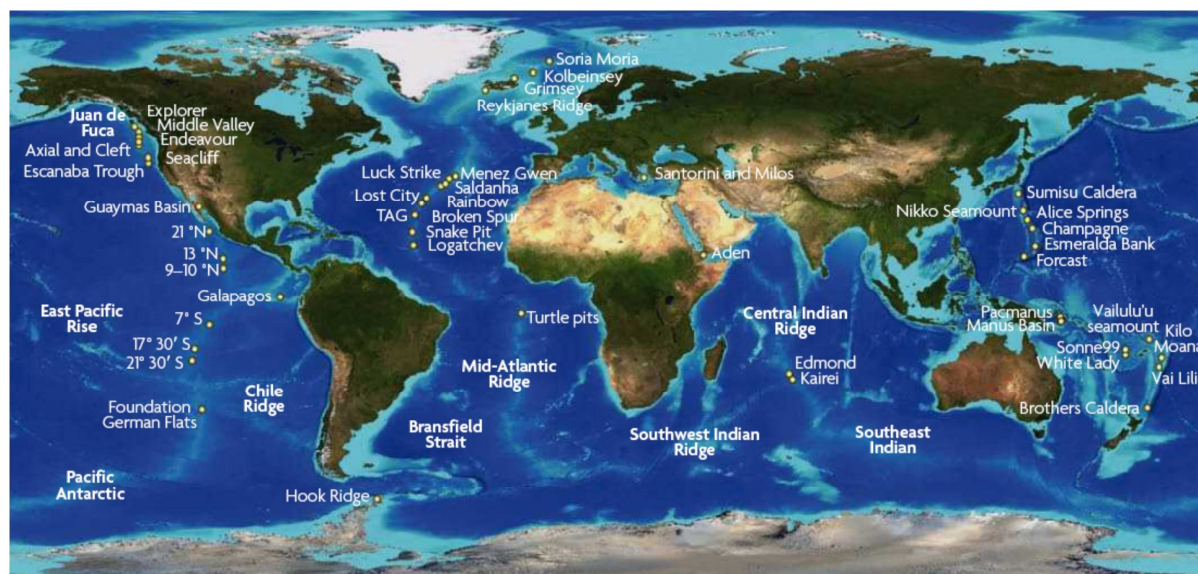
Today hydrothermal technology has been treated as an environmentally benign technology to synthesize almost all the minerals species under sub-natural conditions. Each structure type has a unique physical property such as superconductivity (materials with zero resistance), ferroelectricity, magnetic and electro-optic, etc. Similarly, minerals like hematite, zincite, rutile, magnetite, anatase, spinel, quartz, chalcogenides, etc., in the nanoscale show unique application potential in the field of biomedical, bioimaging, biotechnology, microelectronics, sensors, etc.. Gold in the nanosize was in use from the Roman times giving wonderful shades of colours of gold coatings to glasses and ceramics. Here in the present review the authors discuss the importance of natural hydrothermal processes in the formation of a wide range of rocks and mineral deposits, and also as a tool to design and fabricate a great variety of technological materials.

## NATURAL SUBMARINE HYDROTHERMAL SYSTEMS

In 1977 a large number of spectacular submarine hydrothermal systems have been reported ever since Galapagos spreading center was discovered (Fornari and Embley, 1995). These submarine hydrothermal systems have global significance to ocean chemistry and

geochemistry. Now many biologists and paleobiologists strongly believe that routes of life on earth can be found in hydrothermal ecosystems (Hanley, 1996). Fig. 2. shows the global distribution of sub-marine hydrothermal events. Dick Hanley (1996) describes the geochemical activity of the hydrothermal ecosystems as biotic factory (Byrappa and Yoshimura, 2013).

Everett Shock (1992) states that life originated at warmer temperatures. Such a high temperature at the submarine hydrothermal vents in the presence of various organic biosystems would mix a variety of elements and metals, and provide the required kinetics and free-energy for the formation of abundant mineral deposits, often precious metals of gold, silver, copper, and zinc. Many theories have been proposed that the living organisms once existed in sub-marine hydrothermal vents become fossilized at the very site they lived in. It is believed that the sub-marine hydrothermal systems operate today much in the same manner as they were believed to have functioned in the Precambrian period. These hydrothermal vents having a direct link with heat provide a very broad spectrum of physico-chemical conditions both for the biotic activity and mineralization. The spectacular nature of the submarine hydrothermal ecosystem with features such as black smokers, white smokers, and peculiar ecosystems that are independent of sunlight as a source of reducing power has focused much interest on hydrothermal processes for the explanation of an array of geochemical processes and phenomena (Baross and Hoffman, 1985). According to the model proposed by Abbott and Hoffmann (1984), it is suggested that at the time of formation of ocean (4.2 GA) it is likely that the whole earth was covered with water and that hydrothermal activity was at least 5 times higher than what is observed today. It is well-known that both  $H_2$  and  $CO_2$  are the common gases associated with volcanic activity. The major source of  $H_2$  is believed to originate within the magma from C-O-H-S equilibrium (Abbott and Hoffman, 1984). Similarly, the concentration of  $CH_4$  and helium gases has been discussed in the sub-marine hydrothermal vents. Oxygen and other electron acceptors ( $NO_3^-$ ,  $SO_4^{2-}$ , and  $PO_4^{3-}$ ) and a variety of many unknown chemical components have allowed for the abundant growth of diverse microorganisms in the modern oceans. Similar theories can be proposed for the gold mineralization and charnockitization processes in the presence of  $CO_2$ . Several researchers have carried out Strecker synthesis to produce biomolecules (amino and hydroxyl acids) from starting compounds like ketones, halides, HCN, and ammonia (Schulte and Shock, 1995).



**Fig. 2.** Global distribution of known hydrothermal vents (Courtesy: D. Fornari and T. Shank. Woods Hole Oceanographic Institute, Massachusetts, USA)

## HISTORY OF HYDROTHERMAL TECHNOLOGY

Hydrothermal technology had its origin in Europe, later moved to North America, especially, with the establishment of Carnegie Institute in Washington in 1907. In contrary, hydrothermal activity in Asia began during 1920s. Today several other countries like India, have extensive hydrothermal research activity. Here it is more appropriate to discuss briefly the early activities in Europe, North America, and India for the purpose of comparison.

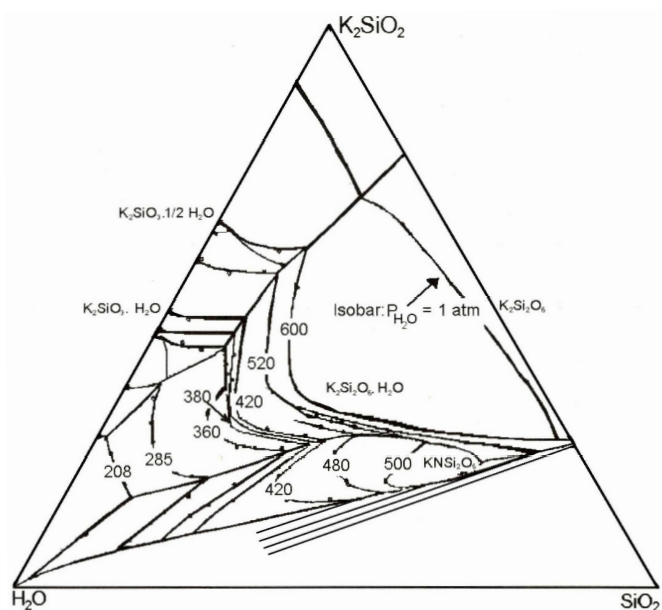
During 19<sup>th</sup> century, much of the hydrothermal technology was related to the design and fabrication of hydrothermal autoclaves and it was confined to Europe alone. In fact, one can identify two schools for autoclave designs - Western school, and Russian school. Although the western school gave more popular designs which are being used world-wide even today, the Russian school designed several new hydrothermal reactors to suit a specific task of either growing mineral species or studying physico-chemical behavior, and so on. Of course the design and fabrication of hydrothermal reactors depended on the availability of suitable refractory alloys. Accordingly, reactors withstanding the pressure of even 200kb, temperature >1500 °C have been developed. In this context, one should not forget the contributions made by European and American researchers. DeSenarmont as early as in AD 1851 designed glass tube-based liner for the autoclave to synthesize carbonates, sulphides, and sulphates. Perhaps, Kennedy, Morey, Bowen, Tuttle, Roy, Niggli, Osborn, Bridgmann, in USA have designed the earliest autoclaves to synthesize silicates, oxides, mica, pyroxenes, etc, during 20<sup>th</sup> century. High Temperature and High Pressure Research Laboratories at the University of Chicago, Harvard University, Pennstate University, AT&T Bell Labs, and Carnegie Institute of Washington, USA, have played a great role in the development of high pressure reactors. Whereas pioneers like Spezia, De Senarmont, Moissan and Chroustshoff have contributed to the development of hydrothermal autoclaves in Europe. Today we have high pressure systems which can work upto 10kb and temperature upto 800 °C in the presence of a strong mineralizer medium. Similarly, the Opposed Anvil High Pressure systems can withstand pressure up to 500 Kb, temperature 1500 °C under dry conditions. Such an approach led to the more simplicity and safety in the later designs from 1950 onwards. With such an advancement in autoclave design and fabrication, the research focus also has shifted merely from synthesizing a variety of mineral species to a more advanced research dealing with phase equilibria, construction of phase diagrams, understanding of physico-chemical conditions of the mineral systems, solubility, thermodynamics, fluid dynamics and so on. The early works of Bowen, Tuttle, Roy, Osborn, Morey, Edgar and Kennedy have constructed phase diagrams for a large number of natural systems within a wide range of temperature and pressure conditions by simulating natural conditions in the laboratory using high pressure reactor systems. Also, these studies have greatly contributed to the understanding of the formation of various rocks and mineral deposits in nature. The interesting aspect of such studies is the knowledge on the behavior of mineralizers, and rise in temperature and pressure limits for the reactors. Here it is appropriate to discuss briefly the hydrothermal research in understanding the natural geological processes of rocks and minerals formation.

In fact, De Senarmont can be considered as the father of hydrothermal geoscience. Daurre was the first one to use natural hot spring water from Plombières (in France) as a mineralizer in the hydrothermal experiment to obtain quartz and feldspar from kaoline. Deville St. Claire in 1857 attempted to transform oxide into corundum under hydrothermal conditions using NaOH as mineralizer for the first time. First ever large mineral species obtained were of 2-3mm long orthoclase feldspar towards the end of 19<sup>th</sup> century. In fact, feldspar and hydrated potassium silicate were obtained by Friedel and Sarasin in 1881. Likewise during 19<sup>th</sup> century more than 80 mineral species like quartz,

feldspars, mica, leucite, nepheline, epidote, pyroxene, hornblende, corundum, diopside, brucite etc, were synthesized (Nassau, 1976). However, the sizes of these mineral species obtained were less than 2-3 mm. Nacken from Germany worked extensively on the hydrothermal synthesis of various minerals including beryl, emerald, quartz, etc., during early 1900s and he was the first one to obtain quartz crystal of 1" diameter. But today more than 2kg size single piece of quartz and more than 5000kg of quartz crystals in a single autoclave can be obtained. However, much of the early hydrothermal work was mainly dealing with the phase-equilibria studies especially relevant to the natural systems with the interest mostly from the geological science side.

Perhaps the first systematic and pioneering study of hydrothermal system began with publication of the work on the ternary system  $\text{H}_2\text{O} - \text{K}_2\text{SiO}_3 - \text{SiO}_2$  (Morey and Fenner, 1917). This work greatly assisted in framing a mechanism for pegmatite crystallization in the presence of a volatile, and also discussed the possibility of a complete solubility in between anhydrous silicate phases and water (Fig. 3).

Here the authors discuss a couple of selective phase equilibria studies representing the evolution of magma and origin of various rock types. O'Hara (1968) has discussed the variations in the partial pressure of the oxygen, and the fluid composition, the influence of polybaric and polythermal crystallization leading to the hydration and fractionation of calc-alkali series magma and high alumina basalt magmas. This work represents the phase equilibria studies within a wide range of pressure (ca)  $P=40\text{Kb}$ . This study covers the most important geological systems such as anorthite-diopside-forsterite and anorthite-forsterite-quartz, quartz-hypersthene-plagioclase-quartz-cordierite-norite, and olivine-clinopyroxene-garnet representing both synthetic and natural systems was on the origin and evolution of basic and ultrabasic rocks (O'Hara, 1968). Plummer and Putnis (2009), and Yardley and Shmulovich (1995) have studied the complex hydrothermal history of granitic rocks representing the earth continental crust through the fluid-rock interactions. The study shows that an externally derived Na- enriched hydrothermal fluid established the progressive albitization of oligoclase. This study throws light on the interactions of gigantic hydrothermal systems with crustal rocks. Arias and Stevens (2016) have studied the thermodynamic modeling to



**Fig. 3.** Isothermal polybaric saturation curves and the isobaric polythermal saturation curve at 1 atm pressure of  $\text{H}_2\text{O}$  vapour (Morey and Fenner, 1917).

understand the phase equilibria of granitic magma. The study deals with the entrainment of a fraction of the mineral assemblage co-existing with melt influencing on the peritectic and non-peritectic assemblages under temperature 650 °C to 950 °C and pressure 0.8 GPa. This explains the geochemical variability depending upon the source invoking variable petrogenic scenario. In recent years there are several thermodynamic computational studies representing a wide range of natural systems covering almost all the origin and evolution and petrogenesis of all the magma types with a variation in pressure and temperature conditions.

The early work on hydrothermal research as discussed earlier was purely on the geological problems and only a few number of researchers were engaged in this research. However, during the second world war, when Brazil imposed an embargo on the supply of high purity natural quartz which is an important mineral used in telecommunication technology, the hydrothermal researchers in many countries like USA, UK, erstwhile USSR, Switzerland, Belgium, Germany started working on the hydrothermal growth of bulk crystals of quartz. In fact, this period is considered as the “golden period” in hydrothermal research. With this there was a sudden surge in the hydrothermal research activity world-wide. Also, other crystals without any natural analogues were synthesized and tested for their application potential in technology. This can be considered as the beginning of hydrothermal growth of gem minerals.

Towards the end of 1970s there was again a decline in the hydrothermal research mainly due to two reasons: there was no scope for further work on the growth of large size single crystals of quartz on one hand and on the other major attempts to grow bigger crystals of other compounds investigated during the 1960s and 1970s failed miserably. It was unanimously decided that the hydrothermal technique is not suitable for the growth of larger crystals other than quartz. Such a decline in the interest was mainly connected to researchers without looking into hydrothermal solution chemistry, kinetics of crystallization processes and also the behavior of the electrolytic solutions (mineralizers) with variation in temperature and pressure conditions. However, the Nobel Symposium organized by the Swedish Academy of Sciences during September 17-21, 1979 on “The Chemistry and Geochemistry of Solutions at High Temperatures and Pressures” is remembered as an eye opener. The presence of pioneers in the field of hydrothermal physical chemistry like Franck, Seward, Helgeson, Pitzer, Perchuk, and so on, drew the attention of hydrothermal researchers and a new trend was set to look into the hydrothermal solution chemistry and the physical chemistry of the hydrothermal systems (Seward, 1979; Helgeson, 1979 and Pitzer, 1979). Following this, Japan organized the first ever International Hydrothermal Symposium during April 1982, which was attended largely by specialists from different branches of science like physical chemistry, inorganic chemistry, solid state physics, material scientists, organic chemists, hydro-metallurgists, earth scientists, hydrothermal engineers, etc (Somiya, 1982). This is the dawn of modern hydrothermal research. Since then, new avenues in the field of hydrothermal research are being explored. The modeling of the hydrothermal systems, study of the hydrothermal crystallization mechanism, thermodynamics and kinetics of the hydrothermal reactions began. Here it is appropriate to describe the emergence of hydrothermal research in India for the benefit of readers. Hydrothermal research in India had a late start. The first ever hydrothermal research laboratory was set up by Prasenjit Saha and D. Bandyopadhyay in mid 1960s, at Central Glass and Ceramics Research Institute (CGCRI), JadHAVapur, Kolkata. They could successfully grow bulk single crystals of quartz weighing upto 1 kg. A large sum of money was invested by CSIR and the focus was also to indigenize the quartz crystals supply required by BEL, Bangalore, and other leading electronic industries in India. However, the quality of quartz did not meet the standard set by the end users in the country. The crystals had more defects and

lesser transparency. This led to the diversification of the focus by the (CGCRI) researchers towards ceramics and fibre-optics communication applications of quartz. Perhaps the first ever research laboratory in India, for hydrothermal work with a focus on Geology, Geochemistry, Mineralogy, Petro-genesis was started at the Mineralogical Institute, University of Mysore, in the year 1967. The state government jointly with the University of Mysore established the Mineralogical Institute under the stewardship of Prof. P.R.J. Naidu and Prof. M.N. Vishwanathiah. Several senior researchers from other national laboratories like Indian Institute of Science and Indian Institutes of Technology were involved in the committee to set the vision and mission of the Mineralogical Institute. High pressure unit with Tuttle-Roy autoclaves systems was procured from M/s Tem-Press Corp., USA, which is presently taken over by M/s Leco Corp., USA, that was originally set up by Prof. Rustom Roy, as a start up at the Penn State University, USA based on his pioneering work on the design and fabrication of high pressure and temperature systems in that University. Researchers like Prof. T.R.N. Kutty and Prof. Anatha Iyer from the Indian Institute of Science (IISc), Bangalore, assisted in the development of this Mineralogical Institute and also trained some of the young researchers of the Mineralogical Institute. The early work mainly dealt with the phase equilibria studies and crystal growth of quartz, chalcogenides, and so on. Similarly, phase equilibria of rare earth carbonates, and rare earth oxides systems were studied. The impetus for such an early study on the geological significance during late 1960s and 1970s triggered the emergence of similar laboratories at IITs particularly in Bombay, Roorkee, and Khargapur, BARC, Bombay and several others including CSIR laboratories and Universities. The work carried out at the Mineralogical Institute of the University of Mysore, was colossal and results were published in several International Journals. Today most of the phase diagrams constructed at Mineralogical Institute currently merged with the Department of Studies in Earth Science are listed in the American Ceramic Society Bulletins. In this context hydrothermal research laboratory at the Department of Studies in Earth Science, University of Mysore is having a historical significance in the Indian context. Today, the laboratory has gained an International reputation, and diversified its research activities from pure Geology to Technology. Several natural systems connected with the origin of charnockites, anorthosites, and other ultramafic rocks have been studied systematically. Besides, an extensive work has been carried out on several natural mineral systems such as chalcogenides, metal oxides, zeolites, diamond, and systematically characterized all the characteristics using sophisticated analytical equipment to ascertain the application potential of these compounds. The laboratory became a center of interdisciplinary and transdisciplinary research, which attracted researchers from other branches of science in a big way. Accordingly, this article has been conceptualized to highlight the development of hydrothermal research from geology to technology.

## ROLE OF VOLATILES

Volatiles play an important role in hydrothermal research whether it is related to the phase equilibria, solubility, kinetics, origin of ore deposits, mineral deposits, synthesis of various bulk, small, micron, and nanosize materials of high purity. The evolution of hydrothermal research and the relevant technology can be well correlated with the evolution of the use of different mineralizers. As mentioned earlier, hydrothermal research began with the use of water as a mineralizer, it means only the OH-volatile. Although water is very effective at very high temperature and pressure conditions, it has the lowest solubility for high melting compounds like diamond, corundum, beryl, garnet, etc. Therefore, the study of the behavior of hydrothermal systems in the presence of other volatiles began as early as 1940s that facilitated



the understanding of various magmatic rocks and mineral deposits. In the fractional crystallization of pegmatites, the role of for example, H<sub>2</sub>O, rare earths, alkalis, B, P, F, has been studied in detail under hydrothermal conditions (Jahns and Burnham, 1969; Jahns, 1982).

The presence of fluorine and chlorine-based mineralizers enhances the cation diffusivities and reduce the melt viscosities. These volatiles play an important role in inducing complexing in aqueous vapor to bring the rare metal transport and the formation of hydrothermal ores (Bailey, 1977; Cerny et al., 1985). Similarly, boron and phosphorous have a great effect on the hydrous silicates melt, especially increase the solubility and facilitate Group IV and Group V elements forming borosilicate, aluminosilicate and phosphates (Wyllie and Tuttle, 1964; Mendel, 1978). However, it is to be noted that P is more compatible with the smaller and more acidic cations of Group I.

Further, the presence of alkalis also likely to lead to zonation of rare earth rich pegmatites. Both theoretical and experimental studies have clearly indicated the interaction of Group I elements with alumina silicate melts, which provide a basis to understand the zonation of alkali alumina silicates in pegmatites (Eichorn, 1858).

De Jong and Brown (1980) and Navrotsky et al., (1985) have proposed that the smaller alkalis Li and Na should exhibit a greater tendency to destabilize silicate melts than K, Rb and Cs. Thus, the pegmatite crystallization can be explained by various volatiles like water, boron, fluorine, phosphorous, and alkalis, on phase equilibria in hydrous aluminosilicate melts. These studies have also yielded the crystallization of pegmatitic magma to nearly 1600 °C. The authors have showed that the rare earth rich pegmatite magma crystallizes at < 500°C under disequilibrium phenomena in super cooled liquids or glasses leading to the intergrowth texture in pegmatite (Morgan, 1986; Fenn, 1986). Later workers have also studied the contribution of other ligands especially chlorine, CO<sub>2</sub>, sulphur, H<sub>2</sub>S, in understanding the geochemical systems of element transport by hydrothermal fluids active in the earth crust.

In contrary to the understanding of the geochemical systems within the earth crust by the earlier researchers, the recent workers are focusing on a wide range of volatiles and ligands including the organics in understanding the hydrothermal system leading to the synthesis of minerals, a host of inorganic materials, and also extraction of chemical elements contained in crustal materials, besides other natural products including, the plants, seeds and leaves. Today hydrothermal technique plays an important role in extraction chemistry both under subcritical and critical conditions with a wide range of volatiles like H<sub>2</sub>O, CO<sub>2</sub> and so on.

Accordingly, several variations have been reported in hydrothermal research like solvothermal, ammonothermal, glycothermal, lyothermal and so on. These variants have a great bearing in the preparative chemistry and metallurgy leading to the synthesis of a wide range of functional materials and metal alloys.

### **Role of Hydrothermal Fluids in Uranium and Rare Earth Elements**

An exact origin of the uranium and rare earth elements mineralization has still evaded the geoscientists, in particular whether these mineralizations are magmatic, or purely hydrothermal or both, although most of the recent studies have supported the combination of both magmatic and hydrothermal processes (Richardson and Birkett, 1996; Dostal et al., 2014; Dostal, 2016). Usually the primary magmatic mineralization is overprinted by late magmatic to hydrothermal fluids rich in rare earth elements (REE), U, Th and so on to deposit as secondary deposits. Quite often the hydrothermal fluids transport rich metals and deposit in the veins, pores, joints and also unconformities – related structures and rocks like breccia, conglomerates, and more permeable sandstones or even deformed and metamorphosed basement as well (Mernagh, et al., 1994; Zhang, et al., 2017). In fact, there is no

direct evidence to prove the role of hydrothermal fluid in the precipitation of U or Th in sedimentary rocks like in sandstone (Adams, 1981). The studies related to their deposition indicate the requirement of higher temperature with decrease in fO<sub>2</sub> and increased *pH*. However, these studies contradict the biogenic origin for these rich metal deposits irrespective of their occurrence in the sedimentary terrain since hydrothermal fluid with temperature over 100 °C do not support bacterial activity. It is important to note that the submarine hydrothermal activity which occurs at much higher temperatures over 200 °C in the presence of various organic biosystems lead to the formation of rich metal deposits (Shock, 1992). In fact, the source of uranium and other rare earth elements has been a subject of debate among the geoscientists for a long time. However, there is a classical opinion that rich metals in hydrothermal deposits must have come often through the differentiation of the silicate magmas and the deposits which are not associated with the igneous rocks, then the rich metals must have come from the rocks through which the hydrothermal solutions pass, and this refers to the sedimentary terrain in particular karst features in carbonates, sandstone, conglomerates, breccia, etc., (Romberger, 1984). Even for the rare earth elements rich mineral deposits, which usually occur abundantly in the carbonatites deposits as in Russia, China, Vietnam, India, and Brazil, it is important to note that the fractional crystallization of the carbonatitic melt with the enrichment by orthomagmatic fluids in the magmatic-hydrothermal fluid phase, which often results in the dissolution and recrystallization of primary to secondary carbonatitic minerals, leading to the concentration of rare earth elements (Broom-Fendley et al., 2016; 2017; Giebel et al., 2017; Witt et al., 2019). The Fe isotopes studies have been carried out to understand the complex interactions between magmatic and hydrothermal processes, which occur in carbonatites and often related to the rare earth elements enrichment (Johnson et al., 2010; Sun et al., 2013). Thus, it is generally accepted that the late magmatic fluids of the magmatic-hydrothermal phase are responsible for the rare earth elements enrichment in the carbonatite complexes across the globe (Chikanda et al., 2019). Besides, the ligands in crustal fluids: Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, F<sup>-</sup>, OH<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and SO<sub>4</sub><sup>2-</sup> facilitate the transport of rare earth metals and forming the respective complexes from ambient temperatures up to 150 °C. Several modeling studies have been carried out to understand the speciation behavior of rare earth elements and their solubility with these ligands in order to understand REE mineralization (Perry and Gysi, 2018).

### **Role of CO<sub>2</sub> as Hydrothermal Fluids**

CO<sub>2</sub> is an important mineralizer in hydrothermal research both for natural and laboratory systems. CO<sub>2</sub> has a critical temperature at around 37 °C. It is one of most important substances in the formation of life and also a variety of rocks and minerals. The studies actually began seriously during the 3<sup>rd</sup> quarter of the previous century and a lot of experimental works have been carried out using CO<sub>2</sub>, H<sub>2</sub>O, Cl, S, etc., rich fluids both individually and mixed, especially after the discovery of rich mineral deposits at the sub-marine volcanic vents. Among these fluids both S-rich and CO<sub>2</sub>-rich fluids played a great role in the transport and fractionalization of metals under geological conditions (Kokh et al., 2016; 2017). Experimental modeling and thermodynamic calculations on these fluids and several electrolytic solutions have been carried out by Benning and Seward (1996). According to their study, the solubility of gold increases with temperature, *pH* and total dissolved sulphur. The equilibrium constants for the uncharged complex, AuHS shows that this species plays an important role in the transport and deposition of gold in ore depositing environments, which are characterized by low *pH* fluids (Benning and Seward, 1996). Kolonin et al., (1997) have carried out thermodynamic modeling of Au-NaCl-H<sub>2</sub>O and Au-NaCl-CO<sub>2</sub>-H<sub>2</sub>O systems to understand the gold solubility in the presence of CO<sub>2</sub> with a variation in the dielectric

constant. This model was validated experimentally at 350 °C and 50 MPa in 1M KCl+0.1 M HCl solutions in the presence of 3MCO<sub>2</sub> and without any CO<sub>2</sub>. These studies indicate that the gold concentration in chloride CO<sub>2</sub> bearing solutions is one order lower in magnitude than in systems without CO<sub>2</sub>. Similar studies have been extended to understand the formation of solubility of several other economically important metals like Fe, CO, Zn, Au, Mo, Pt, Sn, and some common ore minerals. FeS<sub>2</sub>, CuFeS<sub>2</sub>, ZnS, CO<sub>2</sub> rich S-rich, H<sub>2</sub>O-CO<sub>2</sub> fluids, MoS<sub>2</sub>, PtS, SnO<sub>2</sub>, etc., in the presence of CO<sub>2</sub>-H<sub>2</sub>O-S-salt fluids under hydrothermal conditions with temperature varying from 350-450 °C and pressure 600 -700 bars. These studies have shown that solubilities of Au, Mo, Pt, Cu, and Si decrease (within < 1 log unit) with increase in CO<sub>2</sub> content. Whereas for Fe, Zn, Sn solubilities increase significantly (>1 log unit) with CO<sub>2</sub> concentration increasing 0 to 50 wt%. Such a variation is due to the change in dielectric constant of the electrolyte solution under hydrothermal conditions. In fact, the natural fluid inclusion study results are in agreement with these results. The effect of CO<sub>2</sub> fluid on the mobility of (Pt, Mo) is less due to the formation of H<sub>2</sub>S, and oxy-hydroxide complexes. Therefore, CO<sub>2</sub> fluid under geological conditions plays a major role in the fractionation of mineral deposits. Researchers believed that Ni, Cu, Pt, group elements can be carried by CO<sub>2</sub> bubbles through magma away from the Earth mantle and into the upper crust, where they have the potential to form large ore deposits. It is believed that CO<sub>2</sub> fluid is less dense in the magma itself then rises, carrying dense metal rich with it. As the CO<sub>2</sub> and sulphide get closer to the surface, they then part ways, leaving no evidence of CO<sub>2</sub> in the upper crust. The team's evidence of carbonate and sulphide in the lower crustal rocks provides a vital snapshot of this deep process in action before it is eradicated in the upper crust (Blanks et al., 2020). Daryl Blanks (2020) states that "CO<sub>2</sub> has been viewed in recent times as having a negative role in science, considered the villain in causing climate change, but we show that is actually a hidden hero in bringing us the metals essential for the future of clean energy". The author further states that the process of transporting metals by CO<sub>2</sub> is like the initial fuel boosters on a rocket launch to space. "The fuel boosters (CO<sub>2</sub>) are essential in getting the rocket (magma) and its precious cargo (metal-rich sulphide) off the ground, but once spent the fuel tanks separate and the evidence they were there by the time the rocket reaches space is gone".

Supercritical carbon dioxide (scCO<sub>2</sub>) has conditions above 31.1 °C and 7.4 MPa which is considered as green solvent since it is nontoxic and environmentally benign. Therefore, it is extensively used in the processing of several food items (For example, decaffeination of coffee beans), pharmaceutical products (For example, large scale production of tetracycline, paracetamol, ibuprofen, Amoxicillin, etc.), extraction, microemulsion, exfoliation and intercalation of layered materials, drug crystallization and also in the synthesis of a wide range of nanoparticles of native metals (Pt, Au, Ag, Cu, Pd, etc), metal oxides (TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, etc.,) frameworks, porous materials and so on under temperature and pressure conditions not very high. By using this supercritical CO<sub>2</sub> route, one can process bulk materials, thin film coatings, powders and particle suspensions under ambient and near ambient conditions.

### **Role of CO<sub>2</sub> in Deep Crustal Rock Formation Charnockitization**

The influence of CO<sub>2</sub> fluid in the formation of deep crustal rocks particularly in granulitic facies like charnockitic rocks is very important to understand the action of CO<sub>2</sub> in stabilizing the mineral assemblages. CO<sub>2</sub> quantification studies indicate its abundance in charnockite as compared to gneiss, as observed from thermal decrepitation studies (Santhosh,1991). Even today petrogenesis of granulites remains as controversy among petrologists. Several models have been proposed to explain the petrogenesis of charnockites, of which the model (carbonic metamorphism) proposed by (Newton et al., 1980) has

received a greater attention invoking the dilution and driving out of water contained in the rock through the external influx of CO<sub>2</sub>. It is strongly believed that fluids have contributed deep crustal levels to the specific thermal and deformational events such as continental collision or rifting (Newton, 1989) and it is firmly considered that CO<sub>2</sub> present in the upper mantle may have emanated from asthenospheric carbonatic liquids liberated by deep crustal extension, from alkali basalts freezing at various lithosphere levels, or from sub-solidus outgassing of CO<sub>2</sub> enriched deep lithosphere. Similarly, subduction of marine carbonate is also another possibility. However, the presence of such large magnitude of CO<sub>2</sub> fluids, in the evolution of deep crust is yet to be understood clearly by the geologists. A more detailed discussion on the role of CO<sub>2</sub> and other fluids in metal complexes formation and granulitic facies can be obtained from the works of Frost and Frost (1987), Lamb et al., (1987), Jackson et al., (1988), Touret (1992), Huizenga and Touret (2012), and Shogenov et al., (2015).

### **Carbon Capture and Sequestration (CCS)**

The concept of natural hydrothermal system was introduced by the Japanese researchers in early 1990s as geothermal reactor with the geothermal energy as the heat source or driving force to induce mineral reactions or mineralization process. Such an attempt was made using the natural geothermal energy in the Tohoku region, Japan, where the natural hot water springs are abundant, which led to the construction of high pressure and temperature natural geochemical or geothermal autoclave underground. This was considered as completely environmentally benign and very useful to study the alterations of various rocks occurring in the earth's crust in the presence of a variety of fluids and volatiles especially in the granitic and basaltic regions (Takahashi and Nakatsuka, 1994; Nakatsuka, 1996).

In contrary, almost at the same time several researchers in the USA and Europe introduced the concept of mineral carbonation and mineral trapping using CO<sub>2</sub> under high pressure or supercritical conditions, which also works like a natural geochemical or geothermal reactor under CO<sub>2</sub> supercritical pressure. In fact, this comes under climate change mitigation technology with the potential to capture billions of tons of atmospheric CO<sub>2</sub> each year. It is roughly estimated that every year around 20 billion of tons of waste consists of silicate materials from cement kiln, mine waste, fly ash, fuel ash, iron and steel slag, construction and demolition waste, coal combustion, etc. are produced worldwide which can capture more than 400 million tons of carbon (Seifritz, 1990; Renforth et al., 2011). Thus, CO<sub>2</sub> capture and sequestration (CCS) is a fast-emerging technology to reduce global warming by utilizing the geologic media or anthropogenic CO<sub>2</sub> emissions. In this context, deep saline aquifers are the most potential sites for CO<sub>2</sub> repositories leading to geologic sequestration of CO<sub>2</sub>. Similarly, the depleted oil and gas fields, coal fields, sedimentary terrains with higher degree of vertical porosity and permeability, fractured granitic and basaltic terrains can form the potential geological media for carbon sequestration and mineral trapping (Xu et al., 2004; 2006; Gurumoorthy et al., 2004; Rosenbauer and Thomas, 2010; Xiong et al., 2017). The metals like Mg, Ca, Fe, Al, etc., present in these rocks and also mafic and ultramafic lithologies can provoke CO<sub>2</sub> mineralization (Snaebjornsdottir et al., 2020). When captured carbon is injected into the underground geological system, it can permanently fix carbon may be with a negligible amount of CO<sub>2</sub> returned to the atmosphere, of course excluding the over pressurization, mechanical failures, seismic and other tectonic movements of the earth crust. Therefore, geothermal engineers prefer to the optimum utilization of CO<sub>2</sub> injected either through chemical reactions of surrounding rocks and minerals or getting CO<sub>2</sub> dissolved in aquifers to form acidic water thus, making CO<sub>2</sub> from a physical storage to mineral trapping and leading to the immobilization of CO<sub>2</sub> (Carmona et al., 2003; Domingo

et al., 2006; Chang, et al., 2017). It is noted that such ground water or aquifer charged with CO<sub>2</sub> becomes acidic (*pH* = 3-5), depending upon the partial pressure of CO<sub>2</sub> can prompt the dissolution of several minerals especially silicate minerals present in basalt, peridotites, granites and so on. There is an ample scope for exploring such possibilities in the Indian sub-continent as the geologic settings provide vast regions of deep saline aquifers, granitic, basaltic, ultrabasic, and sedimentary basins. In this context, Cambay basin, Cuddapah basin, off-shore basins, Deccan plateau region, and also a host of sedimentary terrains can be the potential sites for CO<sub>2</sub> repository and mineral trapping in India (Gurumoorthy et al., 2004; Jayaraman, K.S., 2007). The biggest barrier in the large CCS deployment in India is the absence of precise data on the geologic storage site, although CCS is considered as the most viable mitigation option in India. It is high time that researchers from various Indian institutions and organizations need to collaborate and prepare an accurate geological storage map for India to capture and store CO<sub>2</sub> (TERI Report, 2013).

## HYDROTHERMAL GROWTH OF SOME SELECTED CRYSTALS

Ever since the term hydrothermal was proposed by Sir Roderick Murchison, several European mineralogists like De Senarmont, Schaftal, Spezia, Bunsen, etc, attempted the growth of a wide range of mineral species in 19<sup>th</sup> century. Their main target was to set up geomimetic conditions in the laboratory and understand the mechanism of their formation. Among all the mineral species, quartz played an important role, and much about the hydrothermal technique could be understood by the earlier workers from the pressure-temperature range, mineralizer type, selection of a suitable alloy, solubility, seeding, creating a suitable temperature gradient and so on with respect to the growth of quartz crystals. This greatly helped in growing several other mineral species like berlinite, AlPO<sub>4</sub> which is isostructural and isoelectronic with quartz having much better electronic properties (Byrappa et al., 1984; Morales et al., 1993) and also ruby, emerald, corundum, diamond, and so on, not only for the sake of understanding the geological aspects, but also to explore their applications potential. The negative solubility of berlinite posed a lot of challenges to the hydrothermal researchers on the whole to successfully synthesize bulk crystals. In this respect, significant contributions have come from the American and French researchers (Kolb and Laudise, 1978; Poignant, 1979).

Although, >130 mineral species were synthesized by the end of 19<sup>th</sup> century, the success rate with respect to the bulk growth of minerals or crystals was restricted mainly to quartz, followed by a very few other mineral species like ruby, tourmaline, and beryl. Rest of the studies gave only small size crystals or particles. A lot of experiments yielded products like very fine, ultrafine, or nanosized particles, and these experiments were discarded as failures. Therefore, in this section, the present authors would discuss only the growth of a few mineral

species of importance, which have a strong bearing on the hydrothermal technology. Mineral species like quartz, berlinite, calcite, zeolite, beryl, ruby, zirconite, cuprite, etc. are discussed here.

In recent years, with an improvement in the understanding of the hydrothermal solution chemistry, the milder conditions are being employed to synthesize even ultra-low solubility materials and high hardness materials. Table 1 gives the experimental conditions for a few characteristic materials employed by the earlier researchers and the present authors group (Byrappa, 2009). The addition of organics into the hydrothermal system can further bring down the growth conditions especially temperature and pressure conditions.

## SUMMARY

Hydrothermal technique has evolved from pure geologic process to one of the most advanced technological processes in the laboratory from understanding the natural geological processes of the formation of various rocks, minerals and ores, to the synthesis of most advanced technological materials and also to explore the carbon capture and sequestration potential of the geologic media. Similarly, a systematic study of the hydrothermal solution chemistry has greatly contributed to the development of knowledge on the role of various volatiles, biomolecules and organics and has posed new challenges in understanding the formation of gold, uranium, rare earth elements, other metallic mineral deposits, charnockites and so on in addition to the lowering of pressure temperature conditions of the formation of high melting functional materials. A proper understanding of the experimental parameters and also the formation of various minerals deposits in nature under diversified geological settings have led to the development of new variants in the hydrothermal technique suitable for the synthesis of high-quality functional materials with specific properties.

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**Table 1.** Current trends in hydrothermal technology

Compound	Earlier Work	Author*
Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	T = 500 – 700 °C P = 500 – 1500 bars	T = 240 °C P = < 100 bars
Li <sub>3</sub> B <sub>3</sub> O <sub>8</sub> (OH) <sub>2</sub>	T = 450 °C P = 1000 bars	T = 240 °C P = 80 bars
NaR(WO <sub>4</sub> ) <sub>2</sub>	T = 700 – 900 °C	T = 20 °C
R=La,Ce,Nd	P = 2000 – 3000 bars	P = < 100 bars
R:MVO <sub>4</sub>	Melting Point > 1800 °C	T =10 °C
R=Nd, Eu, Tm; M=Y, Gd	Synthesized at >1200 °C	P = < 30 bars
LaPO <sub>4</sub>	T < 120 °C P < 40 bars	
Diamond	T > 1000 °C P = 10 Kb	T < 800 °C P =< 3 Kb



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