HANDBOOK OF HYDROTHERMAL TECHNOLOGY

A Technology for Crystal Growth and Materials Processing

by

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Preface

The term *hydrothermal* is purely of geological origin. It was first used by the British geologist, Sir Roderick Murchison (1792–1871), to describe the action of water at elevated temperature and pressure in bringing about changes in the earth's crust, and leading to the formation of various rocks and minerals. Geologists carried out the earliest work on the hydrothermal technique in the 19th century in order to understand the genesis of rocks and minerals by simulating the natural conditions existing under the earth crust. However, materials scientists popularized the technique, particularly during 1940s. Schafhautl who obtained quartz crystals upon freshly precipitated silicic acid in a papin's digestor carried out the first hydrothermal synthesis in 1845. Subsequently, hydrothermal synthesis of a wide variety of minerals was carried out, especially in Europe.

The largest-known single crystal formed in nature (beryl crystal of >1000 kg) and some of the largest quantities of single crystals created in one experimental run (quartz crystals of >1000 kg) are both of hydrothermal origin.

The first successful commercial application of hydrothermal technology began with mineral extraction or ore beneficiation in the 19th century. With the beginning of the synthesis of large single crystals of quartz by Nacken (1946) and zeolites by Barrer (1948), the commercial importance of the hydrothermal technique for the synthesis of inorganic compounds was realized

The general acceptance of plate tectonics theory some 2 ½ decades ago garnered much interest in geochemical processes at plate boundaries which led to the discovery of hydrothermal activity in the deep sea directly on the Galapagos Spreading Center in 1977 and a large number of other spectacular submarine hydrothermal systems of global significance to ocean chemistry and geochemistry. In fact, this discovery has led to a new thinking in marine biology, geochemistry and in economic geology, and has spawned an entirely new term, viz., hydrothermal ecosystems, which means water-containing terrestrial, subterranean, and submarine high temperature environments, which are the sites of investigations for many palaeobiologists and biologists looking for primitive forms of life. It is strongly believed that the roots of life on earth can be found in hydrothermal ecosystems. These ecosystems may also serve as an analog for the possible origin of life on Mars, where a similar environment might have existed or still exists.

Earth is a blue planet of the universe where water is an essential component. Circulation of water and other components such as entropy (energy) are driven by water vapor and heat (either external or internal). Water has a very important role in the formation of material or transformation of materials in nature, and hydrothermal circulation has always been assisted by bacterial activity.

From mid-1970s, exploration of the advantages of hydrothermal reactions, other than the hydrometallurgical and crystal growth aspects, began in Japan, particularly with reference to the ceramic powder processing. A team of researchers from the Tokyo Institute of Technology, Japan, did pioneering work in ceramic processing such as powder preparation, reaction sintering, hot isostatic processing, and so on.

In the last decade, the hydrothermal technique has offered several new advantages like homogeneous precipitation using metal chelates under hydrothermal conditions, decomposition of hazardous and/or refractory chemical substances, monomerization of high polymers like polyethylene terephthalate, and a host of other environmental engineering and chemical engineering issues dealing with recycling of rubbers and plastics (instead of burning), and so on. The solvation properties of supercritical solvents are being extensively used for detoxifying organic and pharmaceutical wastes and also to replace toxic solvents commonly used for chemical synthesis. Similarly, it is used to remove caffeine and other food-related compounds selectively. In fact, the food and nutrition experts in recent years are using a new term, *hydrothermal cooking*. These unique properties take the hydrothermal technique altogether in a new direction for the 21st century and one can forecast a slow emergence of a new branch of science and technology for sustained human development. We have collected a more-or-less complete list of publications in hydrothermal technology and provided the statistical data to show the growing popularity of the technique (Figures 1.10–1.12). The main disadvantage of the hydrothermal system, as believed earlier, is the black-box nature of the apparatus, because one cannot observe directly the crystallization processes. However, in the recent years, remarkable progress has been made in this area through the entry of physical chemists, and the modeling of the hydrothermal reactions and the study of kinetics of the hydrothermal processes, which have contributed greatly to the understanding of the hydrothermal technique. One can understand the hydrothermal chemistry of the solutions more or less precisely, which provides a solid base for designing hydrothermal synthesis and processing at much lower pressure and temperature conditions. The hydrothermal technique exhibits a great degree of flexibility, which is being rightly exploited by a large scientific community with diversified interests. Hydrothermal processing has become a most powerful tool, in the last decade, for transforming various inorganic compounds and treating raw materials for technological applications.

Today, the hydrothermal technique has found its place in several branches of science and technology, and this has led to the appearance of several related techniques, with strong roots to the hydrothermal technique, involving materials scientists, earth scientists, materials engineers, metallurgists, physicists, chemists, biologists, and others. Thus, the importance of hydrothermal technology from geology to technology has been realized. In view of such a rapid growth of the hydrothermal technique, it is becoming imperative to have a highly specialized book on this topic. There are thousands of articles and reviews published on the various aspects of science of hydrothermal research but, so far, the most comprehensive works on this topic were limited to reviews and edited books, and there is not even a single monograph or book available.

The first author, Dr. K. Byrappa, edited a book entitled *Hydrothermal Growth of Crystals* in 1990 for Pergamon Press, Oxford, UK. During early 1995, the authors conceived an idea of writing this handbook and began collecting old records from various sources. The writing of this handbook started in 1997. In this handbook, we have dealt with all the aspects of hydrothermal research covering historical development, natural hydrothermal systems, instrumentation, physical chemistry of hydrothermal growth of crystals, growth of some selected crystals like quartz, berlinite, KTP, calcite, and hydrothermal synthesis of a host of inorganic compounds like zeolites, complex coordinated compounds (silicates, germanates, phosphates, tungstates, molybdates, etc) and simple oxides, native elements, and the hydrothermal processing of materials with an emphasis on future trends of hydrothermal technology in the 21st century.

Many publications on hydrothermal research, especially in the Russian journals, were not easily accessible to us. Our Russian colleagues in the field of hydrothermal research extended great cooperation in this regard. Especially, the help rendered by Dr. L. N. Demianets, Dr. V. I. Popolitov and Dr. O. V. Dimitrova is highly appreciated. The authors are very grateful for the help and encouragement extended by the senior people in this field like Prof. Shigeyuki Sōmiya (Professor Emeritus), Prof. N. Yamasaki (Tohoku University, Japan), late Dr. Bob Laudise (AT & T Bell Labs.), Prof. Rustom Roy (Penn State University), Prof. C. N. R. Rao (Director, JNCASR), Prof. R. Chidambaram (Chairman, Atomic Energy Commission, India), Dr. B. P. Radhakrishna (former Director, Dept. of Mines & Geology), late Prof. J. A. Rabenau (Max-Planck Institute of Physics, Stuttgart), Prof. Ichiro Sunagawa, Prof. J. A. Pask, Prof. Paul Hagenmuller, Prof. H. L. Barnes, late Prof. Saito Shinroku, and Prof. Toshiyuki Sata. Both Prof. Sōmiya and Prof. Yamasaki spent several hours with the authors and provided fruitful discussion. Their suggestions and comments have been included in this book. We would like to extend our special thanks to the most active hydrothermal researchers of the present day, like Prof. S. Hirano, Prof. M. Hosaka, Prof. K. Yanagisawa, Prof. T. Moriyoshi (Director, RIST, Takamatsu), Prof. S. Komarneni, Prof. R. E. Riman, Dr. Don Palmer, Dr. Dave Wesolowski, Dr. S. Taki, Prof. K. Arai, Prof. T. B. Brill, Prof. T. M. Seeward, Prof. Yuri Gogosti, Prof. K. Bowen, Prof. David A Payne, Prof. Fred F. Lange, and Prof. Fathi Habashi, who have helped us by providing their results and data for inclusion in this book. Our colleagues at the Tokyo Institute of Technology, like Prof. Masato Kakihana, Prof. Nabuo Ishizawa, Prof. Eiichi Yasuda, Prof. Akira Sawaoka, Prof. Masatomo Yashima, Prof. Yasuo Tanabe, Prof. Masanori Abe, Prof. Kazunari Domen, and Prof. Kiyoshi Okada, extended great cooperation in our task. Other Japanese friends, like Dr. Yasuro Ikuma, Prof. Tsugio Sato, Prof. Koji Kajiyoshi, Dr. Atsuo Ito, Dr. E. H. Ishida, Prof. Zenbee Nakagawa, Prof. Yusuke Moriyoshi, Prof. Yasumichi Matsumoto, Prof. Tadashi Ohachi (Doshisha University, Kyoto), Dr. Kohei Soga (Tokyo University), Prof. Toshio Yamaguchi and a host of other friends in the field of hydrothermal research, have helped us extensively in completing this great work. We would like to express our sincere thanks to our friends and colleagues from India (late Prof. M. N. Vishwanathiah, late Prof. B. V. Govindarajulu, Prof. J. A. K. Tareen, Prof. D. D. Bhawalkar, Dr. Krishan Lal, Dr. R. V. Anantha Murthy, Prof. A. B. Kulkarni, Prof. T. R. N. Kutty, Prof. P. N. Satish, Dr. B. Basavalingu, Prof. H. L. Bhat, Dr. K. M. Lokanath Rai, and Dr. M. A. Shankara), Russia (Prof. V. S. Balitsky, Prof. V. A. Kuznetsov, Prof. D. Yu Pushcharovsky, Dr. Oleg Karpov, Dr. G. I. Dorokhova, and Dr. E. Strelkhova), Korea (Prof. Choy Jin-ho and Prof. Z. H. Lee), Spain (Prof. Rafael Rodriguez Clemente, and Prof. Salvador Gali), Poland (Prof. Keshra Sangwal), and China (Prof. Shen-tai Song, Prof. Y-T. Qian, and Prof. S. Feng), who were a great source of inspiration and help while writing this book. Here, it is extremely difficult to list all the names of the students, post-docs and research associates from our groups who have helped us greatly. Among them, the help rendered by Mr. B. V. Suresh Kumar, Mrs. B. Nirmala, Mr. J. R. Paramesha, Mr. Dinesh, Dr. W. Suchanek, and Dr. S. Srikanta Swamy is greatly appreciated. Miss S. Vidya, secretary of Prof. K. Byrappa, typed the manuscript. Mr. Murruli of Microsystems, Mysore, did the scanning of drawings, figures and photographs. The manuscript was read and corrected for typographical errors and English usage by Dr. K. T. Sunitha, Chair, Dept. of English, Univ. of Mysore, India (wife of Prof. K. Byrappa), and Miss Shobha M. Gowda, Lecturer in English, University of Mysore (currently in the McGill University, Montreal, Canada). Mrs. Hiroko Yoshioka, Mrs. Fujiko Mori, and Mrs. Keiko Kato, who are the secretaries of Prof. Yoshimura, have greatly assisted the authors in the preparation of this manuscript. We are highly obliged to all our family members—Dr. Sunitha Byrappa, Shayan and Nayan (Prof. Byrappa's family members), Mrs. Akiko Yoshimura, Sayaka, Ayumi, and Hirono (Prof. Yoshimura's family members) for their great patience and cooperation with us during these 3½ years of book writing.

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Finally we would like to express our deep gratitude to Mr. George Narita of Noyes Publications, William Andrew Publishing, for bringing out this book. It is also an added pleasure to acknowledge the role played by the staff of Noyes Publications, especially Mary Bourke and Brent Beckley, and the staff of Write One, New York, for composition. If we have omitted any important topic or any other names of the friends, or citation of the important references in this book, it is not intentional. We have tried our best to cover as much as we could of the hydrothermal research based on the most exhaustive up-to-date literature search. Hopefully, this book will be a most valuable textbook and reference for the students and researchers in the field of hydrothermal technology, both at the beginners' and advanced levels.

September 2000 K. Byrappa
M. Yoshimura

1

Hydrothermal Technology—Principles and Applications

1.1 INTRODUCTION

The hydrothermal technique has been most popular, garnering interest from scientists and technologists of different disciplines, particularly in the last fifteen years. The term *hydrothermal* is purely of geological origin. It was first used by the British Geologist, Sir Roderick Murchison (1792–1871), to describe the action of water at elevated temperature and pressure in bringing about changes in the earth's crust leading to the formation of various rocks and minerals.[1] A majority of the minerals formed in the postmagmatic and metasomatic stages in the presence of water at elevated pressure and temperature conditions are said to be "of hydrothermal origin." This covers a vast number of mineral species including ore deposits. It is well known that the largest single crystal formed in nature (beryl crystal of >1000 gm) and some of the largest quantities of single crystals created by man in one experimental run (quartz crystals of several 100's of gm) are both of hydrothermal origin.

An understanding of the mineral formation in nature under elevated pressure and temperature conditions in the presence of water led to the development of the hydrothermal technique. It was successfully adopted by Schafthaul (1845) to obtain quartz crystals upon transformation of freshly precipitated silicic acid in Papin's digestor.[2] Thus, the hydrothermal technique became a very popular means to simulate the natural conditions existing under the earth's crust and synthesizing them in the laboratory. These studies dealing with laboratory simulations have helped the earth scientists to determine complex geological processes of the formation of rocks, minerals, and ore deposits. As the subject became more and more popular among geologists, new branches of geology emerged as "Experimental Mineralogy" and "Experimental Petrology."

The first successful commercial application of hydrothermal technology began with mineral extraction or ore beneficiation in the previous century. The use of sodium hydroxide to leach bauxite was invented in 1892 by Karl Josef Bayer (1871–1908) as a process for obtaining pure aluminum hydroxide which can be converted to pure Al_2O_3 suitable for processing to metal.[3] Even today, over 90 million tons of bauxite ore is treated annually by this process.[4] Similarly, ilmenite, wolframite, cassiterite, laterites, a host of uranium ores, sulphides of gold, copper, nickel, zinc, arsenic, antimony, and so on, are treated by this process to extract the metal. The principle involved is quite simple, very effective, and inexpensive, as shown below, for example.

$$Al(OH)_3 + OH^- \rightarrow [AlO(OH)_2]^- + H_2O$$

$$AlOOH + OH^- \rightarrow [AlO(OH)_2]$$

The above process is easy to achieve and the leaching can be carried out in a few minutes at about 330°C and 25,000 kPa.[5]

Further importance of the hydrothermal technique for the synthesis of inorganic compounds in a commercial way was realized soon after the synthesis of large single crystals of quartz by Nacken (1946) and zeolites by Barrer (1948) during late 1930s and 1940s, respectively.[6][7] The sudden demand for the large size quartz crystals during World War II forced many laboratories in Europe and North America to grow large size crystals. Subsequently, the first synthesis of zeolite that did not have a natural counterpart was carried out by Barrer in (1948) and this opened altogether a new field of science, viz., molecular sieve technology.[8] The success in the growth of quartz crystals has provided further stimuli for hydrothermal crystal growth.[9]

Today, the hydrothermal technique has found its place in several branches of science and technology, and this has led to the appearance of several related techniques with strong roots attached to the hydrothermal technique. So we have hydrothermal synthesis, hydrothermal growth, hydrothermal alteration, hydrothermal treatment, hydrothermal metamorphism, hydrothermal dehydration, hydrothermal decomposition, hydrothermal extraction, hydrothermal sintering, hydrothermal reaction sintering, hydrothermal phase equilibria, hydrothermal electrochemical reaction, and so on, which involve materials scientists, earth scientists, materials engineers, metallurgists, physicists, chemists, biologists, and others. Although the technique has attained its present high status, it has passed through several ups and downs owing to the lack of proper knowledge pertaining to the actual principles involved in the process. Hence, the success of the hydrothermal technique can be largely attributed to the rapid advances in the apparatus involved (new apparatus designed and fabricated) in hydrothermal research, and also to the entry of a large number of physical chemists, who have contributed greatly to the understanding of hydrothermal chemistry.[10] Further, the modeling and intelligent engineering of the hydrothermal processes have also greatly enhanced our knowledge in the field of hydrothermal research.[11][12]

In recent years, with the increasing awareness of both environmental safety and the need for optimal energy utilization, there is a case for the development of nonhazardous materials. These materials should not only be compatible with human life but also with other living forms or species. Also, processing methods such as fabrication, manipulation, treatment, reuse, and recycling of waste materials should be environmentally friendly. In this respect, the hydrothermal technique occupies a unique place in modern science and technology. The rapid development in the field of hydrothermal research in the last fifteen years, or so, motivated the present authors to bring out this handbook covering almost all aspects of hydrothermal research. Although there is a growing interest among scientists from various branches of science, at the moment there are no books or monographs available in the field of hydrothermal technology. Most of the major works, even by the pioneers in this field, have been confined to reviews and edited books. Table 1.1 lists important reviews and edited books in the field of hydrothermal research.

Table 1.1. List of the Books and Reviews in the Field of Hydrothermal Research

BOOKS

Sl. No.	Author	Title	Publishers
1.	Labachev, A. N. (ed.)	*Hydrodrothermal Synthesis of Crystals*	Nauka, Moscow (1971)
2.	Ulmer, G. C. (ed.)	*Research Techniques for High Pressure and High Temperature*	Springer-Verlag, New York (1971)
3.	Labachev, A. N. (ed.)	*Crystallization Processes under Hydrothermal Conditions*	Consultants Bureau, New York (1973)
4.	Ikornikova, N. Yu	*Hydrothermal Synthesis of Crystals in Chloride Systems*	Nauka, Moscow (1975)
5.	Kuzmina, I. P. and Khaidukov, N. M.	*Crystal Growth from High Temperature Aqueous Solutions*	Nauka, Moscow (1977)
6.	Demianets, L. N., Labachev, A. N., & Emelechenko, G. A.	*Germanates of Rare Earth Elements*	Nauka, Moscow (1980)
7.	David T. Rickard Frans E. Wickman (ed.)	*Chemistry and Geochemistry of Solutions at High Temperature and Pressure*	Pergamon, New York (1981)
8.	Somiya. S. (ed.)	*Proc. 1st Int. Symp. Hydrothermal Reactions*	Japan (1982)
9.	Litvin, B. N. and Popolotov, V. I.	*Hydrothermal Synthesis Inorganic Compounds*	Nauka, Moscow (1984)
10.	Popolitov, V. I. and Litvin, B. N.	*Growth of Single Crystals under Hydrothermal Conditions*	Nauka, Moscow (1986)
11.	Ulmer, G. C. and Barnes, H. L. (eds.)	*Hydrothermal Experimental Techniques*	John Wiley & Sons, New York (1987)
12.	Nesterov, P. V. (ed.)	*Progress in Science and Technology, Crystal Chemistry of Germanates of Tetravalent Metals*	Moscow, VINITI (1989)
13.		*Hydrothermal Reactions ISHR - 89*	Nauka, Moscow (1989)

Table 1.1. *(Cont'd.)*

BOOKS *(Cont'd.)*

Sl. No.	Author	Title	Publishers
14.	Occelli, M. L. & Robson, H. E. (eds)	*Zeolite Synthesis*	ACS Symp. Series 398 Am. Chem. Soc., Washington, DC (1989)
15.	Somiya, S. (ed.)	*Hydrothermal Reactions for Engineering*	Elsevier, Applied Sci. (1989)
16.	Byrappa, K. (ed.)	*Hydrothermal Growth of Crystal*	Pergamon, Oxford (1991)
17.	Cuney, M. & Cathelineau, M. (eds.)	*Proc. 4th Int. Symp. Hydrothermal Reactions*	Nancy France (1993)
18.		*Proc. 1st Int. Conf. Solvothermal Reactions*	Japan, (Dec. 6-8 1996)
19.		*Proc. 2nd Int. Conf. Solvothermal Reactions*	Japan, (Dec.18-20 1996)
20.	Palmer, D. A. & Wesoloski, D. J.	*Proc. 5th Symp. Hydrothermal Reactions*	Gatlinburg, USA (1997)
21.		*Proc. 3rd Int. Conf. Solvothermal Reactions*	Bordeaux, France (1999)

REVIEWS

Sl. No.	Author	Title	Publishers
1.	Morey, G. W.	*Hydrothermal Synthesis*	*J. Am. Ceram. Soc.* (1953)
2.	Roy, R. & Tuttle	*Investigation under Hydrothermal Conditions*	*Phy. Chem. Earth* 1:138 (1955)
3.	Ballman, A. A. Laudies, R. A.	*Solution Growth*	In: *Art and Science of Growing Crystals* (Gilmann, J. J., ed.) Wiley, New York (1963)

Table 1.1. *(Cont'd.)*

REVIEWS ***(Cont'd.)***

Sl. No.	Author	Title	Publishers
4.	Laudise, R. A.	*Hydrothermal Growth of Crystals*	In: *The Growth of Single Crystals,* Prentice-Hall, New York (1970)
5.	Kuznetsov, V. A. & Lobachev, A. N.	*Hydrothermal Method for the Growth of Crystals*	*Sov. Phys. Crystallogr.* 70:775-804 (1973)
6.	Nassau, K.	*Synthetic Emerald: The Confusing History and The Current Technology*	*J. Crystal Growth* 35:211-222 (1976)
7.	Rabenau, A.	*The Role of Hydrothermal Synthesis in Preparative Chemistry*	*Angew. Chem. Int Engl. Ed.* 24:1026–1040 (1985)
8.	Laudise, R. A.	*Hydrothermal Crystal Growth - Some Recent Results*	In: *Advanced Crystal Growth,* Prentice Hall, New York (1987)
9.	Komareni, S. Fregeau, E. Breval, E. &. Roy, R.	*Hydrothermal Preparation of Ultrafine Ferrites & their Sintering.*	*J. Am. Ceram. Soc,* (1988)
10.	Somiya, S.	*Hydrothermal Reactions in Inorganic Systems*	In: *Advance Materials Frontiers* in *Mat. Sci. & Eng.* (Somiya, S.: ed.); *Trans. Mat. Res. Soc. Jpn.*, Vol. 19B, Elsevier Science, B.V. (1994)
11.	Yoshimura, M. & Suda, H.	*Hydrothermal Processing of Hydroxyapatite: Past, Present & Future.*	In:*Hydroxyapatite and Related Compounds*, Brown, P. W. & Constantz, B. (eds.) p. 45–72, CRC Press (1994)
12.	Byrappa, K.	*Hydrothermal Growth of Crystals*	In: *Handbook of Crystal Growth, Vol. 2a,* (D. T. J. Hurle, ed.), Elsevier Science B.V. (1994)
13.	Leco catalogue	Leco corporation	Tem-Press division USA (1999)

1.2 DEFINITION

In spite of the fact that the hydrothermal technique has made tremendous progress, there is no unanimity about its definition. The term *hydrothermal* usually refers to any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions to dissolve and recrystallize (recover) materials that are relatively insoluble under ordinary conditions. Morey and Niggli (1913) defined hydrothermal synthesis as "…in the hydrothermal method the components are subjected to the action of water, at temperatures generally near though often considerably above the critical temperature of water (~370°C) in closed bombs, and therefore, under the corresponding high pressures developed by such solutions."[13] According to Laudise (1970), hydrothermal growth means growth from aqueous solution at ambient or near-ambient conditions.[14] Rabenau (1985) defined hydrothermal synthesis as the heterogeneous reactions in aqueous media above 100°C and 1 bar.[15] Lobachev (1973) defined it as a group of methods in which crystallization is carried out from superheated aqueous solutions at high pressures.[16] Roy (1994) declares that hydrothermal synthesis involves water as a catalyst and occasionally as a component of solid phases in the synthesis at elevated temperature (>100°C) and pressure (greater than a few atmospheres).[17] Byrappa (1992) defines hydrothermal synthesis as any heterogenous reaction in an aqueous media carried out above room temperature and at pressure greater than 1 atm.[18] Yoshimura (1994) proposed the following definition: reactions occurring under the conditions of high-temperature–high-pressure (>100°C, >1 atm) in aqueous solutions in a closed system.[19]

The above definitions hold good for materials synthesis, metal leaching and treatment of waste materials. However, there is no definite lower limit for the pressure and temperature conditions. The majority of the authors fix the hydrothermal synthesis, for example, at above 100°C temperature and above 1 atm. But, with the vast number of publications under mild hydrothermal conditions in recent years, we propose to define hydrothermal reaction as "any heterogenous chemical reaction in the presence of a solvent (whether aqueous or nonaqueous) above room temperature and at pressure greater than 1 atm in a closed system." In addition to this non-unanimity, there is also a lot of confusion with regard to the very usage of the term *hydrothermal*. For example, chemists prefer to use a broader term, viz., *solvothermal*, meaning any chemical reaction in the presence of a solvent in supercritical or near supercritical conditions.[20] However, this term has been introduced recently, and in fact, the early work in this direction was carried out by geologists using CO_2.[21] Japan has already organized two International Conferences and one International Workshop on Solvothermal Reactions.[22]–[24] The third International Conference on Solvothermal Reactions was held in July 1999 in Bourdeaux, France. Similarly, there are several other terms like *glycothermal, alcothermal, ammonothermal*, and so on, depending upon the type of solvent used in such chemical reactions. However, the purpose behind using these different solvents in the chemical reactions is essentially to bring down the pressure-temperature conditions. In this context, Yoshimura has proposed a new term, *soft solution processing,* for processes in which the pressure and temperature conditions reach near or just above ambient conditions.[25] Though this term has a broader meaning, it covers only a portion of the hydrothermal research and refers mainly to any solution processing at or near the ambient conditions. Thus, in the present book, the authors retain a broader term, *hydrothermal,* throughout the text and use other terms only when such occasion arises.

As mentioned above, under hydrothermal conditions, the reactants which are otherwise difficult to dissolve go into solution as complexes under the action of mineralizers or solvents, Hence, one can expect the conditions of chemical transport reactions. Therefore, some workers even define hydrothermal reactions as special cases of chemical transport reactions. Owing to the specific physical properties, particularly the high solvation power, high compressibility, and mass transport of these solvents, one can also expect the occurrence of different types of reactions like:

i. Synthesis of new phases or stabilization of new complexes.
ii. Crystal growth of several inorganic compounds.
iii. Preparation of finely divided materials and microcrystallites with well-defined size and morphology for specific applications.
iv. Leaching of ores in metal extraction.
v. Decomposition, alteration, corrosion, etching.

1.3 MINERALIZERS

In any hydrothermal system or reaction confined to any one of the processes described in Sec. 1 of this chapter, the role played by the solvent under the action of temperature and pressure is very important. It has been interpreted in various ways by many workers. Recently Yoshimura and Suda (1994) have described these processes to understand the action of solvent, for example, water on solid substances under elevated pressure and temperature conditions.[19] This process is represented in Table 1.2.

Through proper interpretation of the above listed processes, one can easily develop a required hydrothermal process corresponding to the material synthesis or crystal growth or materials process using a suitable solvent to increase the solubility of the desired compound. Water is the most important solvent and it was popularly used as a hydrothermal mineralizer in all the earlier experiments. However, several compounds do not show high solubility for water even at supercritical temperature, and hence the size of the crystals or minerals obtained in all the early hydrothermal experiments of the 19th century did not exceed thousandths or hundredths of a millimeter. Therefore, the search for other suitable mineralizers began in the 19th century itself. A variety of aqueous and nonaqueous solutions were tried to suit the preparation of a particular compound. The selection of the mineralizers and their role in hydrothermal systems with suitable examples are discussed in great detail in Ch. 3. The knowledge acquired through the use of several new mineralizers has helped to implement this hydrothermal technique as an effective one in preparative chemistry. Table 1.3 shows the use of hydrothermal processing in various fields of materials synthesis, crystal growth, and materials processing.[19] Before going into the details of this, it is appropriate to discuss the natural hydrothermal systems.

1.4 NATURAL HYDROTHERMAL SYSTEMS

The beginning of hydrothermal research is firmly associated with the study of the natural systems by earth scientists, who were interested in understanding the genesis of various rocks, minerals and ore deposits through laboratory simulations of the conditions existing in the earth's crust. Therefore, it is appropriate to discuss briefly the research on natural hydrothermal systems and its contribution to the development of this field to its present status. Starting from the earliest experiment by Schafthaul in

1845 on the synthesis of quartz,[2] over 130 mineral species were synthesized by the end of 19th century, and the experiments were carried out on various geological phenomena ranging from the origin of ore deposits to the origin of meteorites. Today, it is being popularly used by geologists to solve several existing problems in petrology, geochemistry, mineralogy, ore genesis, and palaeontology. The impetus for the experimental investigations during the 19th century was provided not only by a desire to explain geological phenomena, but also by greatly improved equipment and techniques fostered by industrial revolution. Such investigations helped in unraveling the hitherto unknown natural geological processes of mineral formation. On the other hand, it helped in finding uses for the artificially synthesized single crystals like ruby, emerald, sapphire, quartz, and diamond, in the gemstone industry.

Table 1.2. Action of Hydrothermal Fluid (High-Temperature–High-Pressure Aqueous Solution/Vapor) on Solid State Materials

Classified	Action	Application
1. Transfer Medium	Transfer of Kinetic Energy, Heat and Pressure Forming, etc.	Erosion, Machining Abrasion, HIP
2. Adsorbate	Adsorption/Desorption at the Surface	Dispersion, Surface Diffusion, Catalyst, Crystallization, Sintering, Ion Exchange, etc.
3. Solvent	Dissolution/Precipitation	Synthesis, Growth, Purification, Extraction, Modification, Degradation, Etching, Corrosion, etc.
4. Reactant	Reaction	Formation/Decomposition (hydrates, hydroxides, oxides) corrosion, etc.

Table 1.3. Development of Hydrothermal Processing

1. Crystal Synthesis and Growth	Oxide, Sulfide,Fluoride...(1978 ~)
2. Controlled Fine Crystals Composition, Size, Shape	PZT, ZrO_2, $BaTiO_3$, HAp, ferrite (1978 ~)
3. Crystallized Thin/Thick Films	$BaTiO_3$, $SrTiO_3$, $LiNbO_3$ (1989 ~)
4. Etching, Corrosion	Oxide, Nitride, Carbide
5. Polishing, Machining	Oxide, Nitride, Carbide
6. Combined with Electrical, Photo-, Radio- & Mechano-Processing	Synthesis, Modification, Coating
7. Organic and Biomaterials	Hydrolysis, Extraction Polymerization, Synthesis, Decomposition, Wet Combustion
8. Non-aqueous Solution	
9. Continuous system	

In order to understand the formation of several ore deposits including that of nobel metals, it is necessary to discern the physico-chemical conditions which govern the transport and precipitation mechanisms of these metals in hydrothermal solutions. Several thermodynamic models have been proposed to explain these mechanisms in nature. Relatively much is known, for example, about the hydrothermal chemistry of gold.[27][28] Similarly, the behavior of common rock-forming minerals in a variety of electrolytic solutions has been studied in detail. Here, the authors present only the salient features of these works to provide the background for the hydrothermal technique since the main theme of this handbook is on crystal growth and materials processing. Besides, a quantitative model of the transport and deposition mechanisms is still impeded by a dearth of reliable high temperature and pressure, experimentally based, thermodynamic data. However, there is some remarkable progress made in this direction, thanks to the advances in the thermodynamic modeling, the direct sampling and analyses of the natural geothermal systems, their extinct analogues, epithermal ore deposits, and other geologic environments, primarily by analyses of fluid inclusions.[29] Therefore, an understanding of the mineral-water reaction kinetics is essential to quantifying the behavior of natural and engineered earth systems. Although, several studies have been carried out on the behavior of most hydrothermal systems, the predictions based upon rates from deionized water are unlikely to be representative of processes occurring in complex fluids of natural systems which contain numerous dissolved ions. These constituents have both significant rate-inhibiting and enhancing effects on behavior, even when present in very small quantity.[30][31]

In nature, the most common minerals in soils and rocks are generally in contact with water at a wide pH range. In extreme cases, the pH can be nearly 2 in the presence of sulfides, which oxidizes to give H_2SO_4, and as high as 10 in the presence of alkaline salts like Na_2CO_3. Here, the authors briefly discuss the gold deposition in hydrothermal ore solutions. In this case, the major role is played by the chloride and sulphur-containing ligands.[32][33] The dominant gold complexing ligands are usually sulphide species. The stability constants for gold(I) chloride complexes (for example, at 250°C) are up to twenty orders of magnitude smaller than those of Au(I) hydrosulphide complexes and, therefore, the latter predominates in nature.[36] Despite this observation, the stability constants for Au(I) hydrosulphide complexes under high temperature and pressure environments are not yet well defined. This is particularly true for the low pH region where no satisfactory data are available.

Benning and Seward[35] have proposed three sets of experimental conditions of pH range for gold deposition in nature:

$$\begin{array}{llllllllll}
Au_{(s)} & + & H_2S & + & & + & H_2O & + & H_2\,(gas) & pH \approx 4 \\
Au_{(s)} & + & H_2S & + & NaHS & + & H_2O & + & H_2\,(gas) & pH \approx \text{neutral} \\
Au_{(s)} & + & H_2S & + & H_3PO_4 & + & H_2O & + & H_2\,(gas) & pH < 4
\end{array}$$

The solubility of gold increases with increasing temperature, pH, and total dissolved sulphur. At near neutral pH, an inverse correlation between solubility and pressure has been observed, whereas in acid pH solutions, above 150°C, increase in pressure increases the solubility. The equilibrium constants for the uncharged complex, AuHS show 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.

Recently some thermodynamic modeling in the chloride systems Au-NaCl-H_2O and Au-NaCl-CO_2-H_2O shows that the gold solubility decreases in the presence of CO_2 due to decreasing dielectric permeability of CO_2 bearing solution.[36] This model has been experimentally verified at 350°C and 50 MPa in 1 M KCl + 0.1 M HCl solutions in the presence of 3M CO_2 and without CO_2. It was found that the gold concentration in chloride CO_2-bearing solutions is one order lower in magnitude than in systems without CO_2. Similarly, the silver bearing systems show distinct influence of CO_2 in comparison with gold system. CO_2 has negative solubility effect on gold and silver crystallization and CO_2 acts as a nonpolar component of crustal fluids in the crystallization of many ore deposits.[37] Thus, the recent hydrothermal solution speciation (solvation to ion pairing and complexing) study has greatly contributed to the knowledge and better understanding of various geological problems.

1.5 THE BEHAVIOR OF VOLATILES AND OTHER INCOMPATIBLE COMPONENTS UNDER HYDROTHERMAL CONDITIONS

The physical and thermodynamic properties of silicate melts depend upon melt structure. The structure of a melt is determined by both its composition and the ambient conditions and, with the notable exception of liquid immiscibility, may vary continuously with changes in these parameters. The structures of crystalline silicates vary only within restricted limits. As a result, variation in mineral-melt equilibria caused by changes in either compositions or external parameters may very well reflect the change in properties of the melt phase to a greater extent than those of the crystalline silicates.

The behavior of P_2O_5 is complex. Phosphorus pentoxide (P_2O_5) depolymerizes pure SiO_2 melts by entering the network as a fourfold coordinated cation, but polymerizes melts in which an additional metal cation, other than silicon, is present. The effect of this polymerization is apparent in the widening of the granite-ferrobasalt two-liquid solvus. In this complex system, P_2O_5 acts to increase phase separation by further enrichment of the high charge density cations Ti, Fe, Mg, and Ca, in the ferrobasaltic liquid. Phosphorus pentoxide (P_2O_5) also produces an increase in the ferrobasalt-granite REE liquid distribution coefficients. These distribution coefficients are close to 4 in P_2O_5-free melts, but close to 15 in P_2O_5-bearing melts.

Several attempts to understand the internal evolution of highly fractionated pegmatites focused on the roles of H_2O and other components, especially rare alkalis, B, P, F, are being carried out from time to time. Such studies yield a great amount of data on the role of these volatiles under hydrothermal conditions and also distinguish rare earth pegmatites from other rocks.[38][39] These volatiles exert a significant control on fluid properties, solidus and liquidus temperatures.

1.5.1 Water

Water is an important constituent of any hydrothermal system. It exhibits unique properties, especially under supercritical conditions. These properties have been exploited appropriately in the recent years to disintegrate toxic organics, and recycle or treat waste materials. In nature, also, water plays an important role in the formation of various rocks and minerals and in the creation of life (origin of life). As a component of granitic melts, H_2O depresses solidus and liquidus temperatures,[40][41] lowers melt viscosities,[42]-[45] and promotes coarse grain size.[46]

1.5.2 Fluorine and Chlorine

Fluorine, as H_2O lowers solidus and liquidus temperatures, enhances cation diffusivities, and decreases melt viscosities.[47]-[49] One important difference between F and H_2O is that the DCF vapor/melt is L1 in metaluminous and peraluminous granitic bulk compositions.[50][51] Fluorine decreases the solubility of the melt[52][53] so that, at equal H_2O content of volatile-undersaturated magma at the same pressure and temperature, H_2O is higher in F-bearing melts than in F-absent melt. Metal-fluoride complexing in aqueous vapor may be important in rare-metal transport and formation of hydrothermal ores.[54][55]

1.5.3 Boron

The pronounced effects of boron in hydrous silicate melt are well known. Boron lowers the solidus, and it increases the solubility of H_2O in silicate melts. Lewis acid-base properties suggest that the solubility of H_2O/mole B_2O_3 in melts should increase with increasing boron content because of changes in B-O coordination. Boron also decreases the viscosity of silicate melts presumably through melt depolymerization caused by the synergistic network-modifying effects of boron and water.[56]

In silicate melts, boron forms two common oxyanions: trigonal planar BO_3^{3-} and tetrahedral BO_4^{5-}. The $[BO_4^{5-}/BO_3^{3-}]$ ratio increases with melt alkalinity,[57][58] and boron content.[59] Although boron exhibits strong interaction with silicate melt, non-ideal mixing between borate and silicate melt components is reflected by stable liquid-liquid or metastable glass-glass immiscibility over a wide range of bulk compositions in an hydrous silicate system.[60] The miscibility gap between metal-rich borate and essentially pure silica liquids increases with increasing field strength of added metal cations, with a consequent rise in the consolute temperature. Limited experimental evidence also indicates that the solubilities of other high charge-density cations (e.g., Group IV and Group V elements) are significantly higher in borosilicate melts than in simple aluminosilicate melts.[61]

As in fluorine-bearing systems, the addition of boron to silicate melts leads to an expansion of the liquidus field of quartz.[62] This behavior may reflect removal of cations from coordination with SiO_4^{4-} of the melt framework, resulting in higher SiO_2 through increased polymerization of SiO_4^{4-} tetrahedra.[63] Among Group I cations, boron has a tendency to depress the activities of the higher field-strength ions. The increased solubility of H_2O in borosilicate melts corresponds to a lower H_2O that may stem from direct hydrolysis of borate oxyanions.

1.5.4 Phosphorus

Phosphorus exhibits limited solubility in silicate melt,[64][65] hence the addition of phosphorus promotes phosphate-silicate liquid immiscibility. The phase equilibria data in the systems: SiO_2-P_2O_5, P_2O_5-M_xO_y, and P_2O_5-M_xO_y-SiO_2 show that phosphorus has an affinity for H, and it increases the solubility of H_2O in silicate melts, possibly by: $P = O + H_2O \rightarrow (HO)\text{-}P\text{-}(OH)$.[68] Although experimental evidence of the interaction of phosphorus with other Group I elements is lacking, the common pegmatite assemblage $LiAlPO_4$ (OH,F) + $NaAlSi_3O_8$ [rather than $NaAlPO_4$(OH,F) + $LiAlSi_2O_6$ + H_2O] suggests that P is more compatible with the smaller, more acidic cations of Group I.

1.5.5 Behavior of Alkalis

The zonation of rare element pegmatites is manifested largely by heterogeneous distributions of alkali aluminosilicates. Theoretical and experimental investigations of the interactions of Group I elements with aluminosilicate melts provide a basis for understanding the zonation of alkali aluminosilicates in pegmatites.

Both De Jong and Brown (1980), and Navrotsky, et al. (1985), proposed that the smaller alkalis Li and Na should exhibit a greater tendency to destabilize silicate melts than K, Rb, and Cs.[53][60]

A number of salient pegmatite characteristics can be explained by the effects of high concentrations of boron, fluorine, and phosphorus on phase equilibria in hydrous aluminosilicate melts.

1.5.6 Crystallization Temperatures

Comparatively high concentrations of B, P, F, and Group I elements serve to depress pegmatite magma liquid to approximately 650°C (within the stability fields of petalite or spodumene), and solidus to < 500°C. The low liquidus temperatures permit rare-element pegmatite magmas to migrate to metamorphic conditions of the anadalusite-cordierite/staurolite facies.[69][70] The physical migration of magma may be facilitated also by the lower melt viscosities of the H_2O-, B-, and F-rich pegmatite system. Because of the low temperature interval of crystallization, however, rare element pegmatite magmas may experience rapid increases in melt viscosity with only slight cooling, as glass transition temperatures are approached (e.g., as in the macusanite analogue). As a result of increased kinetic barriers to crystallization, internal disequilibrium may prevail (an important and poorly defined parameter in pegmatite crystallization is the rate of cooling, but evidence from wall-rock studies indicates that rare element pegmatite magmas are hosted by rocks at temperature < 500°C (e.g., Morgan, 1986).[71] Common textural features of rare element pegmatites, such as graphic intergrowths and radial or banded fabrics, can be interpreted as disequilibrium phenomena in supercooled liquids or glasses.[72] Experiments with dry macusanite, however, present alternative possibilities. In these experiments, pegmatitic fabrics, mineral assemblages, and zonation have been generated at or near equilibrium conditions with high concentrations of B, P, and F but low water content.

Numerous experimental investigations of aqueous systems at high temperature and pressure have been undertaken using conductivity, potentiometric, spectrophotometric, solubility, PVT and calorimetric, neutron diffraction, EXAFS, and other related methods. These studies yield a vast amount of information on cation-oxygen pairing and their increased or decreased distances with varying temperature. Likewise, the anion-water distances, for example, as in the case of iodide-oxygen (water) bond lengths, indicate that the solvation shell expands slightly with increasing temperature. Similarly, molecular dynamics simulation studies on the alkali metals hydration in high temperature water up to 380°C have been carried out recently, demonstrating a small expansion of the first hydration shell around chloride with increasing temperature.[73] More or less complete data is available on the formation of simple, neutral ion pairs for dilute alkali metal halide solutions at high-pressure/temperature conditions. However, the understanding of the formation of polynuclear species is still not been clearly understood. Some workers have studied the ion pairing and cluster formation in a 1M NaCl solution at 380°C and near critical pressure.[74] These studies indicate the presence of simple monocationic ions and ion pairs together with triple ions such as Na_2Cl^- and $NaCl_2^-$ as well as the $Na_2Cl_2^-$ and more complicated polynuclear species. Similar studies on other solutions are available in the literature. All these studies have greatly contributed to the understanding of the geochemical system wherein the metal-complexing by other ligands is the most important aspect. However, there is a major lack of overall experimental data pertaining to the metal complex equilibria in supercritical aqueous systems as well as in binary solvent systems such as H_2O-CO_2. Such data are of enormous importance to the understanding of geochemistry of element transport by hydrothermal fluids active in the earth's crust.

In the last couple of years, a new concept, viz., *geothermal reactor,* introduced by Japanese workers is slowly catching the attention of hydrothermal engineers.[75][76] The principles of geothermal reactors include the direct use of geothermal energy as a heat source or driving force for chemical reactions. It helps to produce hydrothermal synthesis of minerals and a host of inorganic materials, extraction of useful chemical elements contained in crustal materials such as basalt, and use them as raw materials for hydrothermal synthesis. Thus, the concept of geothermal reactor leads to the construction of a high temperature and pressure autoclave underground. This has several advantages over the conventional autoclave technology.

Figure 1.1 shows the schematic sketch of a typical geothermal reactor for mineral synthesis.[76] The major advantages of the geothermal reactor are:

1. Synthesis of ceramic materials by hydrothermal reaction is possible without using fuel or electricity as main energy source.
2. The system does not discharge the used heat.

3. Outer tube with a slit in the bottom must be strong enough to keep the inner space of the tube against the pressure by the wall of formation, but inner double tube does not need the strength against the inner pressure as usual autoclaves.
4. Area of the plant is small because of the vertical long reactor in the ground.
5. It is highly useful to study the alteration of various rocks occurring in the earth crust in the presence of fluids of various compositions. Such studies have been carried out for granite and basalts.[75]

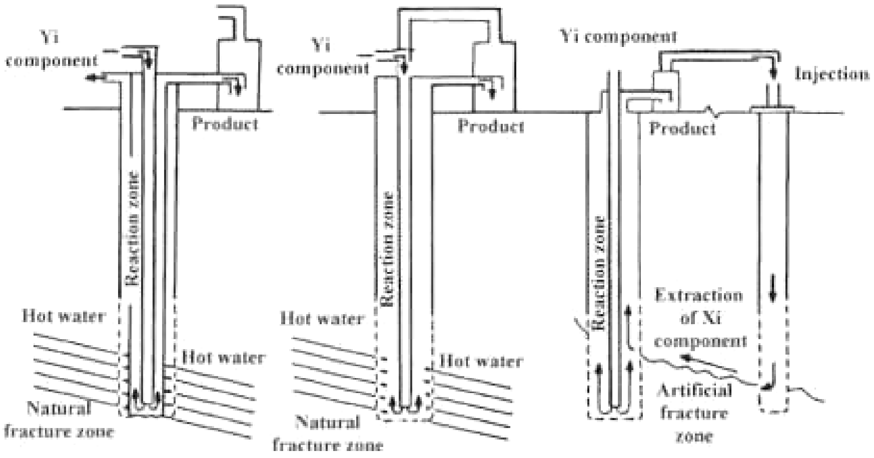

Figure 1.1. Geothermal reactors for mineral synthesis.[76]

The main disadvantage of the geothermal reactor is that the flow characteristics of high temperature slurry accompanied with the chemical reaction must be well understood for controlling the reaction. The volumetric capacity of the geothermal reactor is very large compared to that of usual autoclave, and the operation must be continuous. The merit of the geothermal reactor and its cost of operation can be realized only if the target material is to be developed in large quantity.

1.6 SUBMARINE HYDROTHERMAL SYSTEMS

The general acceptance of plate tectonics theory some 2½ decades ago has garnered much interest in geochemical processes at plate boundaries which has led to the discovery of hydrothermal activity in the deep sea directly on the Galapagos Spreading Centre in 1977,[77] and a large number of other spectacular submarine hydrothermal systems (like Red Sea Rift Valley, Juan de Fuca Ridge-North Pacific Ocean; 21°N East Pacific Rise, Kamchatka, Kurile Islands, Atlanti’s II Deep in Red Sea, Lake Kivu, and so on) of global significance to ocean chemistry and geochemistry.[78] In fact, this discovery has led to a new thinking in marine biology and geochemistry, and in economic geology and has spawned an entirely new term, viz., *hydrothermal ecosystems*, which means water-containing terrestrial, subterranean, and submarine high temperature environments which are the sites of investigations for many palaeobiologists and biologists looking for primitive forms of life. It is strongly believed that the roots of life on earth can be found in hydrothermal ecosystems. These ecosystems may also serve as an analogue for the possible origin of life on Mars, where a similar environment might have existed or still exist. The conditions at the hydrothermal ecosystems mimic, to some extent, the conditions on early earth because of the presence of both heat and water. These conditions were abundant at around 3.5 Ga, when there was much greater vulcanism and a higher ambient temperature on earth. Dick Henley (1996) describes the geochemical activity of the hydrothermal ecosystems as biotic factory.[79] According to Everett Shock (1992), life thrives in submarine hydrothermal conditions because they have a (geologically supplied) source of chemical disequilibrium which brings in redox reactions.[80] Further, he states that life originated at warmer temperatures. This was also supported by simple experiments on organic synthesis under hydrothermal conditions. These higher temperatures would mix various elements and supply the energy for the formation of simple compounds. Abundant mineral deposits at hydrothermal ecosystems imply that they provide a fossil record of their biological inheritance. Often the minerals deposited are precious metals such as gold, silver, copper, and zinc. These are common outpourings from hydrothermal vents. Thermal waters usually contain high concentrations of dissolved components which are deposited when the hot spring discharge gases are released and the temperatures fall, leading to the deposition of mostly calcium carbonate, silica, iron and manganese oxides. Thus, any living organisms that once existed in the vents become fossilized at the very site it lived in. All these theories proposed that the life existed some 3.5 billion years ago.

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.[81] The submarine hydrothermal systems reveal that most primitive organisms found in modern environments are thermophiles (for example, *archea*). Many scientists believe in a "redox neutral" in the primitive atmosphere. The most important aspect is the possibility that the iron vapor and reduced carbon liberated from impacting objects like meteorites would leave the ocean reducing for a long period. In addition, those submarine hydrothermal systems are the only environments where primitive life would have been protected against postulated meteoritic impacts and partial vaporization of the ocean. The presence of supercritical fluids like H_2O, CO_2, or CH_4, are the main constituents of any hydrothermal system. They serve as excellent solvents of organic compounds and would probably be of great potential for several of the chemical reactions eventually leading to the origin of life. Further, the pressure and temperature gradients existing in natural hydrothermal systems have a dramatic effect on the properties of the hydrothermal fluids. This is known from the current experimental data on many electrolytic solutions and some nonaqueous solutions.[82]

The submarine hydrothermal systems operate today in much the same manner as they are believed to have functioned in the pre-Cambrian period. They provide a wide range of closely linked gradients in both physical and chemical conditions obviously having a direct link with magmatic heat. Thus, the biological communities (biotic family) occupying vast and relatively stable soft bottom habitats of the sea are characterized by low population densities, high species diversity, and low biomass, compared to those inhabiting the unstable conditions of submarine hydrothermal ecosystems which exhibit high densities and biomass, low species diversity, rapid growth rates and high metabolic rates.

Despite such an understanding of the hydrothermal ecosystem, there are many unclear aspects like period of formation and depth. As mentioned earlier, the available evidences indicate that the ancient ocean was a chemically reducing environment, probably warm or hot (> 30°C to > 100°C),[83] shallow (maximum depth of 1000–2000 m), and considerably more active, tectonically and hydrothermally, than it is today.[84] The model proposed by Abbott and Hoffman (1984) suggests that, at the time of formation of the ocean (4.2 Ga.), it is likely that the whole earth was covered with water and that hydrothermal activity was at least five times greater than at present.[85] The overall rate of sea floor spreading and subduction has declined steadily over the evolution of the earth. Figure 1.2 shows the geological and geochemical features of hydrothermal circulation of seawater through the oceanic crust at mid-ocean ridges.[86] Rona et al. (1983) have found two types of vents occurring along spreading ridge crests of the East Pacific Rise and Juan de Fuca Ridge in the Pacific.[87] The fluids emanating from these vents are enriched with magmatically derived elements and complexes. Depending upon the degree of mixing, we can expect a variety of chemical components in different quantities which serve as the primary energy sources for the extensive microbial communities as represented in Figs. 1.3 and 1.4. All the biologically important trace elements are also known to be associated with submarine hydrothermal vents. However, the actual reactions involved in the production of various chemical components are not clearly known. It is well known that both H_2 and CO are common gases associated with volcanic activity. The major source of H_2 is believed to be the oxidation of magnetite to hematite, while CO is believed to originate within the magma from C-O-H-S equilibrium.[88] Similarly, the concentration of CH_4 and helium gases has been discussed in the submarine 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 a diverse microorganisms in the modern oceans.

In order to prove the above theories and discoveries, several workers have proposed the thermodynamics of strecker synthesis in hydrothermal systems and also the hydrothermal synthesis of several amino acids under laboratory conditions. Schulte and Shock (1995) and Shock (1995) have worked out the strecker synthesis to produce biomolecules (amino and hydroxy acids) from starting compounds (ketones, aldehydes, HCN and ammonia).[88][89] They have evaluated their work quantitatively using thermodynamic data and parameters for the revised Helgeson-Kirkham-Flowers (HKF) equation of state. Although there is an overwhelming thermodynamic drive to form biomolecules through streckers synthesis under hydrothermal conditions, the availability and concentration of starting components limit the efficiency and productivity of strecker reactions. Some representative reactions for strecker synthesis are given below:[89]

$$\begin{array}{lcl}
\mathrm{RCHO} + \mathrm{NH_3} + \mathrm{HCN} & = & \mathrm{RCH(NH_2)CN} + \mathrm{H_2O} \\
\text{aldehyde / ketone} & & \text{amino nitrile} \\[1ex]
\mathrm{RCH\ (NH_2)CN} + \mathrm{H_2O} & = & \mathrm{RCH(NH_2)CO(NH_2)} \\
\text{amino nitrile} & & \text{amino amide} \\[1ex]
\mathrm{RCHO} + \mathrm{HCN} + \mathrm{H_2O} & = & \mathrm{RCH(NH_2)COOH} \\
\text{aldehyde/ketone} & & \text{amino acid}
\end{array}$$

There are several reports on the laboratory hydrothermal synthesis of amino acids to justify the origin of life on the earth. It is appropriate to mention that the organic synthesis on the whole is not new and, in fact, it began in the previous century. However, the organic synthesis under hydrothermal conditions with reference to the origin of life began in a systematic way only during 1980s, after the discovery of hydrothermal activity in the deep sea on a Galapagos spreading rich in thermophile organisms (Fig. 1.5 a and b) during 1977. The reader can get additional information from the works of Fox and Windsor (1970); Marshall (1987); Shock (1990, 1992); Hennet et al. (1992).[90]-[94] These workers have synthesized amino acids in a temperature range of 150°C to 275°C from aqueous solutions containing KCN, NH_3, HCHO, CO_2, H_2, O_2, NaCN, NH_4HCO_3. Miller (1953)[95] and Amend and Shock (1988) in Ref. 97 have shown that the autotrophic synthesis of all twenty protein-forming amino acids was energetically favored in hot (100°C), moderately reduced, submarine hydrothermal solutions relative to the synthesis in cold (18°C), oxidized, surface sea water.[95] Although the above studies do not support the challenge raised by several others over the life in submarine hydrothermal ecosystems, these studies definitely have set a new trend in hydrothermal research.

This field of research is growing very fast and a large number of publications are coming on diversified aspects of submarine hydrothermal ecosystems. The reader can refer to some of the most important reviews for further studies.[95]-[97]

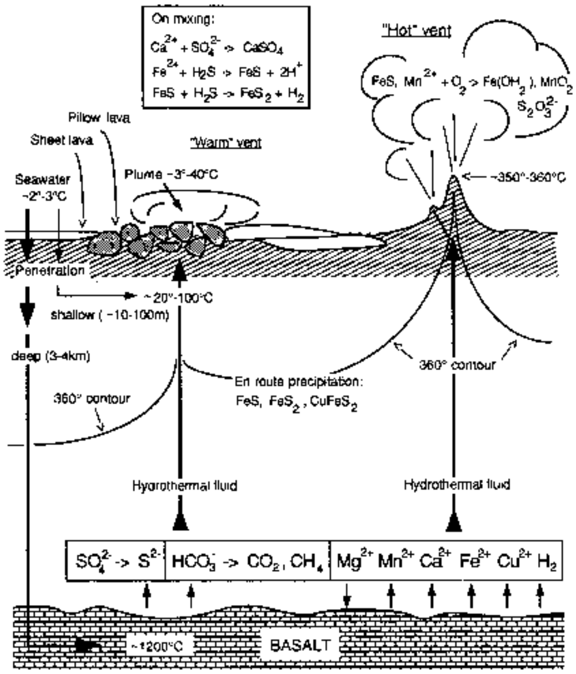

Figure 1.2. Major processes during the hydrothermal circulation of seawater through the oceanic crust at mid-ocean ridges. *(Courtesy H. W. Jannasch)*

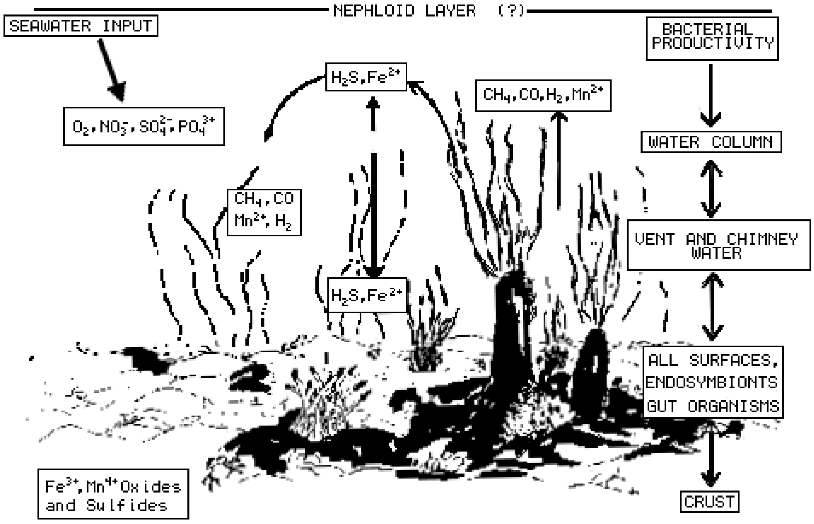

Figure 1.3. Microbial community.[81]

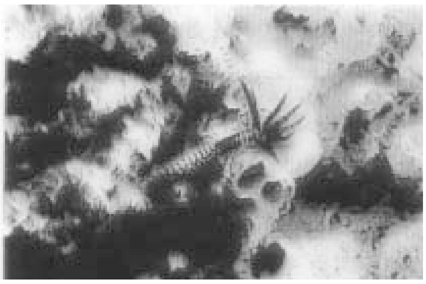

Plate 1. The Pompei worm *Alvinella* at 9°N on the East Pacific Rise. The densely-packed tubes form the wall of a chimney. One worm has emerged: to the upper right, the tips of the tentacles of several others can be seen at the tube openings.

Plate 2. A dead vent field on the Galapagos Rise near Rose Garden. Partially dissolved shells of vesicomyid clams fill the extinguished vent opening. But there are a few survivors - mussels filter-feeding for ambient suspended particles.

Plate 3. Barnacles encrust the edge of a vent opening at the Mariana back-arc spreading center. Alvinoconchid snails live in the openings where temperatures were measured at 10-25°C. Bresiliid shrimp and bythograeid crabs scavenge off the surfaces of rock and other animals. The cloudiness of the water is caused by suspended bacteria.

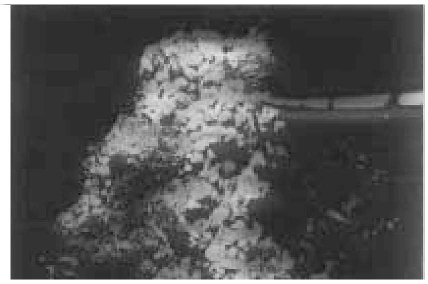

Plate 4. The tip of a chimney at the Mariana vent emitting 250°C effluent. Animals avoid this hot spot, but are able to live only a few centimeters below it, where the temperature is only 25°C. Alvinoconchid snails, bresiliid shrimp, bythogracid crabs and limpets can be seen.

Figure 1.4. Microbial community. Photos are reproduced from Ref. 97.

Plate 1. The Rose Garden vent on the Galapagos Rise in 1979. Vestimentiferan tube-worms and mussels dominate. Bresiliid shrimp and archacogastropod limpets walk on them.

Plate 2. Bresiliid shrimp at a Mid-Atlantic Ridge vent.

Plate 3. Serpulid polychacies and a dandelion in the near-field at the Rose Garden. Most of the serpulids are retracted into their tubes, but the tentacles of several are spread for capturing food particles from the water.

Plate 4. Spaghetti worms cover pillow lava at the periphery of Rose Garden.

(a)

Figure 1.5. Hydrothermal activity in the deep sea (a, b). Plates are reproduced from Ref. 97.

Plate 5. The huge thicket of vestimentiferan tube-worms at the main vent fissure at Rose Garden in December, 1979. Mussels live among the worms, principally at the base of the tubes.

Plate 6. The population of vestimentiferans has been drastically reduced, and mussels have proliferated to form a great pile over the fissure opening.

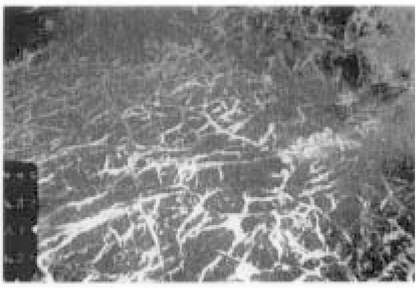

Plate 7. The rift valley on the East Pacific Rise at 9°N in April 1991. A recent lava flow has blanketed the valley. Wide-scale venting has encouraged bacterial growth, but there are not yet any animals grazing on the mats.

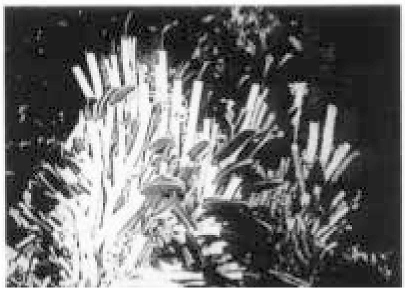

Plate 8. The same general area in December, 1993, a little over two and a half years later, showing vigorous colonization by vestimentiferans. The bacterial mats have disappeared.

(b)

Figure 1.5. *(Cont'd.)*

1.7 HYDROTHERMAL CRYSTAL GROWTH AND MATERIALS PROCESSING

After the successful application of the hydrothermal technique in hydrometallurgy in the previous century, the other important application of this method began with the artificial production of bulk single crystals of quartz and also with the synthesis of zeolites during late 1930s and 1940s. The hydrothermal method of crystal growth has several advantages. It is very important for its technological efficiency in developing bigger, purer, and dislocation-free single crystals. The method has been widely accepted since 1960s and practically all inorganic species, starting from native elements to the most complex oxides, silicates, germanates, phosphates, chalcogenides, carbonates, and so on, have been obtained by this method. The technique is being employed on a large scale to prepare piezoelectric, magnetic, optic, ceramic and a host of other materials both as single crystals and polycrystalline materials. In the recent years, several new advantages of the hydrothermal technique have been described by many workers and they are discussed in Chs. 5 to 10 in great detail. The hydrothermal technique, in contrast to other conventional techniques, offers several advantages:

i. Compounds with elements in oxidation states that are difficult to obtain, especially important for transitional metal compounds, can be obtained in a closed system by the hydrothermal method [e.g., ferromagnetic chromium (IV) oxide].

ii. The hydrothermal method is also useful for the so-called low temperature phases, e.g., α-quartz, α-berlinite, and others.

iii. For the synthesis of metastable compounds, such as subiodides of tellurium, Te_2I, the hydrothermal method is unique.

Commercial production of quartz and zeolites began during 1940s, but it was during 1940s and 1950s that the study of hydrothermal phase equilibria became quite popular owing to the appearance of new designs in autoclaves, particularly the Tuttle cold-cone sealed autoclaves which became popular as test tube type autoclaves.[98] The main advantage of the phase equilibria studies under hydrothermal conditions is that it is a closed system; one can study the influence of temperature, pressure and compositional variations individually. These studies helped to understand the phase formations in many inorganic systems, which had direct bearings on the natural systems as well. They also helped in the crystallization of several new phases which do not have the natural analogues. Moreover, these studies laid a firm foundation for the growth of some most complex inorganic single crystals which did not have analogues in nature. During 1960s, there was a question about the search and growth of hitherto unknown compounds of photo-semiconductors, ferromagnets, lasers, piezo- and ferrielectrics, so the hydrothermal method gained greater attention. This also led to the studies concerning the solubility, solvent-solute interaction, kinetics, and thermodynamic aspects of crystal growth. A large number of groups appeared in Europe, Asia and North America, and also the number of crystals obtained by hydrothermal method increased exponentially. Further, the studies concerning the phase equilibria paved a way for the emergence of a new technology, viz., *ceramics processing technology*.[99]

From mid-1970s, exploration of the advantages of hydrothermal reactions other than the hydrometallurgical and crystal growth aspects began in Japan, particularly with reference to the ceramic powder processing. A team of researchers from the Tokyo Institute of Technology, Japan, did pioneering work in ceramic processing such as powder preparation, reaction sintering, hot isostatic processing, and so on. The powder prepared by the hydrothermal technique is not agglomerated, but is fine-grained, highly pure, with controlled morphology, has a narrow size distribution, and consists of single crystals. The technique has several advantages like high reaction rate of powders, good dispersion in liquid, almost pollution free, does not require very expensive and highly sophisticated equipment, energy saving processing, and many times it produces new phases. These aspects are discussed in the subsequent chapters of this book.

In the last decade, the hydrothermal technique has offered several new advantages like new homogeneous precipitation using metal chelates under hydrothermal conditions, decomposition of hazardous and/or refractory chemical substances, monomerization of high polymers like polyethylene terephthalate, and a host of other environmental engineering and chemical engineering issues dealing with recycling of rubbers and plastics instead of burning, and so on. The solvation properties of supercritical solvents are being extensively used for detoxifying organic and pharmaceutical wastes and also for replacing toxic solvents commonly used for chemical synthesis. Similarly, it is used to remove caffeine and other food-related compounds selectively. In fact, a new term, *hydrothermal cooking*, is being used by the food and nutrition experts in recent years.[100] These unique properties take the hydrothermal technique altogether in a new direction towards the 21st century and one can forecast a slow emergence of a new branch of science and technology for sustained human development. An understanding of the structure, dynamics and reactivity of water and other aqueous electrolyte solutions with the advancement in instrumentation like neutron diffraction, x-ray, Raman and NMR spectroscopic approaches, have greatly contributed to the emergence of this new branch of science and technology employing hydrothermal techniques. As is well known, water is environmentally the safest material and the cheapest of all solvents. It can act as a mineralizer or a catalyst under elevated pressure-temperature conditions. The thermodynamic and transport properties of supercritical water are remarkably different from those of ambient water. The solubility of nonpolar species increases, whereas that of ionic and polar compounds decrease. As a result of the drop of the polarity of water, the molecular mobility increases due to a decrease in the solvent viscosity (η). Drastic changes of ionic hydration are brought about by the decrease in the dielectric constant (ε) and density (ρ). Table 1.4 gives the values of dielectric constant, density and viscosity of water varying with temperature and pressure in comparison with the ambient values of 78.3, 0.997 g cm^{-3}, and 0.890 mPa, respectively.[101] The temperature dependence of the saturation vapor pressure is illustrated up to the critical point in Fig. 1.6.[101] Below 150–200°C, the saturation vapor pressure is relatively low. Above this temperature, however, the vapor pressure rises rather sharply. Such anamolous properties of water with pressure-temperature variations are associated with the hydrogen bonding, which has attracted the attention of solution chemists. Thus recent advances in hydrothermal solution chemistry have paved a new path to materials processing techniques with minimum energy consumption in comparison with larger energy consumption to create melt, vapor, gas or plasma. Figure 1.7 shows free energy vs. temperature diagram in a single component system. Similarly, Fig. 1.8 shows the pressure-temperature range for material preparation or processing. A portion of the hydrothermal field falls within the biocompatability range, which can be further supported with the recent findings in the field of submarine hydrothermal or biohydrothermal research.

Table 1.4. Values of ε_r, ρ (g cm^{-3}), and η (mPa s) of Water at High Temperatures and High Pressures*

p/MPa	Parameter	t/°C					
		200	250	300	350	400	450
10	ε_r	35.1	27.4	20.4	1.2	1.2	1.1
	ρ	0.871	0.806	0.715	0.045	0.038	0.034
	η	0.136	0.108	0.087	0.022	0.025	0.027
20	ε_r	35.3	28.0	21.2	14.1	1.6	1.4
	ρ	0.878	0.816	0.733	0.600	0.101	0.079
	η	0.139	0.110	0.091	0.070	0.026	0.028
30	ε_r	35.9	28.4	22.0	15.7	5.9	2.1
	ρ	0.885	0.826	0.751	0.646	0.357	0.148
	η	0.141	0.113	0.094	0.076	0.044	0.031
40	ε_r	36.3	28.9	22.6	16.7	10.5	3.8
	ρ	0.891	0.835	0.765	0.672	0.523	0.271
	η	0.114	0.115	0.097	0.080	0.062	0.039
50	ε_r	36.6	29.3	23.1	17.6	12.2	6.6
	ρ	0.897	0.843	0.777	0.693	0.278	0.402
	η	0.146	0.118	0.099	0.083	0.068	0.051
60	ε_r	37.0	29.7	23.6	18.2	13.3	8.5
	ρ	0.903	0.850	0.788	0.711	0.612	0.480
	η	0.148	0.120	0.101	0.086	0.073	0.059
70	ε_r	37.3	30.0	24.0	18.8	14.2	9.9
	ρ	0.909	0.857	0.798	0.726	0.638	0.528
	η	0.150	0.122	0.104	0.089	0.077	0.065

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* Cited from IAPWS Release on the Values of Temperature, Pressure and Density of Ordinary and Heavy Water Substances at their Respective Critical Points, 1992.

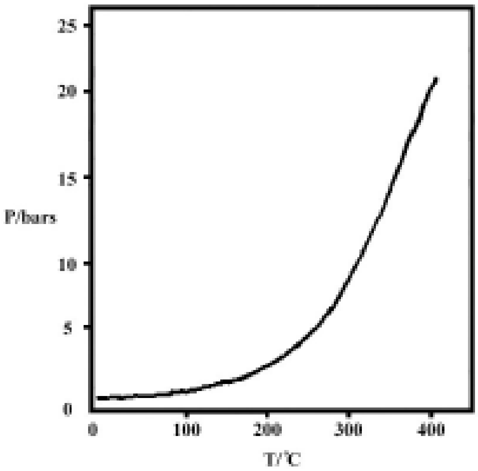

Figure 1.6. Temperature dependence of saturation vapor pressure.

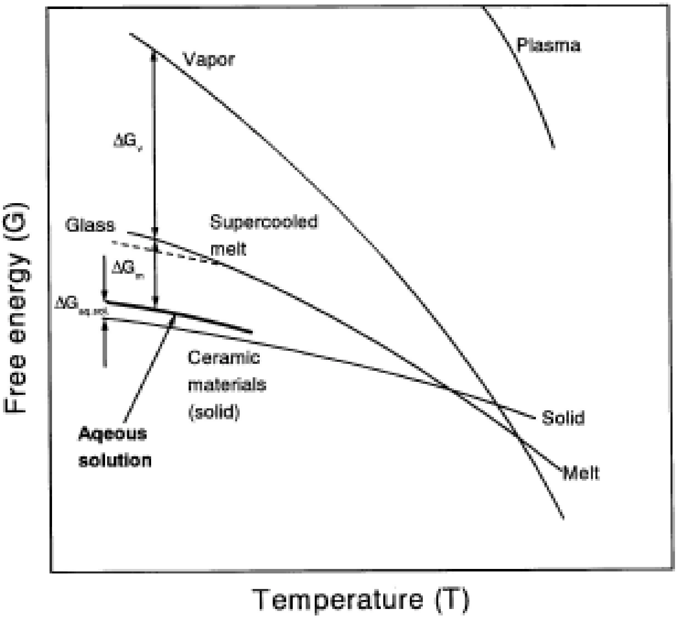

Figure 1.7. Schematic energy diagram (G-T) in a single component system.

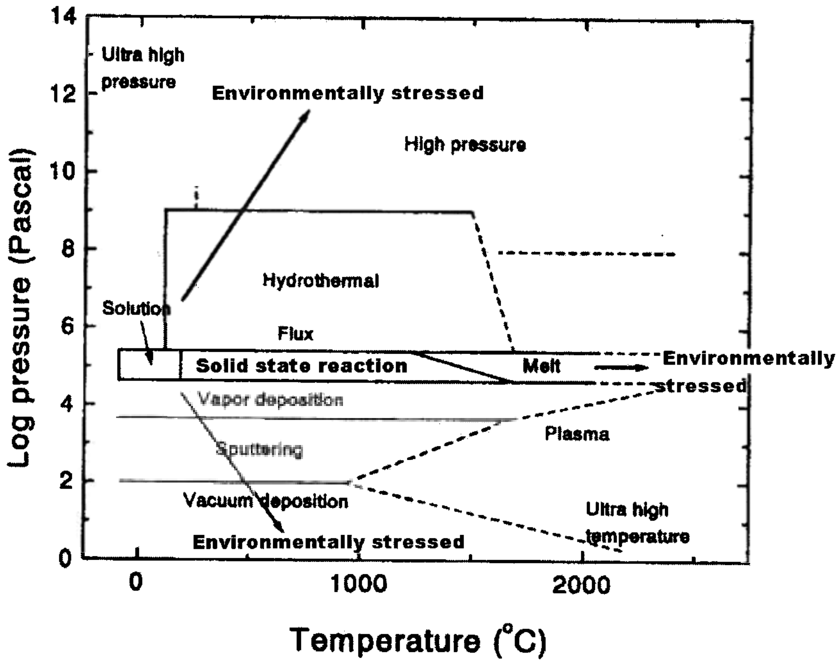

Figure 1.8. Pressure-temperature range for material preparation.

1.8 STATISTICS OF PUBLICATIONS AND RESEARCH IN HYDROTHERMAL TECHNOLOGY

The statistical data on the hydrothermal research give a picture about its developments. Throughout the course of its evolution from geoscientists to modern technologists, the hydrothermal technique has captured the attention of scientists and technologists from different branches of science. Today it is a highly interdisciplinary subject and the technique is popularly used by geologists, biologists, physicists, chemists, ceramists, hydrometallurgists, materials scientists, engineers and so on. Figure 1.9 shows various branches of science either emerging out from the hydrothermal technique or closely linked up with the hydrothermal technique. One could firmly say that this family tree will keep expanding its branches and the roots in the years to come.

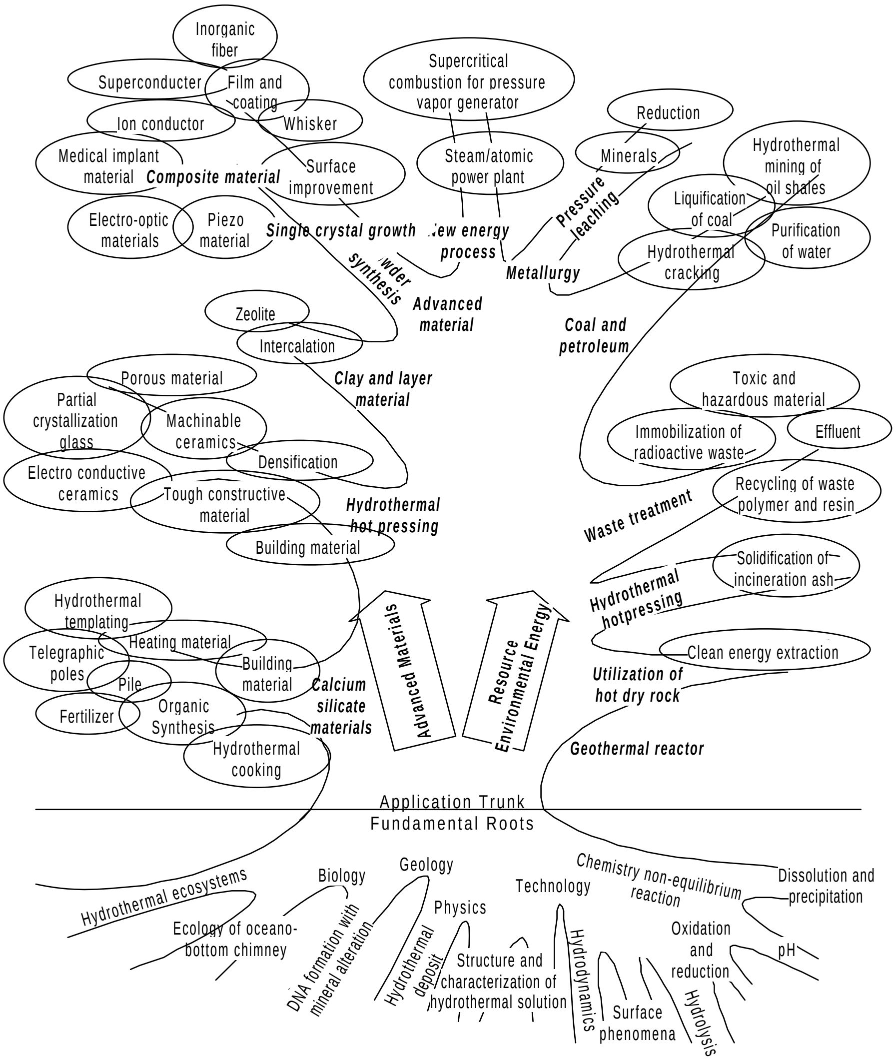

Figure 1.9. Tree showing the interdisciplinary natureof hydrothermal technology. *(Figure courtesy of N. Yamasaki, modified by K. Byrappa.)*

In view of such a rapid growth of the hydrothermal technique, it is becoming imperative to have a highly specialized book on this topic. There are thousands of articles published on various aspects of hydrothermal research. In the initial days of the hydrothermal research, there was a dearth of diversified journals, thus much of the hydrothermal research data from the 19th century to the beginning of the second half of this century was published in essentially *Earth Science Journals*, *Chemistry Annals*, and *Bulletins*. Since then, success in the growth of large single crystals of quartz and, subsequently, a large number of other minerals and inorganic compounds, as well as the progress achieved in the instrument side in attaining higher pressure and temperature conditions, led to the slow diversity of the field. Today a large quantum of work on hydrothermal research is being published in more than one hundred journals, and the number is still growing. Owing to the limitation of space and with an intention to focus on the main theme of the book, we give below only the important journals which publish the work on hydrothermal research:

Journal of Crystal Growth
Journal of Materials Research
Journal of Materials Science
Journal of Materials Science Letters
Materials Research Bulletin
Materials Physics and Chemistry
Advanced Materials
Materials Science Forum
Materials Letters
Journal of Solid State Chemistry
European Journal of Solid State and Inorganic Chemistry
Progress in Crystal Growth and Characterization of Materials
Crystal Research and Technology
Crystallography (Russian Journal)
Izvestia Academy Nauk Inorganic Materials (Russian)
Solid State Communication
Doklady Academy Nauk (Russian)
Journal of American Ceramic Society
Chemistry of Materials

Journal of Applied Physics
Physics and Chemistry of Earth
Journal of American Chemical Society
American Mineralogist
Canadian Mineralogist
Geochimica Cosmochimica Acta
Zeolites
Journal of Ceramic Society of Japan
Bio-materials
Japanese Journal of Applied Physics
Ceramics Transactions
Materials Science and Engineering
Materials Science Research
Materials Technology
Journal of Microporous Materials

Although there are thousands of research publications on hydrothermal research, so far, the most comprehensive works are limited to the scale of only reviews and edited books and there is not even a single monograph available. In connection with the hydrothermal technique for crystal growth and materials processing, the books and reviews listed in Table 1.1 are very useful.

We have made a very sincere effort to collect a more-or-less complete list of publications related to the field of hydrothermal technology, especially with a higher reliability in the last decade. Therefore, it is interesting to discuss briefly the statistics of this field of research. Figure 1.10 shows the number of publications year-wise and this number is increasing sharply with the entry of scientists from other branches of science. As evident from Fig. 1.11, the preparative chemists and ceramists have dominated this field, particularly with the recent advances in the advanced materials and electronic ceramics. It is interesting to note that the hydrothermal technique of material synthesis, although began in the previous century, has gained its momentum during the postwar period. Prior to that, majority of the compounds synthesized under hydrothermal conditions were essentially the natural analogues, as the main thrust was on the study of the origin of rocks, minerals and ores through laboratory simulations.

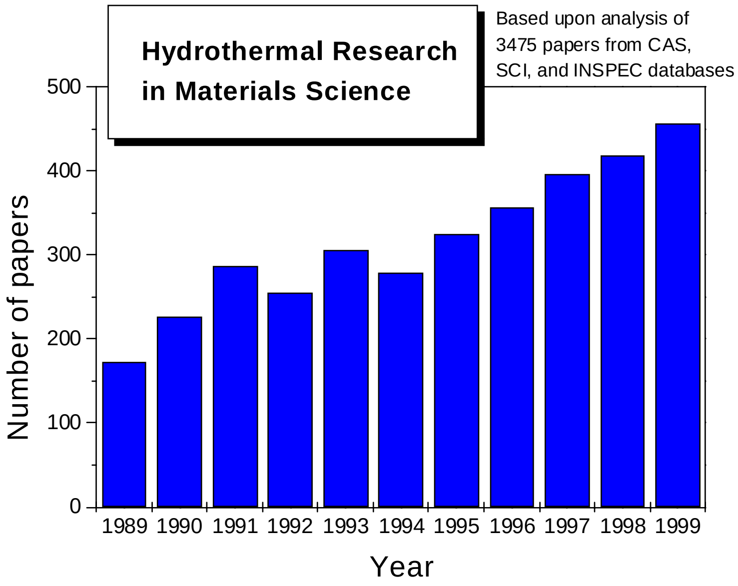

Figure 1.10. Number of publications year-wise.

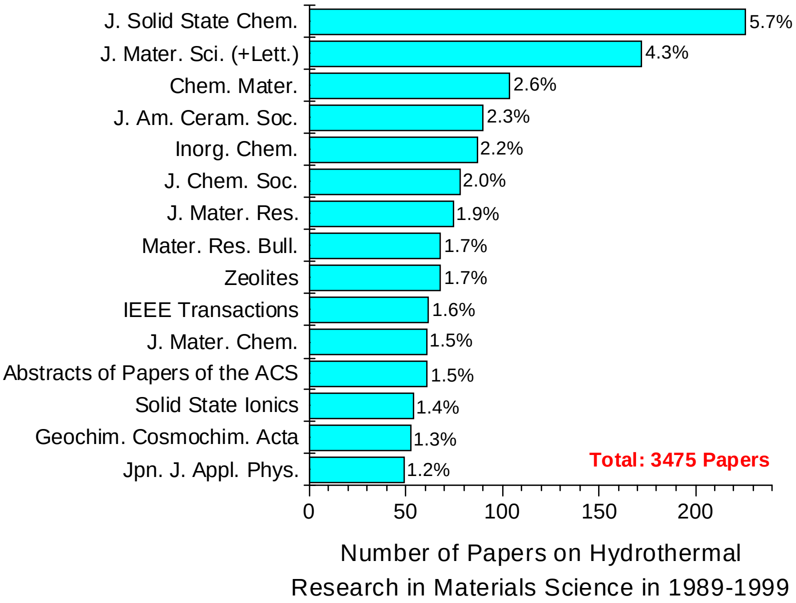

Figure 1.11. Number of papers on hydrothermal research in materials.

With the availability of the improved equipment and also with the knowledge on the preparative chemistry routes to synthesize many inorganic compounds, with or without natural analogues under hydrothermal conditions, the popularity of the technique grew fast. Today, the number of compounds without any natural analogue synthesized under hydrothermal conditions is more than the number of compounds with natural analogues synthesized. With the advent of new mineralizers, a wide variety of organic and inorganic compounds hitherto unknown are being prepared by hydrothermal technique. The technique is being popularly used for crystallization of materials, crystal growth, materials processing, thin film preparation, and so on. As evident from the synthesis of silicates, phosphates and oxides followed by the ceramics are very popular materials being obtained under hydrothermal conditions. The popularity of this field is probably connected with the better understanding of the hydrothermal solution chemistry and the effective use of several new mineralizers which have virtually changed the scenario, particularly with reference to the pressure and temperature conditions of synthesis of materials which were obtained under very high pressure and temperature conditions. For instance, rare earth tungstates, rare earth silicates and so on are being obtained under mild hydrothermal conditions.[102]

Hydrothermal research had its origin in Europe, and later spread its activity to North America during the early 20th century. The hydrothermal research in Asia began in the 1920s in Japan. Today, Japan has emerged as a leader in this field of research on par with the USA. However, the hydrothermal research is becoming quite popular in several other countries, particularly in the last three decades. The countries engaged in hydrothermal research are listed below in alphabetical order: Australia, Belgium, Brazil, Bulgaria, Chile, China, Canada, Denmark, France, Germany, Holland, Italy, India, Japan, Korea, Norway, Poland, Russia, Switzerland, Spain, Sweden, Taiwan, UK, Ukraine, USA. Amongst these countries over 75% of the hydrothermal research is going on in Japan and USA. Figure 1.12 shows the countries actively engaged in hydrothermal research.

The above statistical data on hydrothermal research clearly illustrate a growing popularity of the technique, covering various branches of science. The main disadvantage of the hydrothermal system, as believed earlier, is the black-box nature of the hydrothermal autoclave, because one can not make any direct observation of the crystallization processes. Though several attempts were made to observe the crystallization

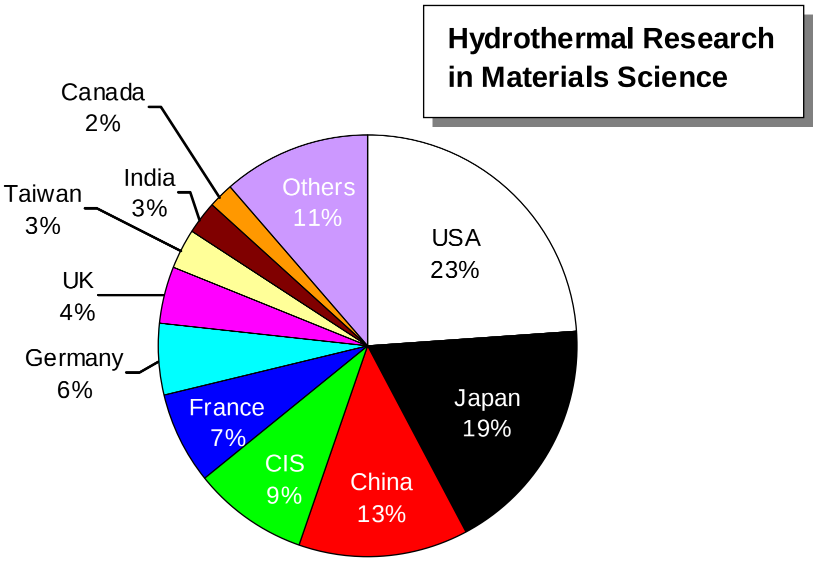

Figure 1.12. Number of papers on hydrothermal research in materials.

processes through special ruby windows for these autoclaves, not much success has been achieved because of the high pressure and temperature of the system. However, in recent years, remarkable progress was made in this area through the entry of physical chemists and the modeling of the hydrothermal reactions, and the study of kinetics of the hydrothermal processes have contributed greatly to understand the hydrothermal technique. One can now understand the hydrothermal chemistry of the solutions more or less precisely, which provides a solid base for hydrothermal synthesis and processing at much lower pressure and temperature conditions.[29][103] These developments are slowly removing the concept of the black box for the hydrothermal system, and one can make use of thick-walled silica autoclaves to carry out hydrothermal experiments up to a temperature of 300°C and pressure up to several hundreds of bars, to facilitate direct observation of the hydrothermal processes taking place in a given system. Already some groups in Russia, Japan and USA have begun work in this direction and numerous publications have appeared. These developments have given the hydrothermal technique an edge over other techniques for the preparation of pure materials as it is a closed system providing a more controlled diffusion. Besides, the role of pressure together with temperature helps enhanced molecular arrangements including those of organic molecules as supported by the synthesis of organic amino acids and other life forming complexes, and also the natural submarine hydrothermal ecosystems. Thus the hydrothermal technique exhibits a great degree of flexibility or adaptability which is being rightly exploited by a large scientific community with diversified interests.

1.9 HYDROTHERMAL MATERIALS PROCESSING

Hydrothermal materials processing is becoming a popular field of research, particularly after the successful development of ceramic processing technology during 1970s. Further there is a growing interest to enhance the hydrothermal reaction kinetics using microwave, acousto-wave simulations, mechanical mixing, and electrochemical reactions. These processes have made the hydrothermal technique more attractive to ceramists and preparative chemists because of the enhanced kinetics. The duration of the experiments is reduced by two orders of magnitude, at least, which makes the technique more economic. The microwave hydrothermal technique is especially handy for the synthesis of PZT and other oxide ceramics. Added to this, the crystal size, morphology and level of agglomeration of the different ceramic oxides can be controlled through careful selection of ratio of starting materials, pH, time, and temperature. Submicron size powders of TiO_2, ZrO_2, Fe_2O_3, $KNbO_3$, $BaTiO_3$, $PbTiO_3$ and their solid solutions have been prepared by this way. This has made the technique a more valuable one in the low temperature production of fine ceramic powders, clays, and zeolites.[17][104][105]

Similarly, ultrasonic energy, sonochemical simulation is used to prepare novel materials and accelerate the chemical reactions. In this way, hydrothermal reactions can be carried out at very rapid rates, and several new phases and high temperature phases can be obtained in minutes.

Hydrothermal epitaxy began during 1970s in connection with the development of magneto-optic and magnetic bubble domain devices, especially thin and highly crystallized magnetic films of yttrium iron garnets and their solid solutions on gadolinium gallium garnet substrates.[106][107] It did not capture the attention of specialists owing to the higher experimental pressure and temperature conditions involved ($T > 500°C$, $P > 1$ kb). However, in the last five years, the work in this direction has been revived. With the use of electrochemical reactions under hydrothermal conditions, it has become possible to grow highly pure and dislocation free crystalline thin films of various perovskite type oxides like $BaTiO_3$, $SrTiO_3$, $CaTiO_3$, and so on, under much lower pressure (< 100 bars) and temperature (100–200°C) conditions over a variety of substrates.[108]-[110] The method offers a high success rate and there are efforts to obtain functionally gradient materials through hydrothermal electrochemistry. With an increase in the demand for the composites, the hydrothermal technique offers an excellent facility for coating of various compounds on metals, and ceramics. For example, the coating of HAp or bone like apatite layers on chemically treated Ti metals, organic polymers and other metals has emerged out as a promising field.[111]-[113] This is discussed in detail in Ch. 10.

The hydrothermal technique has become very useful for the production of whiskers, which are finding extensive applications in modern technology. For example, whiskers of HAp are being produced under mild hydrothermal conditions. Although, the crystal growth of whiskers with controlled morphology is not a new field, it was already on the verge of extinction during the last decade. A few years ago, some reports on the growth of whiskers which are biocompatible under mild hydrothermal conditions appeared, giving a fresh lease on life to this field of research concerning whiskers crystal growth.[114][115] Amongst the popular whiskers crystal growth, the most popular one is the biocompatible HAp whiskers of nanometer size and this can be prepared at temperatures < 200°C, and pressure < 2 MPa within a few hours. Whiskers prepared by the hydrothermal method have a more controlled and better morphology, uniformity in size and purity in composition compared to the HAp whiskers produced by other methods. The whiskers obtained by other methods usually contained contaminants like carbonates, heterogeneity in shape and size. The hydrothermally prepared whiskers are finding promising applications mostly as reinforcements in composites, and thermal insulation. They are highly biocompatible, as they contain nontoxic species, such as Ca, P, OH^-, and are noncarcinogenic, chemically inert both outside and inside the living bodies. This is discussed in greater detail in Ch. 10.

The hydrothermal hot-pressing technique is becoming a very simple and most effective processing technique for the preparation of solid bodies from inorganic powders under mild hydrothermal conditions.[116][117] This technique is especially useful for the solidification of thermally decomposable powders such as carbonates, sulphates and nitrates at high temperatures. The solidification process is thought to be similar to liquid-phase sintering under pressure. In this technique, the starting powder containing water is continuously compressed from the outside of an autoclave under hydrothermal conditions. The powder is then treated at autogeneous pressure, while it is compressed at much higher pressure than the vapor pressure inside the autoclave. The water still remaining in the compacts after the hydrothermal hot pressing can be easily drained out by drying in air. By this means, porous ceramics can be easily prepared. This technique becomes handy for the solidification of radioactive wastes[119] and sludge ashes.[120]

Corrosion is a major problem in industries and power stations. Corrosion afflicts all metals, alloys and even advanced ceramics. The commonly observed problems of corrosion include exfoliation, stress-corrosion cracking, intergranular corrosion, and dealloying. From the perspective of engineering, the prediction, monitoring, and mitigating the corrosion problem is highly cumbersome. Once the attack is initiated, it makes localized corrosion a major problem in industries, power plants and reactors. In this respect, the supercritical solvents oxidation, particularly of water can be of great help to solve many of the problems associated with corrosion and erosion. In these systems, the toxic and corrosive ions are treated and made to form a solid crystalline coating of the metal surfaces as oxides or as oxychlorides. Several aqueous and nonaqueous solvents have been tried on a variety of metals, alloys, and ceramics, which greatly contribute toward solving the major industrial corrosion problem. The reader can get additional information from the works in Refs. 121–127.

Hydrothermal processing has become a most powerful tool, in the last decade, to transform various inorganic compounds and also to treat the raw materials for technological applications. The hydrothermally treated raw materials become very highly reactive as a function of solvent used in the preparation of advanced materials. One can find an extensive literature data available on this topic covering a wide range of oxides and hydroxides, carbosils, and so on. Similarly, the hydrothermal transformation, for example, montmorillonite and other variety of clays into the most useful zeolites with larger pore volumes, is a subject of great interest, because of its efficiency and economy.[105] In the last couple of years, the hydrothermal technique has been widely employed for metal intercalated nanocomposites preparation. Several variety of clay minerals which have two-dimensional layer structures[128] like montmorillonite, beidellite, hectorite, saponite, nontronite, etc., are attractive materials, because of their properties like cation exchange and swelling-shrinking in the interlayers. They readily produce pillared clays upon hydrothermal treatment. The preparation of pillared clays involves essentially the cation exchange with hydroxy polymeric cations followed by dehydration and dehydroxylation of the polymeric species to prop the layers apart with ceramic oxide pillars in the interlayers.[129] These pillared layers are successfully intercalated with transitional metals. Likewise, the hydrothermal technique is very useful for stabilizing the metastable phases. Also, for example, the water rich natural phyllosilicates, which have lower thermal stability can be made more stable chemically and thermally through replacement of $(OH)^-$ groups by oxygen atoms.[130] By these means, several phyllosiloxides have been prepared by many workers.[131]

All the above information on hydrothermal technology provides enough support for the growing popularity of this technique for materials synthesis, crystal growth, and materials processing.

The scope of this book has been restricted to recent developments under each one of the applications described above with the exception of the natural hydrothermal systems which are not within the perview of the present handbook. Although we have given the historical aspects of the technique in Ch. 2, the emphasis has been focused mainly on the crystal growth and materials processing through the ages.

This chapter clearly reveals the fact that the hydrothermal technique is drawing the attention of scientists from different branches of natural science. The future of this technique lies in this kind of multidisciplinary approach. More and more new findings and applications in this field are not only contributing to the scientific knowledge of the hydrothermal technique, but are also posing new problems. The role of organics in hydrothermal systems for example, has to be studied more seriously, which would definitely twist the geological thinking to a greater extent. It is well known that the organics in hydrothermal systems not only lead to the formation of new phases or new structures, and stability of metastable phases, but can also bring down the pressure and temperature conditions of crystallization. In nature, we can expect a very wide range of chemical components including hydrocarbons, which greatly contribute to the crystallization of rocks, minerals, and ore deposits. The role of these organics in the earth's crust has not been understood properly by geoscientists in the context of thermodynamics, and kinetics of crystallization. It is expected that such studies will definitely propose much lower temperature and pressure conditions of crystallization for various rock bodies, and add many more new questions to experimental petrology.

Thus, the future of hydrothermal research (both crystal growth and materials processing) is not towards higher pressure and temperature conditions, but definitely towards the lowering of the pressure and temperature conditions, which will facilitate *in situ* observation. This will also provide new stimuli for the fabrication of simpler (may be even silica and composites based) and larger autoclaves. As the design and fabrication of the autoclaves becomes simpler and easier, the cost will automatically go down, thereby making them more attractive to specialists. In the last fifteen years, as we see from the statistics discussed earlier in this chapter, more new applications for hydrothermal technique are being reported continuously. It is predicted that it will merge with soft solution chemistry and soft solution processing by being more compatible with biosphere. It will come out as an important tool for the development of advanced materials with limited resources and energy consumption. These materials are less hazardous to living species, also environmentally friendly without firing or sintering at ultrahigh temperatures, or melting or plasma or vaporizing. Because the energy consumed in attaining the melt or vapor or plasma conditions is very high, it proves to be environmentally unfriendly. Hence, the future of hydrothermal technology lies in promoting the lower pressure and temperature conditions for crystal growth and materials processing. We have made an attempt to expose the reader to the above mentioned aspects of hydrothermal growth and materials processing in the forthcoming chapters.

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2

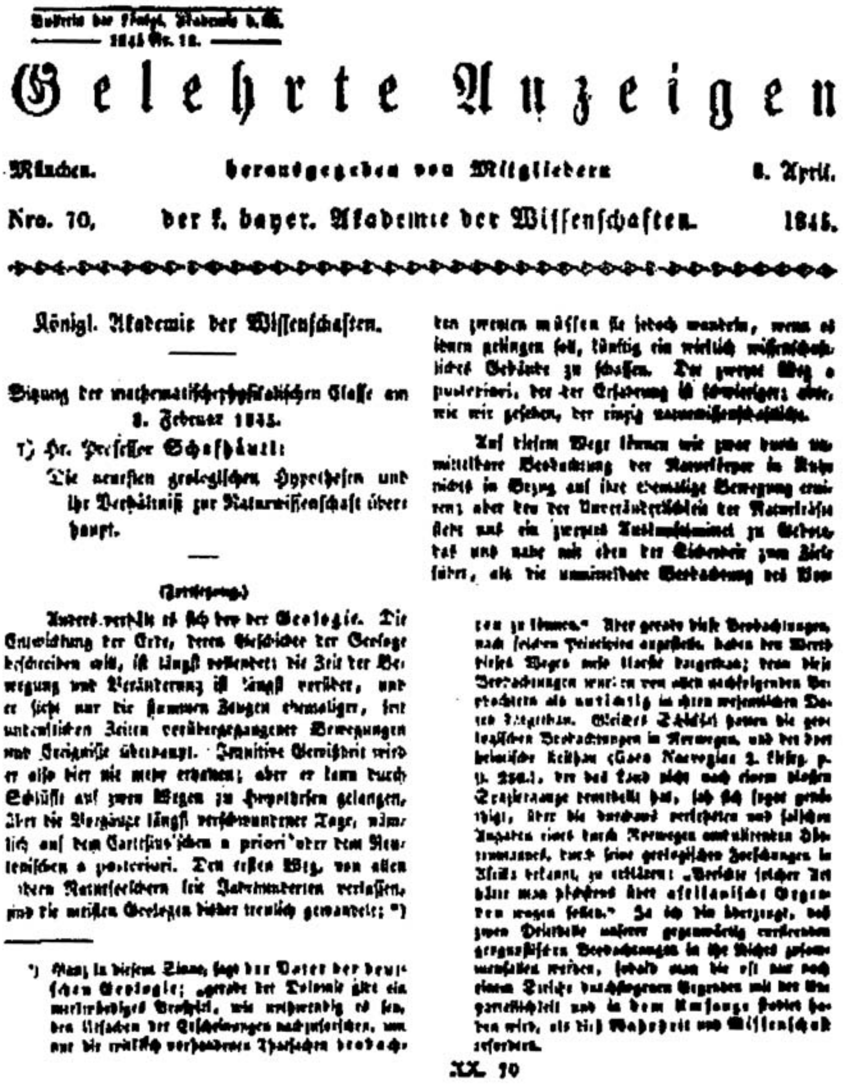
History of Hydrothermal Technology

2.1 INTRODUCTION

In the ancient times, Romans used to celebrate the year-end and year-beginning in great festivities in honor of the God Janus, in whose honor the month January is named. The God Janus is a deity with two heads: one looking to the past and the other looking to the future (Fig. 2.1).[1] Here, we have made a sincere attempt to explore and review the early history of the hydrothermal technology that has an extremely promising future.

Figure 2.1. The God Janus.

As mentioned earlier, Sir Roderick Murchison, a British Geologist, was the first to use the term *hydrothermal* in the mid 19th century.[2] The first publication on hydrothermal research appeared in 1845 (Fig. 2.2). This reports successful synthesis of tiny quartz crystals upon transformation of freshly precipitated silicic acid in Papin's digestor by K. F. E. Schafthaul.[3] Following this, mineralogists, especially from France, Germany, and Italy, started synthesizing various other minerals. Although the size of the crystals or minerals they obtained did not exceed thousandths or hundredths of a millimeter, their main objective was to create or simulate, in the laboratory, the natural conditions existing in the earth's crust. If, in nature, minerals and mineral assemblages were formed at elevated temperature and pressure conditions in the presence of volatiles—mainly water, it will be quite impossible to simulate the natural conditions or processes responsible for the formation of rocks and minerals except under the *hydrothermal conditions*. Thus, the early interest in hydrothermal research was merely in the synthesis of a particular mineral or in obtaining compounds similar to natural minerals rather than to carry out any systematic investigation pertaining to phase relations or geochemistry of the earth's interior. Even the conditions under which they worked were, in general, simple and sometimes lacking precision. The minerals obtained by the earlier workers are chiefly those which are stable or at any rate, phanerostable, over a wide range of conditions, for example, quartz, and feldspar. As the resultant products obtained were very tiny, accurate chemical analysis or identification of the phase by optical microscopic methods was quite doubtful and many a times led to speculations. Besides, the experiments were carried out in glass tubes in which it was difficult to attain higher pressure-temperature conditions; also water was used in most cases as a solvent. Therefore, the crystals obtained were very small, and the purity of the crystals could not be studied satisfactorily. Most of the experiments during the 19th century under hydrothermal conditions, with some exceptions, were related to silicate synthesis. Therefore, the contribution from the glass tubes to the resultant product could not be precisely understood. After the introduction of steel autoclaves and suitable metal linings, attempts were initiated to reach higher pressure-temperature conditions to obtain other compounds and purer phases. However, no attention was paid to the chemistry of the solvent, the frequent appearance of the metastable phases, solubility relations, kinetics, phase equilibria and related phenomena. Thus, the frequent appearance of the metastable phases also complicated the earlier studies.



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Sitzung der mathematiſch-phyſikaliſchen Claſſe am 8. Februar 1845.

1) Hr. Profeſſor Schafhäutl:

Die neueſten geologiſchen Hypotheſen und ihr Verhältniß zur Naturwiſſenſchaft überhaupt.

(Fortſetzung.)

XX. 70

Figure 2.2. The first publication on the hydrothermal research. *(Courtesy of Prof. S. Somiya.)*

Most of the work on hydrothermal research during 19th century was confined only to Europe, especially to the Mineralogy, Petrology, and Geochemistry laboratories in Germany, France, Switzerland, and Italy. Bunsen (1845) carried out the hydrothermal experiments for the first time using thick walled glass tubes to contain high-temperature–high-pressure liquids and prepared strontium and barium carbonates.[4] Wohler (1848) recrystallized apophyllite by heating apophyllite in water solutions at 180–190°C under 10–12 atm pressure.[5] In fact, all the early hydrothermal experiments, until 1881, were carried out in simple glass tubes with sealed ends, of course, with an exception of one or two attempts with steel tubes. Even the term *hydrothermal bomb* was not used by earlier workers and they simply referred to them as autoclaves or tubes. The greatest contribution in the 19th century was by H. De Senarmont, the founder of hydrothermal synthesis in geoscience. He used glass tubes containing gel, SiO_2 and H_2O, HCl, or CO_2, enclosed in steel tubes, and heated at 200–300°C. The resultant product was a six-sided quartz prism with pyramidal termination.[6] When the solution contained $NaHCO_3$, CO_2 and some realgar, very little quartz was obtained. It was probably Daurree (1857), a French mineralogist, who first used a steel tube to synthesize quartz and wollastonite at about 400°C with water as a solvent. The most important aspect of his experiments was the pressure balance he introduced for the first time. The starting substances were taken in a sealed glass tube with water as a mineralizer, and this glass tube was placed inside a steel tube.[7] The space between the glass tube and steel tube was filled with water. He carried out a series of experiments with this design and a varied concentration of the starting materials to obtain several other minerals. Similarly, he conducted experiments on the recrystallization of felspars, micas, and pyroxenes.

Daurree's other significant contribution was his attempt to use natural hot spring water from Plombieres as a mineralizer and this led to the deposition of a small quantity of quartz in two days' time. In addition, he treated kaolin with Plombieres water under hydrothermal conditions and obtained felspar and a small amount of quartz. Here it is interesting to note that, after the discovery of hydrothermal activity in the deep sea on the Galapagos during the 1970s, active research is going on using the natural submarine hydrothermal vent fluid to study the origin of life (organic synthesis). This led to the establishment of the relation between the submarine hydrothermal activity and rich mineralization of a very wide spectrum from native elements to sulphides, oxides, and so on.[8]-[10] The literature survey on the early hydrothermal research shows that several attempts were made to transform zeolite minerals and kaoline in the 19th century,[5]–[11] but it was only during 1940 that Barrer succeeded in synthesizing for the first time zeolite, that is, *analcime*, using the hydrothermal technique.[12] Although Deville St. Claire (1857) attempted to transform bauxite into corundum under hydrothermal conditions using NaOH as mineralizer, the experimental results were not definite. Perhaps he was the first one to use a mineralizer other than water.[13] In fact, many of the earlier workers, including von Chroustshoff, found that the glass tubes they were using were frequently attacked under hydrothermal conditions. However, they do not mention anything about precautions taken in this regard, as they were more concerned in obtaining a product corresponding to some natural minerals. During 1873, von Chroustshoff first proposed the gold lining of steel autoclaves to prevent corrosion. By introducing gold lining for the steel autoclaves, he could achieve a temperature of 350°C to synthesize tridymite phase of quartz and increased experimental duration.[15]

With the introduction of steel autoclaves along with noble metal linings, the tendency to reach higher pressure-temperature conditions than the usual 5 to 10 atm began. However, majority of the works up to 1880 remained pertaining to quartz, felspar, and related silicates. Thus, many of the earlier authors even define hydrothermal technique as the "one used in the synthesis of silicates." In 1880, Meunier carried out an experiment using water vapor passed over $AlCl_3$ and Mg contained in an open tube, heated to a low red heat and obtained mainly spinel. In some parts of the tube, he even observed tiny crystals of periclase and corundum.[15]

Followed by this work, Hannay (1880) claimed to have synthesized artificial diamond by the hydrothermal technique.[16] Similarly, Moissan (1893) also claimed to have synthesized diamond artificially as large as 0.5 mm from charcoal.[17] Though the success of these experiments was treated as dubious, they certainly provided a further stimulus for hydrothermal research, particularly the development of high-pressure techniques. It is interesting to note that the results of some of these earlier works were treated as dubious. This is probably in connection with the small size of their resultant products. The first ever large size crystals obtained by the earliest workers was that of hydrated potassium silicate, which was about 2–3 mm long, by Friedel and Sarasin (1881).[18] In this case, while growing orthoclase and felspar, hydrated potassium silicate was obtained as an additional phase containing surplus potassium silicate. Here it is appropriate to quote one or two earlier experiments for the curiosity of the readers and to show their experimental conditions. Chroustshoff (1887) obtained quartz by heating a colloidal solution of SiO_2 to 250°C, almost every day for 6 months. He started his experiments with 4 tubes, 3 of which soon burst. Some crystals as large as 8 mm long and 3 mm wide, of type of vein quartz with $(10\bar{1}0)$, $(10\bar{1}1)$, $(01\bar{1}1)$ faces were crystallized. Perhaps this is the first systematic work on the growth of quartz. Although, the experimental duration was quite long, almost 6 months, he could obtain quartz crystals as large as 8 mm long and 3 mm wide.[19] In another experiment, Chroustshoff (1890) used a thick-walled evacuated glass tube of 25 cc volume, containing a mixture of colloidal SiO_2 solution, colloidal $Fe(OH)_3$, colloidal $Fe(OH)_2$, lime water, freshly precipitated $Mg(OH)_2$, and several drops of a NaOH-KOH solution which he heated for 3 months at 550°C. The resultant product contained, among other things, long, thick, dark-colored prismatic crystals of hornblende, 1 mm long, 0.5 mm thick, with (010), (110), (011) faces.[20] The most interesting point to be noticed here is that the experimenter obtained a mineral in 3 months under hydrothermal conditions having no bearing on its petrogenesis and no relation to any known equilibrium. Morey (1953) quotes this as a horrible experience of the experimenter.[21] Here, the reader should notice the duration of each experiment and the size and type of the minerals obtained. This is definitely related to the lack of knowledge in areas of solvent chemistry, kinetics, and solubility of the compound. Despite very low growth rates achieved in the 19th century, the earlier workers in hydrothermal research continued to synthesize a very wide range of mineral species. According to Morey and Niggli (1913), over 80 mineral species are supposed to have been synthesized during 19th century.[22] The list includes quartz, felspars, mica, leucite, nephelite, epidote, hornblende, pyroxene of minerals from the silicate group and several non-siliceous minerals like corundum (Al_2O_3), diaspore ($Al_2O_3 \cdot H_2O$), and brucite ($Mg(OH)_2$).

For the sake of convenience, the authors describe the further development of the hydrothermal research in coherence with the autoclave design, development, and pressure-temperature range. It is well known that the study of hydrothermal processes is merely the study of certain aqueous systems at high temperature, usually near to and often above the critical temperature of pure water, therefore considerable amount pressures are developed at these temperatures by water or aqueous solutions. The experimental difficulties of such a study are many, but are largely connected with the choice and control of working conditions and the selection of a suitable autoclave to withstand the pressure at high temperatures over a long period of time. It was soon after Chroustshoff (1873) proposed the gold lining for the steel autoclaves that many earlier researchers began to work on new designs and new lining materials for autoclaves to obtain the most ideal conditions for the synthesis of several high temperature oxide minerals. Probably Friedel and Sarasin (1881) termed their hydrothermal autoclave as *hydrothermal bomb*, because of the high pressure working conditions in their experiments.[18] Obviously new metals and alloys available during that time were tested. For example, De Schulten (1882) even used a copper bomb to synthesize analcite by heating a mixture of sodium silicate, sodium aluminate, and lime water at 180°C for 18 hours.[23] Similarly, Sir Ramsay and Hunter (1882) used a cast iron bomb.[24] Bruhns (1889) used steel bombs lined with platinum, with a cover held down by bolts and made tight by means of a copper washer, which was protected by the action of the mineralizer on platinum.[25] Other contemporary workers used this design. Perhaps the simplest design of the autoclave, made of a nickeled gun-barrel or silver lined steel tube closed by a screw cap and copper washer, was developed by Doetler (1890). Using this type of autoclave, Doetler has done an extensive work by obtaining several mineral recrystallized species like chabazite, okenite, heulandite, analcite, natrolite, and so on.[26] However, in most of these works from 1870s to 1890s using the above mentioned type of autoclaves, experimental uncertainties were introduced owing to the lack of a perfectly tight closure, which resulted in the leakage of water, thereby causing variations in the pressure conditions (and hence the concentration) of water during the course of experiments. Friedel (1891) obtained corundum crystals by heating a solution of NaOH with excess of Al_2O_3 at a higher temperature at that time, 530–535°C.[27]

Towards the end of 19th century, Spezia from the Torino Academy of Science began his classical work on the seeded growth of quartz. His contribution to the field of hydrothermal research is remembered even today. Spezia (1896) found that plates of quartz kept at 27°C for several months with water under a pressure 1750–1850 atm did not lose its weight and also showed no etch figures. Thus, he concluded that pressure alone has no influence on the solubility of quartz.[28] Subsequently, Spezia studied the action of Na_2SiO_3 in the solubility of quartz with temperature. He found that when alkali was present in the system, SiO_2 separated out as quartz and the rhombohedral faces of the quartz were easily attacked, and on the other hand, on the same faces were the greatest depositions of SiO_2 from Na_2SiO_3 solutions. The more rapid growth of the quartz crystals along the *c*-axis was explained.[29]

During the 19th century, much work was done on the geological side of hydrothermal research and the entire work was confined to Europe, particularly Germany, France, Italy, and Switzerland. It was only towards the turn of 19th century that the science of hydrothermal technology moved to North America, which was assisted by the American Industrial Revolution. Further, the establishment of the Geophysical Laboratory at the Carnegie Institute of Washington, USA, in 1907, probably marked the most important milestone in the history of hydrothermal technology. Although a great deal of research was carried out on hydrothermal technology in the 19th century, the facilities for large scale hydrothermal research before the end of the World War II were virtually nonexistent, except the Carnegie Institute of Washington, where Bowen began his hydrothermal research and later moved to the University of Chicago, Bridgman's high pressure laboratory at Harvard University during 1940s and 1950s, Kennedy's at the University of Chicago, and Tuttle's at Penn State University. This situation dramatically changed with the development of the test tube type pressure vessel by Tuttle in which high pressures up to 5 kbar could be maintained at temperatures of 750°C for a long period of time. However, before going into the contributions of these great personalities, we shall discuss the early contributions during the turn of the 19th century and the beginning of 20th century. As mentioned earlier, the entire activity on hydrothermal research was concentrated in Europe and there was no activity in North America or Asia, including Japan, China, India, and Taiwan, which are included today in the top ten countries actively engaged in hydrothermal research. Perhaps the first North American published work on hydrothermal research was by Barus (1898), who essentially worked on the impregnation of glass with water to such an extent that it melted below 200°C. He used steel bombs for these experiments.[30] Subsequently, Allen (1906) obtained very fine quartz crystals by heating a solution of $MgCl_2 \cdot 6NH_4Cl$ and Na_2SiO_3 for 3 days at 400–450°C. Also, large crystals of 2 mm long, often barrel shaped with short rhombohedral terminal faces, were obtained. Allen used steel bombs closed by a Cu disc held in place by a screw on steel cap, used either $MgCl_2 \cdot 6NH_4Cl$ solutions or a mixture of $MgCl_2$ solution with $NaHCO_3$, and either amorphous SiO_2 or Na_2SiO_3, heated for 3 to 6 days at 375–475°C to obtain magnetite, quartz, fosterite, etc.[31] However, the early American hydrothermal research was carried out using the autoclaves of

European designs. Around the turn of the century, it was again the German workers who were active in the field of new designs, especially Tammann and Boeke from Tottingen who carried out extensive studies with reference to many carbonate and silicate reactions in the newly designed bombs at higher pressure and temperature conditions with CO_2 pressure.[32] Perhaps this is the beginning of the solvothermal research, although the term *solvothermal* was introduced by French chemists in 1971.[33] The autoclaves used by Tammann and Boeke were all heavy steel vessels 10" diameter, 18" long, with soft metal gaskets which formed the seal when compressed by a set of radially deployed screws and nuts. The heating was internal with a resistance furnace.

With the establishment of the geophysical laboratory in Carnegie Institute of Washington, USA, Bowen established a fine hydrothermal research laboratory. Obviously, all the major contributions to the field of hydrothermal research from USA in the early 20th century are solely from this laboratory and have received worldwide recognition. Bowen took up a systematic study of the phase equilibria in high temperature silicate systems and, around the 1920s, he framed the most important petrologic principle, viz. *Bowen's Reaction Principle,* shown in Fig. 2.3.[34]

These ideas of Bowen have been, without question, one of the rare landmarks in the history of petrology. The main opposition for this principle was that the extrapolation of experimental phase equilibrium results was based on the data he obtained from systems made from relatively few and chemically pure components to natural systems. Subsequently, Bowen continued his research in this field, worked on several complex systems, and revised his earlier proposed reaction series slightly. While Bowen was working on the petrologic problems, Morey, Niggli, and Fenner were actively studying the silicate systems with water as one of the components. Morey first designed a simple, gasketed, sealed steel autoclave of 25 to 100 ml volume in the year 1913. It became very popular because of its simplicity and ease to handle. Later, the autoclave that bore his name was widely used for working up to the temperature of 450°C and 2 kbar pressure.[35] The details of the design and construction are discussed in Ch. 3. The first American autoclave designs were those of Adams and Smyth, again from Geophysical Laboratory of Carnegie Institute of Washington in 1923,[36] which later led to the modified versions by Goranson in 1931.[37] Figure 2.4 shows the schematic diagram of the autoclave design of Adams and Smyth. Before the development of these autoclaves, hydrothermal research was confined only to lower pressure and temperature limits because the externally heated vessels failed as a result of creep and oxidation of the alloy used. On the other hand, the pressure vessels designed by Adams and Smyth were internally heated and externally cooled by circulating water. These developments in the 1920s are regarded as important milestones in hydrothermal research. They set a new trend in search of new alloys, and extended pressure and temperature limits. Using this set up, Goranson (1931) carried out a systematic study pertaining to the solubility of water in a liquid having the composition of the Stone Mountain Granite, and this investigation was considered as the most outstanding advancement in the application of hydrothermal laboratory studies to petrologic problems. The driving forces for the volcanic activity were related to the crystallization of hydrous silicate liquids.[37]

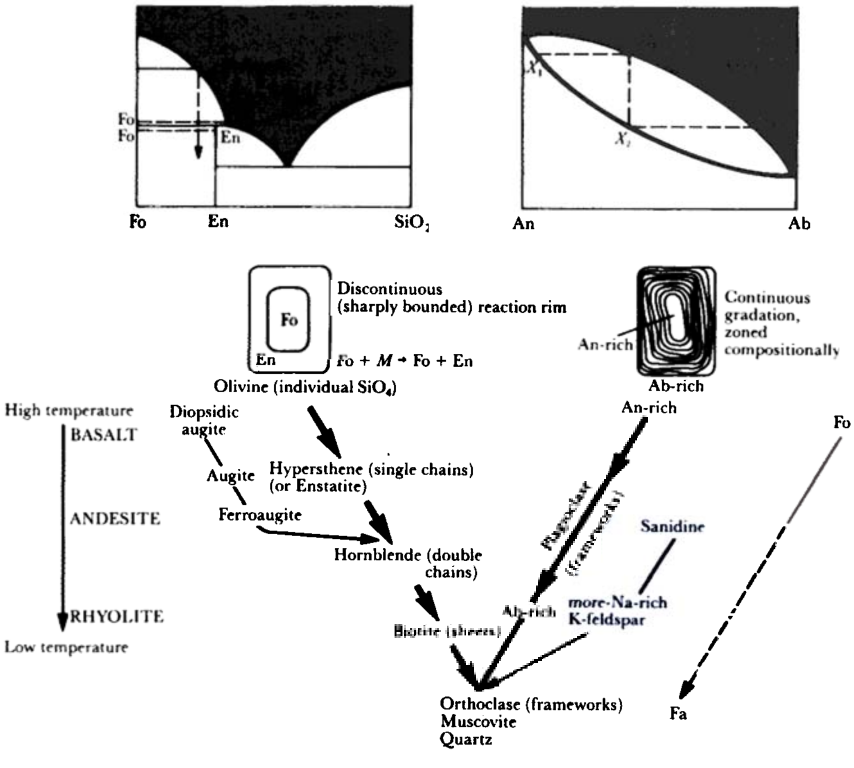

Figure 2.3. Bowen's Reaction Principle.[34]

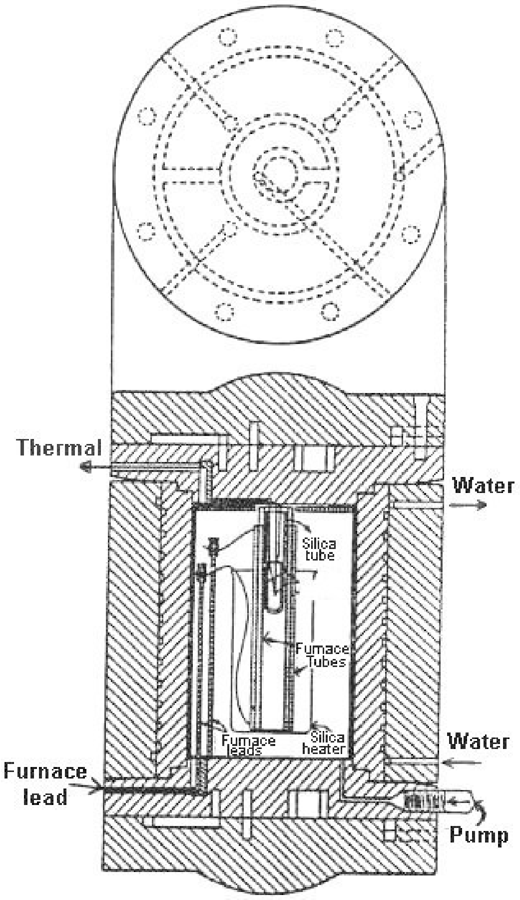

Figure 2.4. Schematic diagram of the autoclave design of Adams and Smyth.[36]

During this time, hydrothermal research began in Eastern Europe and Asia on a small scale, and much later in China and India—maybe after the Second World War. Here the reader should observe that the hydrometallurgy was quite an established field of research in many countries in Europe, North America, Eastern Europe, and Asia, particularly after the discovery of bauxite leaching by Karl Josef Bayer (1871–1908).[38] While writing the history of hydrothermal technology, the authors paid more attention to crystal growth and materials science rather than metallurgy or metal extraction. Therefore, historical references are not made for hydrometallurgical processes. As the authors of this monograph are from Japan and India, a brief history of the hydrothermal research in these two countries is given. Today, Japan is the second most active country in the world for hydrothermal research next to the USA, and India stands in the 9th position next to Taiwan, with respect to the hydrothermal research in Materials Science (Fig. 1.12). If the hydrothermal research in geological science is also included, India's position goes up to the 7th place (based on the statistics prepared from Chemical Abstracts, Science Citation Index and INSPEC data bases from 1989 to 1997). More details on the statistics can be obtained from Ch. 1. According to Prof. Shigeyuki Somiya,[39] in Japan the hydrothermal work was first initiated in 1926 by Dr. Tominosuke Katsurai, and the work was related to hydrometallurgy. He worked on the soda treatment of aluminum ore through hydrothermal extraction. Following this, Prof. Shoichiro Nagai reported the synthesis of calcium silicate in 1931.[40] Perhaps this was the beginning of hydrothermal synthesis in Japan. Before going into the further developments which took place during the World War period, let us discuss briefly the progress achieved by the earliest workers of 20th century in the area of hydrothermal phase equilibrium studies.

Pioneers like Bridgman, Cohen, Morey, Niggli, Fenner, and Bowen in the early 20th century changed the scenario of hydrothermal research. They carried out an impressive amount of basic research along with their European counterparts, especially Tammann. Much of this early work was concerned with the setting up the pressure scale and testing. The results were predicted from thermodynamics. However, the total research effort was small and the study passed into a period of dormancy except for phase equilibria studies in some systems relevant to the natural systems. This was connected with the need for materials with a combination of high strength and corrosion resistance at high temperatures. Thus, the interest was again mostly geological, and the bulk of research is from the geological science side. It is fortunate for chemical science that most of the early geological workers appreciated the necessity for considering very simple chemical systems before there was any hope of understanding complexities of natural systems. Thus, the early work of Geophysical Laboratory of the Carnegie Institute of Washington was heavily biased towards pure chemistry.[41]

Here it is appropriate to discuss one or two important systems studied in early 20th century. Perhaps the first systematic and pioneering study of the hydrothermal system began with the publication of the work on the ternary system H_2O-K_2SiO_3-SiO_2 by Morey and Fenner (1917).[42]

This work gives a more precise account of the pressure and temperature conditions throughout the experiment. Besides, nutrient materials were prepared from highly pure substances and consequently the composition of the charges used in each experiment was precisely known. The paper carried great significance to geological science as it demonstrated clearly the possibility of a complete solubility between anhydrous silicate phases and water, which in turn assisted in framing a mechanism for pegmatite crystallization in the presence of a volatile. Morey and Fenner (1917) studied this system from 200°C to >1000°C.[42] The work comprises of the determination of the composition and properties of the various stable solid phases which can coexist with solution and vapor within the above temperature range, of the composition of the solutions in equilibrium with the solid phases, of the change in composition of these solutions with temperature, and the approximate determination of the corresponding 3-phase pressures. Morey and Fenner used the famous Morey autoclave in all their work on phase equilibria studies in different systems. The isothermal polybaric saturation curves and the isobaric polythermal saturation curve at 1 atm pressure of H_2O vapor is shown in Fig. 2.5.

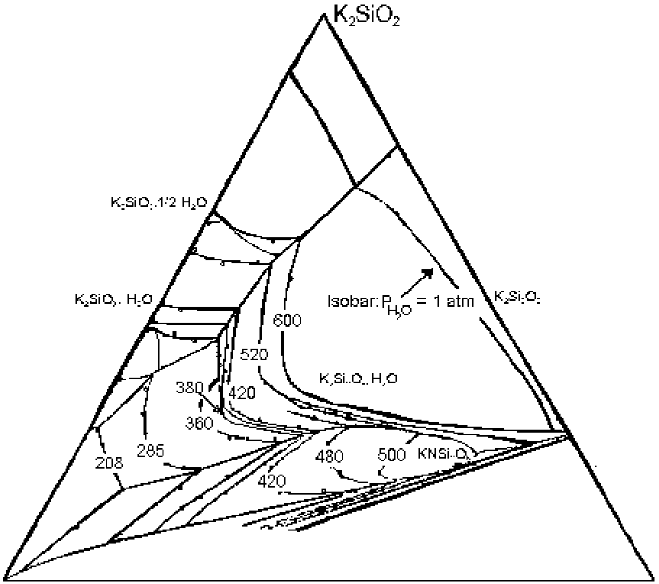

Figure 2.5. The isothermal polybaric saturation curves and the isobaric polythermal saturation curve at 1 atm pressure of H_2O vapor.[42]

The most significant aspect of this work is that a new trend can be observed here with reference to the theoretical relations governing the equilibrium in binary and ternary systems containing a volatile component, and a short discussion of the proper application of the term *solubility*. Besides Morey and his group, another group from the same laboratory led by Bowen was very active during that time. The study of the *p-v-t* relations of water became popular during the late 1920s. The works of van Nieuwenburg and Blumendahl (1932) followed by Keenan and Keyes are the most significant ones.[43][44] Later, Kennedy (1950) oriented his famous PVT data on water.[45] The Kennedy's diagram is shown in Fig. 2.6.

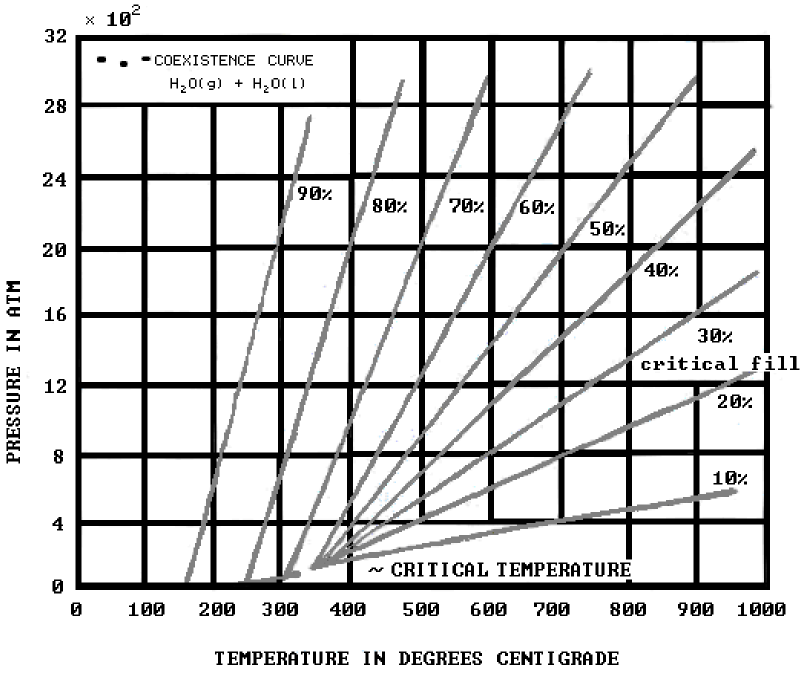

Figure 2.6. PVT diagram of water.[45]

Hitherto, the hydrothermal researchers were quite satisfied with the synthesis of inorganic compounds which resembles or which is similar to natural mineral. They did not bother much about the size of the crystals obtained. The growth rate was extremely low because of the lack of accurate knowledge on the proper solvent, and with such slow growth rates, the hydrothermal research was less promising. Only a few number of people were engaged in this research studying the phase relations in various systems including that of water, and the interest was mainly on Geoscience. However, when Brazil imposed an embargo on the supply of high purity quartz which was a strategic material for the telecommunications purpose during the second world war, hydrothermal researchers began to think seriously about the growth rate of crystals. At that time, Brazil was the only country in the world for the source of electronic grade natural quartz, and even today, the situation is the same. Thus, the crisis owing to the shortage of pure quartz forced many researchers to jump into the field of hydrothermal research with a sole objective of growing large size single crystals of quartz. Many countries like the USA, UK, Germany, and the erstwhile Soviet Union were into the field and the success achieved was immense. Therefore, the period from the late 1930s to 1940s is referred to as the "golden period" in the hydrothermal research, not only because of the enhanced research activity, but also because of the many new discoveries with reference to autoclave designs and other important technological materials.

The authors feel that it is highly appropriate to discuss briefly the historical contribution made by the German hydrothermal researchers with reference to the increased growth rate and growth of large size single crystals of quartz. In contrast to the slow rate of growth achieved by the earliest workers like De Senarmont and Spezia, the captured German reports show that Nacken, using natural alpha-quartz as seed crystals and vitreous silica as the nutrient, had grown quartz crystals in an isothermal system and had succeeded in obtaining large single crystals of quartz from a small seed.[46] Prof. Richard Nacken (1884 to 1971) worked on the synthesis of various minerals from 1916 onwards, but left this field. In 1927 or 1928, he started working only on the hydrothermal growth of quartz crystals. On Nacken's work, Sawyer writes (cited by Bertaut and Pauthenet, 1957) that, "...Nacken made quartz crystals of 1" diameter by using hydrothermal method and the conditions are given as…" followed by some biographical data. Similarly, Nacken's emphasis on the quartz growth has also been documented by Sawyer. Almost at the same time, Nacken made emerald single crystals by the hydrothermal method and also beryl or corundum crystals for watch bearings. He prepared a large number of synthetic emeralds by using a trace of chromium to produce the color and could obtain hexagonal prisms of emerald weighing about 0.2 gm in a few days.[47] However, much of the work carried out by Nacken during late

1930s and 1940s remained as intelligence reports since he could not publish much.[48] During 1950, Nacken published his work on quartz that remains a classic even today.[49] Figure 2.7 shows a photograph of the quartz crystals obtained by Nacken.[49] As mentioned earlier, Doetler was the first one to use closed nickeled gun-barrel autoclaves, way back in 1890. It attained its prominence during World War II when several laboratories from many countries began working on the growth of large size crystals of quartz. This is also partly connected to the availability of alloys containing Mo and other important metals, which provided better strength to the alloys. Many countries attempted to grow large single crystals of quartz using old cannon barrels with closed ends during early 1940s. In this regard, the contributions of Lobachev and Shtenberg are important. By the mid 1940s, many laboratories, particularly from the USA, Germany, Russia, and the UK, were actively engaged in the growth of large quartz crystals. At this time, Tuttle (1948) designed a cone-in-cone seal for a small vessel with no threads to seize. However, the Tuttle apparatus could not achieve high pressure and temperature conditions, and it did not become very popular.[50]

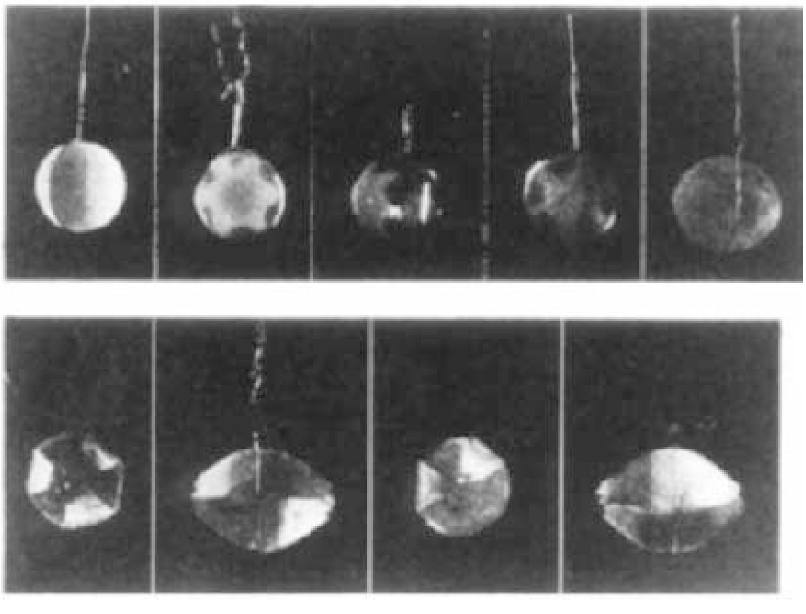

Figure 2.7. Photographs of the quartz crystals obtained by Nacken.[49]

Later, Rustom Roy modified another vessel that had been designed by Tuttle but never exploited. It proved to be much simpler and highly versatile. This modification by Roy is popularly known as the "test-tube bomb," which is made up of Hastelloy; Rene 41; Stellite 25 or Udimet, with 1–1½" o.d. × 8" long, having a 3/16"–¼" diameter hole drilled down to ½" of the bottom. It was threaded at one end and closed at the other.[51] A more detailed description of the design and construction of this autoclave is given separately in Ch. 3. The greatest advantage of this test-tube bomb was not only the ease of operation, but also a large number of such vessels could be served by one pressure source. This integrated system of several vessels, each with its own gauge with one pressure generator, became a standard hydrothermal laboratory apparatus. Figure 2.8 shows a picture of such an assembly of 10 autoclaves of test-tube type, with one pressure generator source, operating simultaneously.

Figure 2.8. Picture of an assembly of 10 autoclaves in the laboratory of K. Byrappa.

Many laboratories throughout the world have this apparatus for studies concerning phase equilibria, materials synthesis, crystal growth, particles preparation, materials processing, diamond synthesis, and so on. The recent modifications of these test-tube bombs have been extended further for higher pressure and temperature conditions. The credit goes to the pioneers of this apparatus, Tuttle, Roy, and Licastro, who could set up a Tem-Press Company to manufacture these autoclaves at Penn State University. Thus, during the 1950s, the trend in hydrothermal research was towards the development of new designs, again to attain higher pressure and temperature limits with the better alloys available. This also led to the study of phase relations in several systems within a broader pressure-temperature range. In this regard, the contribution of Kennedy (1950), Morey and Hesselgesser (1951), Tuttle and England (1955), and Della Roy and Rustom Roy (1956) are very important.[52]-[54] The SiO_2-H_2O system was studied in great detail. Followed by this, many other laboratories in Europe, North America, erstwhile Soviet Union, and Japan took up the study of phase equilibria in several simple and complicated systems.[55] These studies laid a firm foundation for the ceramists and physical chemists, after many years, to develop a new technology. At this time, Prof. Yamasaki, Prof. Kumitomi, Prof. Ohara, and Dr. Akitsu were doing an excellent work in hydrothermal research in Japan. Some of them were closely associated with the industries like Toyo Communication Co. Ltd. and Nippon Dempa Co. Ltd., which resulted in the successful growth of large size quartz single crystals. Though they started in a very small way during the postwar period, Japan is now the largest producer of commercial quartz in the world. Japan alone produces >50 % of the world's annual production, it has the largest autoclaves in the world.[56] Figure 2.9 shows the quartz crystals obtained by Walker during 1950s.[57]

Figure 2.10 shows the quartz crystals obtained at AT&T Bell Labs during the 1970s,[58] and Fig. 2.11 shows the growth of quartz crystals in the world's largest autoclave located at the Toyo Communication Co. Ltd., in Japan during the 1980s.[56] In one experimental run, about 4000 to 4500 kg of quartz is produced. The early success in producing commercial quartz crystals in Japan during the postwar period paved the way for several others in the field. Some prominent ones are Prof. T. Noda, Prof. Doimon, Prof. R. Kiyoora, and Dr. Y. Itoh. When the North American laboratories were concentrating mainly on the development of new designs of autoclaves, the study of phase equilibria, and commercial production of quartz, Japan concentrated essentially on the growth of quartz crystals, and achieved its goal in becoming the world's largest producer.

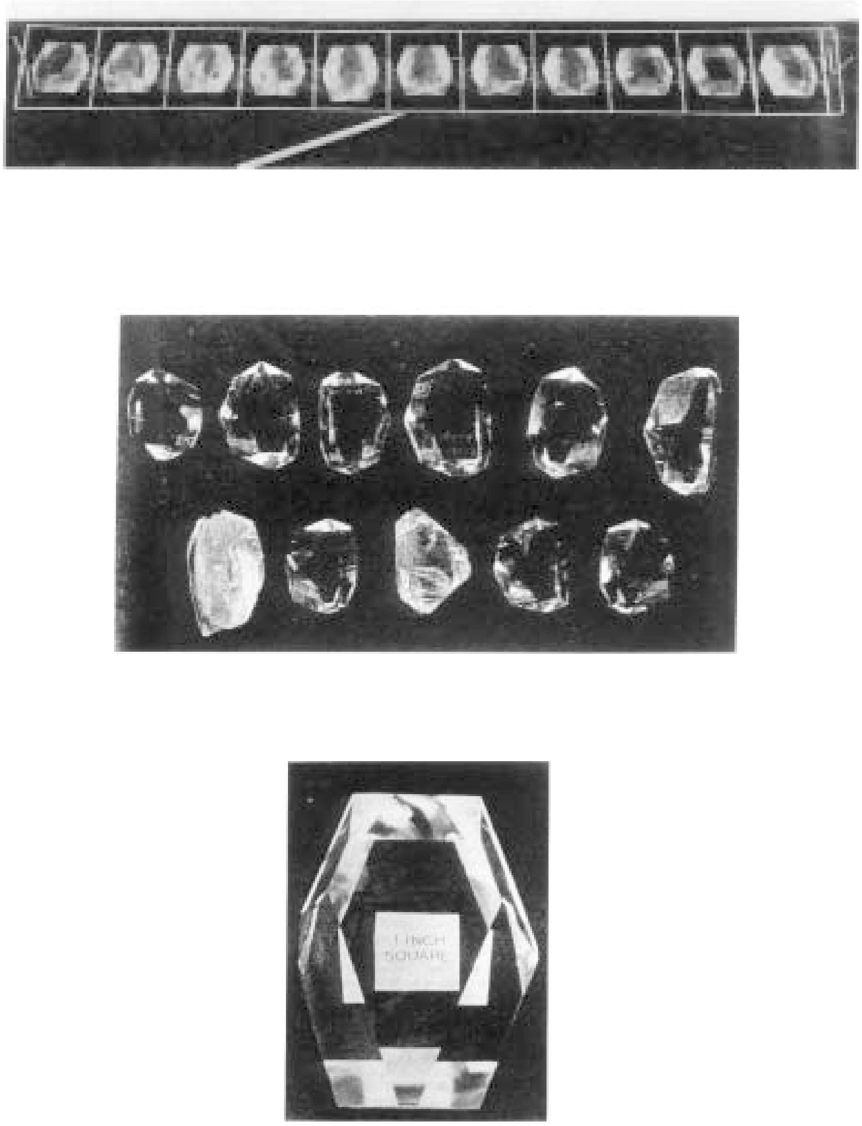

Figure 2.9. Quartz crystals obtained by Walker.[57]

Figure 2.10. Quartz crystals obtained at AT&T Bell Labs. *(Photo courtesy of R. A. Laudise.)*

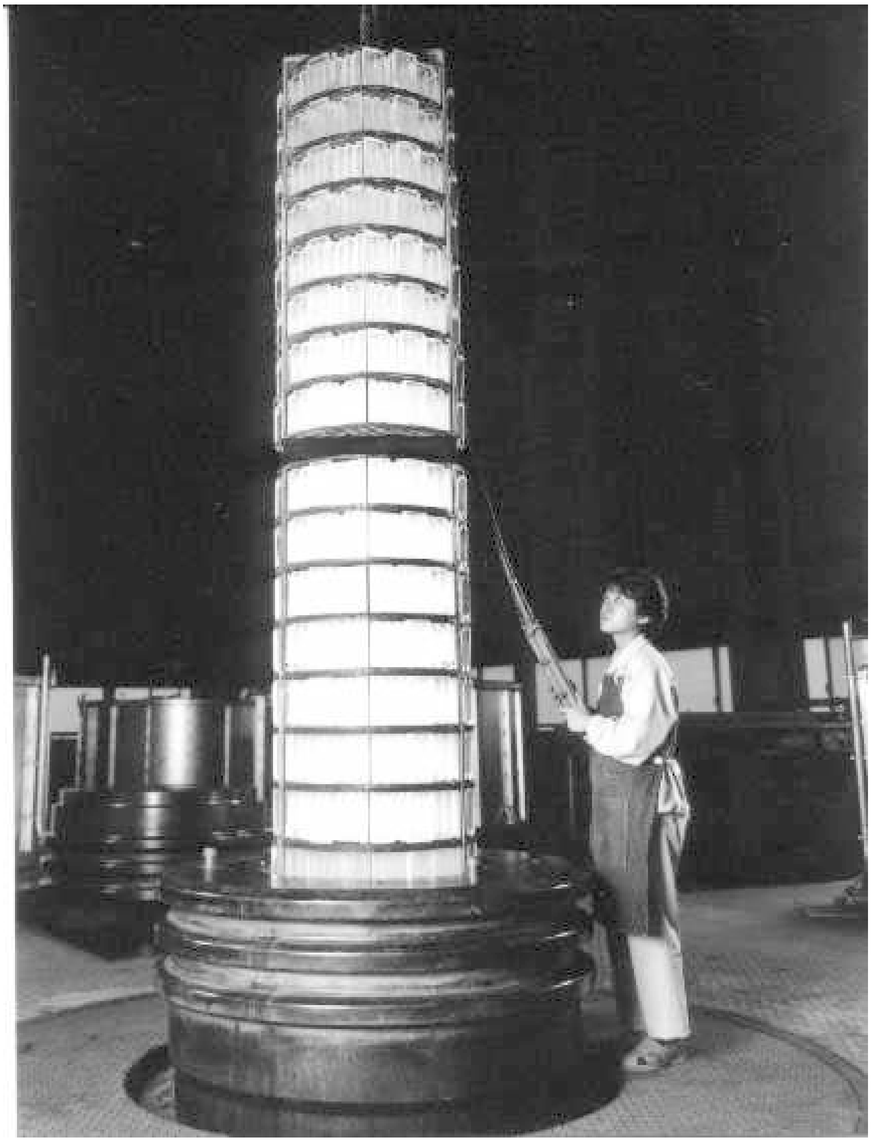

Figure 2.11. Growth of quartz crystals in the world's largest autoclave. *(Photo courtesy of Dr. Taki.)*

The study of ternary and other more complex systems during the 1950s was very important, not only from the point of view of geological science, but also from the inorganic chemistry point of view, as several new compounds which were hitherto unknown or not found in nature could be crystallized. Some of the important systems studied under this category are: MgO-SiO_2-H_2O, Al_2O_3-SiO_2-H_2O, BaO-Al_2O_3-H_2O, SrO-SiO_2-H_2O, K_2O-SiO_2-H_2O, Na_2O-SiO_2-H_2O, CaO-SiO_2-H_2O, CaO-Al_2O_3-H_2O, CaO-Al_2O_3-SiO_2-H_2O, and so on. More accurate phase equilibria data were obtained for the earlier studied systems. At this time many laboratories in the erstwhile Soviet Union attained a special prominence and led to the rapid growth of this branch of science not only in terms of laboratories, but also in terms of research personnel.

At one time, in the erstwhile Soviet Union there were more than 1000 researchers in this field. During the 1960s, an intensive study of the hydrothermal process of synthesis and growth of single crystals which did not have the analogues in nature began. During the 1970s, there was a quest for the search and the growth of hitherto unknown compounds of photo-semiconductors, ferromagnets, lasers, piezo- and ferroelectrics and, in this regard, hydrothermal technology attracted a great attention. Many other nations, including China and India, got into the field of hydrothermal growth of crystals. Several established laboratories in the world began to study systematically various aspects of the hydrothermal growth of crystals such as the physicochemical principles, kinetics, designing new apparatus, growing new compounds, and so on. This marks a significant change in the trend of hydrothermal research. Specific aspects of the hydrothermal method as a modeling tool to understand the natural processes of mineral formation changed dramatically into an important method characteristic for inorganic chemistry. During the early 1980s, a new sealing for the autoclave was designed, that is, *Grey-Loc* sealing, which facilitates the construction of the very large size autoclaves with a volume of 5000 liters.[59] The world's largest autoclave is located in Japan works with such a Grey-Loc sealing mechanism. The details of the sealing mechanism is discussed in Ch. 3.

Towards the end of the 1970s, on the whole, the hydrothermal field experienced a declining trend for two reasons: there was no scope for further work on the growth of large size single crystals of quartz on the one hand, and on the other hand, large scale attempts to grow bigger crystals of other compounds investigated during the 1960s and 1970s failed. It was unanimously decided that the hydrothermal technique is not suitable for the growth of large crystals other than quartz. The focus at this time was on Czechrolskii, MOCVD, and MBE. This is largely connected to the general approach of the hydrothermal researchers to grow large single crystals without looking into the hydrothermal solvent chemistry and kinetics of the crystallization process. Although Franck started working on the study of the behavior of electrolytic solutions with temperature and pressure conditions way back in the 1950s,[60][61] it did not attract the hydrothermal researchers' attention immediately. They thought that the conditions under which Franck worked were confined to the lower pressure and temperature conditions, whereas the hydrothermal technique actually belonged to the higher pressure and temperature conditions at least until recently. In fact, Ballman and Laudise, in their famous article published in the book: *Art and Science of Growing Crystals* edited by Gilman, write that "crystal growth is more an art than science."[62] 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, and so on, drew the attention of hydrothermal crystal growers and a new trend was set to look into the hydrothermal solvent chemistry and the physical chemistry of the hydrothermal systems.[63]-[66] 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, materials scientists, organic chemists, hydrometallurgists, hydrothermal engineers, etc.[67] 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 reactions began. New designs of the reactors to suit the specific requirements of research into areas like crystal growth and materials processing were developed. Unfortunately, this period also marks the fall of the Russian domination in the field of hydrothermal research. Japan emerged as a leader in hydrothermal research on par with the US. The decade-wise evolution of the hydrothermal research with regard to its objective and apparatus used is given with appropriate remarks in Table 2.1.

Table 2.1. Evolution of Hydrothermal Technology with Time

Period	Focus	Equipment	Remarks
1850-1900	Mineral synthesis, imitation of natural conditions	Simple reactors, glass reactors, digestors	Lower growth rate, tiny particles, geological interest
1900-1940	Mineral synthesis, improvement in PT conditions, German domination	Morey autoclaves, flat closures	Lower growth rate, silicates, carbonates, Germany, Russia, France, USA, geological interest
1940-1950	Large size and large scale production of quartz, beginning of zeolites, clays, and micas	Test-tube type (cold-cone-sealed), welded closure modified Bridgman type	Cold-cone-seal type autoclaves made revolution, *PVT* diagrams systems
1950-1960	Phase diagrams for natural systems	Morey, Tuttle-Roy, welded closures, modified Bridgman	The dawn of modern hydrothermal research
1960-1970	Synthesis of technological materials, new inorganic compounds without natural analogues	New designs from USSR, commercialization of the autoclaves, improved sealing, larger size of the autoclaves	Russian School dominated, Japanese labs appeared

Table 2.1. *(Cont'd.)*

Period	Focus	Equipment	Remarks
1970-1980	A variety of new materials synthesis, ceramic processing in a bigger way, advanced materials	New designs, improved PT conditions, Grey-Loc sealing, Large autoclaves	Appearance of many hydrothermal labs in several countries
1980-1990	Decline in interest on hydrothermal research. Importance of the technique in materials science, physical chemistry of hydrothermal solutions		Japan organized 1st Int. Conf. Hydrothermal Reactions. Beginning of the entry of physical chemists
>1990	Diversification of hydrothermal technique, age of solvo-thermal, physical chemistry of hydrothermal solutions	Design of new reactors to suit the specific applications: batch reactors, flow reactors, and so on.	Entry of organic chemists, environmental scientists, fall in Russian domination and beginning of the Japanese domination

Today, the hydrothermal technique is being applied widely by various specialists from different branches of science including organic chemistry, biochemistry, biotechnology, food and nutrition, environmental safety, and so on, as shown in Fig. 1.9. These developments in hydrothermal research form the main theme of this book.

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