PRECIPITATION AND PATTERN FORMATION UNDER
FAR-FROM-EQUILIBRIUM CONDITIONS

DISSERTATION

Presented to the Graduate Council of the
University of North Texas in Partial
Fulfillment of the Requirements

For the Degree of

DOCTOR OF PHILOSOPHY

By

Peng Chen, B. S., M. S.
Denton, Texas
August, 1995
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Precipitates of a series of alkaline earth metal (barium and strontium) carbonates, chromates, phosphates, and sulfates were formed at high supersaturation by diffusion through silica hydrogel, agarose hydrogel, and the freshly developed agarose-silica mixed gels. The reaction vessels could be a small test tube, a recently designed standard micro slide cassette and a enlarged supercassette. Homogeneous nucleation is thought to have taken place, and particle development led to the formation of an unusual category of materials, known as Induced Morphology Crystal Aggregates (IMCA), at high pH under far-from-equilibrium conditions. Standard procedures were developed in order to produce homogeneous gels. Particle development led to characteristic style of pattern formation, which I have called monster, spiral, and flake. Among these IMCA, barium carbonate, chromate, and sulfate were moderately easy to grow. Barium phosphate was very difficult to grow as IMCA due to formation of poorly crystalline spherulites. IMCA of strontium carbonate, chromate and sulfate could be developed at high basic pH in the presence of silicate. Strontium carbonate sheet morphology displays a unique property, double internal layer structure, which was identified by backscattering electron imaging (BEI). Selected electron diffraction (SAD) revealed a new crystal phase which was called "Dentonite". Precipitate particles were isolated using a non-destructive isolation technique. Optical microscopy
was widely used to examine particles in situ and scanning electron microscopy and X-ray dispersive energy (EDX) spectroscopy were applied to particles ex situ, together with ESCA for surface analysis. Growth patterns were found to be strongly dependent on pH.

Other related pattern formation processes were also investigated including normal and dendritic structures, spherulitic structures and periodic pattern formation. Some interpretations were proposed in terms of mechanism.

Chemical additive effects were examined experimentally in the calcium phosphate system. The effect of external ionic strength was investigated, and it was found that a certain concentration of sodium chloride (0.2 M) approximately equals a fraction of pH unit (-0.2).
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CHAPTER I

THEORIES OF PRECIPITATION AND PATTERN FORMATION UNDER NEAR- AND FAR-FROM-EQUILIBRIUM CONDITIONS

1.1 Far-From-Equilibrium Phenomena

Equilibrium is really a very special situation. Chemical equilibrium is an absolutely dynamic state; bonds are continually being formed and broken. All reaction rates in the system are perfectly balanced in the equilibrium state, near which systems normally show relatively simple linear behavior. On the other hand, far-from-equilibrium phenomena are among in biological processes and have major scientific importance. Examples include precipitation behavior, chemical waves (Ross, 1984), animal pattern formation, biomineralization (Mann, 1983-1989; Pamplin, 1991), materials modifications (Heywood, 1992), the origins of life (Braterman, 1987; Cairns-Smith, 1985), some types of crystal engineering, and almost all biological processes (Williams, 1984; de Silva, 1991).

1.1.1 Aspects of Far-From-Equilibrium Phenomena

A system whose dynamics is described by nonlinear kinetic laws is termed as a far-from-equilibrium system which can be characterized as breaking expected symmetry in time and/or in space. Such systems have been studied under other
circumstances, away from very restricted equilibrium conditions. So, it is not surprising that such investigations could reveal a much wider range of possible behaviors. Classical thermodynamics makes few restrictions and gives little guidance to the possible behavior under far-from-equilibrium conditions. Among well-known recognizably nonlinear phenomena is the Belousov-Zhabotinskii oscillating reaction in a closed or open system. A closed system here means a system which can exchange energy but not matter. An open system is one that can exchange matter and energy with its surroundings. An example is the Continuous Flow Stirring Tank Reactor [CSTR], in which certain chemicals are pumped in and precipitated out so as to keep the concentrations in solution as constant as possible.

Inorganic precipitates, particularly highly insoluble inorganic materials, commonly show pattern construction, such as Liesegang ring formation, a form of spatial patterning which reduces the homogeneity of a system (Stern, 1967). Liesegang ring formation is a characteristic diffusion-reaction process under far-from-equilibrium conditions. It has been found in almost all varieties of chemical reaction systems, ranging from gas phase reactions to alloy melting processes, as long as diffusion boundary conditions are satisfied (Field, 1985, 1989). Liesegang rings formed in oxidation-reduction reaction systems can also be easily observed in a laboratory.

Recently, Henisch has developed microcomputer simulations for Liesegang rings using both the competitive growth and the reaction-diffusion model (Henisch, 1991). In the competitive particle growth model, the smaller size particles have higher
solubility. If both small and large size particles are in the same system, large ones will become larger, and small ones will become smaller until they completely disappear. Hypothetical experimentation in diffusion related systems can be simulated by his programs. This work catches the growing trend of using computer simulations to supplement real world experiments; NASA and the Pentagon are already conducting many investigations such as space shuttle development and new tactical nuclear weapons testing using only computer simulations. As Henisch indicates, many results can not be intuitively predicted, simply because they are the consequence of complex interactions between the various descriptive parameters of the modelled system. For example, in the Liesegang ring simulation, the first ring will survive to the final stage while many others will vanish.

1.1.2 Diffusion and Fick's Laws

Diffusion is the transport of dissolved material as a consequence of the casual character of the thermal motion of molecules. If the transport of material through the medium is what controls particle growth velocity, this is defined as a diffusion controlled crystal growth process. One characteristic of this process is that polydisperse precipitates tend to become more monodisperse. Some such processes are effectively irreversible, for example the formation of highly insoluble inorganic precipitates. More detailed studies must consider particle size distributions as well as individual shape (Grindrod, 1991).

Diffusion controlled processes are an important class of transport-controlled
processes in nature (convection is another transport controlled process). Diffusion-controlled processes may generate numerous patterns. They can be contrasted with reaction-controlled processes, where many collisions occur before each event. Slow diffusion processes always lead to more perfect nuclei. One feature of diffusion-controlled particle growth is that the shapes will depend strongly on the shapes of the original seed or nucleus. Also, edges and corners have a tendency to grow faster than centers of the faces when diffusion is controlling the growth rate (Langer, 1980, 1989).

In any situation where a concentration gradient exists, diffusive processes will work to remove that gradient. Such a process is called Brownian Diffusion. Brownian Diffusion is a totally random walk process at the molecular level. Furthermore, local diffusion (or secondary, such as membrane in this study) also makes the situations even more complicated. Overall diffusions actually contain Brownian and local Brownian processes.

The flux of material, $F$, across an interface is defined by Fick' first law:

$$F = - D \frac{\partial c}{\partial x}$$

where $D$ is the diffusion coefficient (with units of length $^2$ time $^{-1}$) and $\partial c/\partial x$ is the concentration gradient. The negative sign indicates that the flow of materials proceeds down the concentration gradient, i.e. from high to low concentration. The diffusion coefficient $D$ is generally dependent on temperature. Experimentally measured diffusion coefficients $D$ over a wide range of temperature often fit and can be expressed by the Arrhenius equation as:

$$D = D_0 \exp(-Q/kT)$$
where \( D_0 \) and \( Q \) are to a first approximation independent of temperature (Ghez, 1988).

However, Fick's first law does not directly show the variation of flux \( F \) in terms of time. Now, if the flux \( F \) is differentiated with respect to time and after a series of rearrangements (see e.g. Henisch, 1988), Fick's second law of diffusion for one dimension is obtained, and can be expressed as:

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}
\]

Fick's second law cannot in general be solved exactly analytically when material is being removed from the system, e.g. by precipitation. However, given recent advances in computation, it is sometimes possible to find realistic numerical solutions with reasonable precision. The iteration method is a common mathematical technique used to solve the diffusion equations. The solution is not exact since it neglects the influence on the concentration field from neighboring particles.

1.2 Survey of Precipitation

Precipitation of particles is of wide interest. Applications include preparation of new ceramics, new composite materials, cements, supported catalysts, and geological diagenesis and cementation. Precipitation of inorganic materials is a process in which a new, solid, phase is formed-usually as a result of a chemical reaction of at least two components contained in the original phase. For low solubility materials, this process is typically characterized by high relative supersaturation ratios (1.3, below) [up to several thousands, e.g. iron oxide] compared with the low relative supersaturation [0.001 - 0.1] for an ordinary crystallization process. Perhaps due to
the high supersaturation, contemporary opinion on this process is much more uncertain and divided (Mullin, 1972).

1.2.1 Induced Morphology Crystal Aggregates (IMCA)

The term "Induced Morphology Crystal Aggregates" or "IMCA" was introduced by Juan-Manuel Garcia-Ruiz in 1979 (1979-1994) to describe strangely shaped particles of barium carbonate grown by precipitation in silica gel. Currently, it is believed that there are three important factors which contribute to IMCA formation. First of all, silica is a necessary component. Second, the cation of the insoluble material must apparently be an alkaline earth, i.e. Ca, Sr, Ba; many transitional metal ions have been attempted in experiments with no definite evidence for IMCA. Third, the pH plays a central role (Dominguez, 1986, 1987).

1.2.2 Distinctive Properties of Silica

Over the last few decades, silicon (as silica or silicate) has been recognized as an essential trace element in the formation of bone, teeth, cartilage, and connective tissue in mammals as well as participating in several other important mammalian metabolic processes. In addition, silicon has been implicated as the causative agent in silicotic lung diseases and cancers. Silica is unique among plant materials, both for the baroque beauty and endless variety of their siliceous "shells" or frustules and for the absolute dependence of many species upon silicon for growth and development (Simpson, T. L., 1978).
1.3 Supersaturation

Supersaturation of a system may be expressed in many different ways, but the most common dimensional expressions are the concentration driving force $\Delta C$, $\Delta C = C^* - C$, which is also called absolute supersaturation. The supersaturation ratio SSR can be expressed as: $SSR = C^* / C$ (which is dimensionless). Alternatively, the relative supersaturation ratio can be expressed as $\delta = \Delta C/C = (C^* - C)/C = SSR - 1$, or $\delta = \Delta C \times 100\%/C$, where $C$ is the equilibrium saturation, and $C^*$ is the concentration of the solution at the given temperature (Myerson, 1990). The driving force of diffusion in a chemical concentration gradient is due to the bulk thermodynamic quantities, such as chemical potential gradient in nonideal solutions (Vere, 1987).

The behavior of newly created nuclei in supersaturated solutions depends on their size. They can either grow or redissolve, but the process they undergo should result in a decrease of the free energy of the system. Particles or nuclei with radii smaller than $R^*$ (critical radii, Figure 1.1) will dissolve. The size of the critical nucleus is dependent on temperature, since the volume contribution of free energy is a function of supersaturation, and, normally, the size of the critical nucleus will increase with temperature (Smith, D., 1990).

During the nucleation process in solution as described in Section 1.4, a second phase is being created as the solid phase. Assuming any nucleus is spherical with radius $R$, and if $-A$ is the contribution per unit volume of the Gibbs free energy of the nucleus, and $B$ is the contribution per unit area of the spherical surface energy at the interface of the nucleus, the overall Gibbs free energy in nucleation can be expressed
as:

\[ G = 4\pi BR^2 - \frac{4}{3} \pi AR^3 \]

Differentiating \( G \) in terms of \( R \) gives

\[ \frac{dG}{dR} = 8\pi BR - \frac{4}{3} \pi AR^2 \]

and letting \( \frac{dG}{dR} = 0 \) for a critical nucleus of radius \( R^* \) gives

\[ R^* = \frac{2B}{A} \]

Hence,

\[ G(R^*) = \frac{16\pi B^3}{3A^2} \]

The coupling between the surface and the curvature of the interface yields the thermodynamic measurement of supersaturation (SSR) which can be expressed by the Gibbs-Thompson equation in the general form:

\[ R^* = \frac{2mB}{kdT \ln(SSR)} \]

where \( d \) is density, \( k \) is the Boltzmann constant, \( T \) is absolute temperature, \( m \) is molecular weight. At this level, it is clearly seen that the driving force has to be provided by supersaturation to overcome the Gibbs free energy barrier (Figure 1.1).

Supersaturation is a necessary requirement for crystallization thermodynamically, but it is not a sufficient one. For example, some solutions never crystallize spontaneously even at maximum supersaturation due to their chemical nature. The maximum supersaturation is the supersaturation limit that can be reached under given conditions. The value of maximum supersaturation depends primarily on the nature of the solute and solvent as internal factors. Nevertheless, external factors also dramatically affect this value. Those factors include temperature, various
mechanical effects, electrical fields, light irradiation, ultrasound, cooling rate, stirring speed, and impurities (Khamskii, 1969).

Figure 1.1. Schematic representation of the Gibbs free energy change $dG$ as a function of size illustrating the nucleation process (Henisch, 1988, p.94).

1.4 Theory of Precipitation

The formation of chemical precipitates consists of at least three stages: nucleation, growth, and the stable stage. The most important stage which dominates the properties and characteristics of precipitation is the nucleation process. Nucleation is a process of higher order than is crystal growth, and requires higher supersaturation. Indeed, nucleation is the predominant process at high enough concentration. In addition, most behavior development has been done at this interval of time.
Essentially, two major nucleation processes can be discerned. These are the primary nucleation process which include homogeneous nucleation (spontaneous) and heterogeneous nucleation (induced by foreign particles), and secondary nucleation consisting of induced (by crystal) nucleation (Khamskii, 1969). At high supersaturation, the precipitated particles are usually small in size and large in numbers. The driving force for precipitation is still determined by the activity coefficients of important species in solution.

It is still unclear how chemical precipitates are formed. However, some very advanced techniques such as femtosecond ($10^{-12}$ s) laser spectroscopy might provide the right approach for studying their formation in depth through the examination of their interface. (Liu, 1993)

1.4.1 Nucleation

Nucleation phenomena are relevant to many branches of science from crystal growth and particle formation to the microphysics of clouds. Nucleation is the elementary process leading to the formation of crystals and particles in general. The groundwork on nucleation theory and phase transitions was done by Raleigh and J.W. Gibbs during the early part of the 20th century; utilizing a thermodynamics basis (Abraham, and references thereafter, 1974). The classical concept of crystal nucleation was based on the assumption that fluctuation in the supercooled phase can overcome the nucleation barrier caused by the surface of the nuclei. Nucleation processes are described by the Boltzmann distribution, that is, the nucleation rate increases rapidly
with decreasing temperature over a relatively narrow temperature interval due to the rapid decrease in $\Delta G$ which is closely correlated to temperature. The major pioneering studies were done by David Turnbull at Harvard (Cargill, 1987). His work laid out the experimental and theoretical foundations of contemporary nucleation theories in great detail (Cahn, 1987). Nucleation is a fundamentally important process which determines the number, size, structure and morphology of precipitated crystals. Unfortunately, our understanding of the nature of such precipitation formation is by no means complete. Part of the difficulty stems from the fact that individual nuclei are too small to be treated by bulk thermodynamic theories and to be detected by normal scattering techniques. But they are also too large to be treated by individual atomic concepts and be fully characterized by techniques such as conductivity measurements.

The Gibbs energy is required to form stable nuclei whether they are spherical or others from homogeneous medium which is a thermodynamic barrier of nucleation. The critical radius on top of this energy barrier can be expressed as:

$$R^* = \frac{2mB}{kdT \ln(SSR)}$$

Clearly, the greater the degree of supersaturation, the smaller will be the size of the nuclei (1.3, 1.4). For the most complicated systems, the treatment of nucleation contains numerous limitations. The first and most obvious is reached for high supersaturation. In the case where the critical nuclear radius $R^*$ is reduced to the order of only a few unit cells, the interaction between opposite surfaces must give rise to a unit surface free energy which is size dependent. Also, many of the simplifications included in the expression are only suitable for reasonably large numbers of molecules.
A second limitation is the assumption of a strictly crystallographic growth, permitting the use of the crystalline product thermodynamic data as measurements from macroscopic experiments. The initially crystallized material may not have sufficient perfection for these substitutions. Finally, the limitation of the nuclei to the equilibrium shape (well-behaved, only one theoretically stable shape, ideal shape) neglects other possible nucleation directions. Although those nonequilibrium shapes are less probable, their number may be large, and in the final analysis the magnitude of higher activation energy may be more important than the single lower energy pathway.

Binsbergen (1972) has made an attempt to try to describe the nucleation process taking into account all possible routes. His calculations are based on a molecular model for primitive cubic crystals. However, no critical size parameters could be given since the nuclei did not correspond to equilibrium shapes. Classical nucleation theory can explain many experimental results adequately except for shape, which unfortunately is the property that dictates early particle morphology.

Figure 1.2. Schematic representation of concentration variation as material is added to a system before and after nucleation as a function of time.
1.4.1.1 Homogeneous Nucleation

Any crystal must have its beginning as a small crystal with a large specific surface area. This initial process leading from the solution to a growing crystal is called primary nucleation or homogeneous nucleation. A primary nucleus must be formed via a path of positive $\Delta G$ before a thermodynamically stable crystal of sufficient size can be grown. This maximum in $\Delta G$ corresponds to the critical size nucleus, or cluster. Nuclei with a negative $\Delta G$ are called stable nuclei or microcrystals. This breakdown of the overall crystallization into a nucleation step followed by growth is described in the literature on crystallization (Abraham, 1974).

The Gibbs Free Energy ($\Delta G$) barrier to crystallization can only be overcome by a local random fluctuation of order. The larger the required critical size of the nucleus, the longer will be the time needed for the primary nucleation process (Gordon, 1959). Experimental evidence such as supercooling or supersaturation is required. The rate of homogeneous nucleation is comparatively slow. This occurs not only because it is in a homogeneous solution environment, but also because it is related to solid-liquid phase transformations. Therefore, it is not surprising that the maximum level of nucleation rate is critically dependent on the ease with which the crystallizing unit can cross the phase boundary. Brostow has an excellent thermodynamic treatment of classical nucleation processes (1985).

1.4.1.2 Heterogeneous Nucleation

Primary nucleation is called homogeneous nucleation as discussed above if no
preformed nuclei or foreign surfaces are involved. A foreign surface frequently reduces the nucleus size needed for crystal growth since the creation of the interface between crystal and substrate may be less hindered than the creation of the corresponding free crystal surface. The resulting enhanced nucleation process is called heterogeneous nucleation. A heterogeneous nucleation course makes use of a foreign preexisting surface to reduce the free energy opposing primary nucleation. Then, following the theory outlined in Section 1.3.1.1 for homogeneous nucleation, the critical nucleus is smaller if there is a reduction in free energy when the nucleus contacts a preexisting surface. A lower overall free energy of nucleation, $dG^*$, would then lead to a faster nucleation rate. Most macromolecules are crystallized through heterogeneous nucleation processes. Such crystallization requires a lower degree of supersaturation.

Much of the specific mechanism of the heterogeneous nucleation process is still unclear. As reported in experimental results in the literature, heterogeneous nucleation in steps, cracks, holes, or other surface irregularities would be more advantageous than heterogeneous nucleation on a flat surface which has a smaller available interfacial area (Bond, 1975).

Heterogeneous nuclei are usually larger in size and should be easily recognizable by their morphologies. The process of heterogeneous nucleation described by the classic concept also illustrates the strong temperature dependency of the number of active nuclei. In heterogeneous nucleation, foreign particles help to create new solid phase nuclei and reduce the surface energy to decrease the necessary
Gibbs free energy by lowering the critical radius. Therefore, little supersaturation is necessary.

1.4.1.3 Other Nucleation Processes

In addition to the primary nucleation described above, secondary nucleation also plays an important role especially in the crystal growth stage; and many individual factors can affect this process such as temperature, stirring, supersaturation, crystal size etc.. However, this kind of nucleation is much more complicated than expected and is not as critical in most cases either morphologically or thermodynamically. Nucleation from the presence of crystals in supersaturated solutions is called secondary nucleation. According to Nyvlt, three groups of secondary nucleation processes can be further separated (1985). The first is Apparent Secondary Nucleation in which seeding can be accomplished with crystal dust, polycrystalline breeding or macro abrasion. The second is True Secondary Nucleation, a process which includes three different formations of nuclei (from solid phase, i.e. crystal seeding; from a dissolved substance in solution; from the transition phase at the crystal surface). The last one is sometimes called Contact Nucleation, which is characterized by the heterogeneous nucleation on a surface. A typical example is nucleation by a glass rod in solution. Small molecules are different from macromolecules in their nucleation behavior because of their size. For example, homogeneous nucleation may not take place in macromolecules which are 5 to 10 nm in size. Very often, self nucleation and/or heterogeneous nucleation processes are
more important for these macromolecules (Wunderlich, 1973, 1976).

Self-nucleation is particularly important for macromolecules because of a large temperature range in which crystals do not melt, but even nucleated melts do not crystallize. Crystals for self-nucleation can also be created on deformation which shifts the melting point of macromolecules to higher temperatures because of rubber-elastic effects. Turnbull proposed that crystal fragments grown in small cracks of a foreign surface may have an elevated melting point and thus survive the initial dissolution or melting of the bulk of the polymer and serve as nuclei on subsequent cooling (Cargill, 1987). Once formed, nuclei remain active until they are dissolved by heating above their dissolution temperature. Low molecular weight solutions which lack high molecular weight fractions may perhaps show self-nucleation by several molecules as was suggested by Blundell (1968). This is similar to small molecule nucleation behavior where it is difficult to overcome the energy barrier to form nuclei.

1.4.2 Growth of Precipitates

During crystal growth, a phase transformation occurs, connected with mass transfer from the original phase. This is an extremely complicated process related to the boundary between two entirely different phases, at which properties change drastically. Therefore, the crystal growth stage is much more important than the ultimate, most stable stage. Crystal growth is a surface phenomenon strongly influenced by adsorption which, as a consequence, may change the crystal shape. For crystals of fixed mass, one shape has a lower surface free energy than others. This
gives the equilibrium shape of the tiny crystals. However, particles do show different shapes at the same temperature, only one of which can be the equilibrium shape. In most cases, the shape of a crystal is not the equilibrium shape but is determined by the dynamics of its growth.

The formation of a finely divided precipitate is not the end of the process thermodynamically. The system tends to shift the thermodynamic equilibrium until all the precipitates are gathered in one crystal to reach the minimum total surface free energy. The transformation towards this final equilibrium state is called ripening, or secondary growth. Ostwald ripening is one of the processes involved in which smaller particles are dissolved and larger ones grow (larger swallows smaller). This is a very common phenomenon in crystal growth. Coagulation is another secondary crystal growth process in which particles come into contact and adhere to form larger ones. Coagulation is totally dominated by Brownian motion in nature.

The crystal grows by the deposition of ions layer upon layer. Each layer is made up of rows and each row is formed by the deposition of ions, or low order aggregates. There are several known processes, of which two are most important. The first one is nucleation controlled growth. This involves a mononuclear layer and dominates when the rate of growth is a fraction $[1/6]$ of the diffusion controlled rate. A growth rate between $1/6$ to $1$ is a diffusion controlled, polynuclear layer dominated process. Some experimental results support these processes (Nielsen, 1964). But the most common type of crystal growth is the dislocation controlled process. Dislocations may arise spontaneously, just as surface nuclei do, or originate from some
unpredictable event during the early stages of the growth process. Intergrowth of crystals filling up in a dendrite with occasional misfits when the branches meet, or growth around a foreign particle or on a foreign nucleus, will give inexact matching between lattices (Rao, 1985). Some earlier experiments have shown that growth spirals quite often are Archimedean rather polygonal (Nielsen, 1958). The spiral step (one step-up distance, or one layer) as the rate determining step is defined as the dislocation controlled growth process, at least in microscopic and especially submicroscopic crystals. The growth spiral may be rate determining at measurable supersaturation (Nielsen, 1964).

![Figure 1.3. Dislocation-controlled spiral crystal growth (Verma, 1953, p.155).](image-url)
1.5 Pattern Formation

Fundamental research focusing on pattern formation has important significance for humankind. Special structures can be seen from pattern configurations of objects ranging from snowflakes to galaxies (Ponman, 1992). Some of the patterns can be described well by the language of Euclidian geometry, particularly those with regular shapes. There are many important spatial patterns found in nature and in the research laboratory which are either irregular or fragmented; these are difficult to describe using Euclidian geometry. Fortunately, recent mathematical progress provides alternative concepts and possibilities to describe those special geometries. However, to draw clear lines between those different concepts is enormously difficult (Young, 1986). Furthermore, pattern formation and crystal organization are relevant to topics such as the origin of life, order from chaos, turbulent problems... and so on. They are all extremely important issues to our future guiding the deep space search (criteria should be set to guide purposely search). Life is not just a collection of structures, but also a collection of processes. The origin of life, and the development from uncomplicated structures to complicated structures, from primary processes to manifold processes, has taken place over long periods of evolution. Life itself is certainly an extremely complicated subject for sure (Quin, 1988). Between these long periods of evolution, some processes may disappear after stages in which they are featured are completed. But what kind of driving force is necessary to make them take place? Is every system capable of evolution (Braterman, 1986)?

Any inequality in the diffusion coefficients can support pattern formation over
some range of experimental far-from-equilibrium conditions. These instabilities are induced by the inequality of the diffusivities. Turing first noticed this instability which is caused by diffusion driven instability in a closed system (1952). It is a typical case of chemical diffusion pattern formation. In general, pattern formations, especially those not permanent to space, are conceptually different than permanent pattern formation of objects unless space and time are seen as parameters, as may be happening at a moving interface.

1.5.1 Self-similar Structures

That there is no characteristic length scale (no fixed length) in the system is the most profound property of fractals. This is called the self-similarity. In other words, every piece of a fractal looks like the whole fractal. Fractal formation is the same as self-similar formation in nature. One of the most important characteristics is the system's initial condition which has a dramatic impact in determining the pattern formed (Avnir, 1989).

Since the term "fractal" was first introduced by Benoît B. Mandelbrot in 1970s, this relatively fashionable branch of science has undergone great changes. From astronomy to the biological sciences, some kinds of unpredictable irregularities in natural phenomena can be studied with fractals. The fractal geometry concept is very different than Euclidian geometry and topology (Mandelbrot, 1977, 1990). Fractal concepts cannot be explained in terms of the classical concepts of Euclidian geometry which is based on three fundamental elements (point, line and surface) to describe.
everything. On the other hand, fractal geometry is expressed by a noninteger
dimensionality, such as 1.200, 2.610, 2.800 and smaller dimensionalities as 0.3, 0.5
etc. This mathematical language uses non-integer dimensions to widely describe
irregular shapes such as mountains, trees, coastlines and other unusual shapes which
cannot be described by Euclidian geometry. Strictly speaking, the ideal fractal has a
self-similarity property. A natural fractal that only has a statistical sense is not
actually self-similar overall but can be considered as statistically self-similar because
every level has the same basic structure (Feder, 1988). There are two major important
properties of fractals: self-similar features and embedding dimension. Self-similar
features are scale invariant as described above, i.e. the magnification of any part of a
fractal, will appear the same as the original, even after multiple magnifications.
Typical properties of fractals are related to their volume with respect to their linear
size embedding dimension. Fractals are actually a class of highly irregular shapes that
have myriad counterparts in nature, such as islands, continent, coastlines, snowflakes,
and pulmonary membranes. Fractals can be treated mathematically; classical fractals
include Brownian paths, Cantor sets, and Koch curves. The Hausdorff dimension is
the main parameter of a fractal (Mandelbrot, 1982). Hausdorff dimension serves as an
excellent measure of irregularity and fragmentation and gives meaning to ideas such as
curves of dimension greater than 1 and surfaces of dimension greater than 2 (Vicsek,
1989).

Ronald Hoffmann frequently mentions that chemistry is about shapes, how
things look, how things fit together, and how shapes change. Therefore, the fractal
concept could provide another alternative to describe chemistry, but it has a very long way to go. Thousands of different shapes of snowflakes can be found in the book of Bentley and Humphreys (1931). Even after many years of investigation, the formation of snowflakes as a general interesting subject remains unknown in terms of formation mechanism (Mulvey, 1981). The diversity of natural patterns can be very difficult to control because the exact conditions can not be known, but all the snowflakes have six sided stable symmetric structures (Berry, 1969). This is a very suitable example to show that nature is imperfect and complicated as well as beautiful (Burke, 1966).

1.5.2 Dendritic Structures

An intricate tree-like evolution morphology with a main branch and regularly spaced side branches is termed a dendritic structure. It is a very common form of growth observed during the solidification of isotropic or mildly anisotropic materials (Tirmizi, 1989). Also, it is a typical example of spontaneous pattern formation in nature which occurs during unstable solid-liquid or solid-vapor interface reorganization. Dendrites are complex time-dependent solidification fronts which have a fractal appearance and properties. Dendritic growth is inherently a dynamically unstable process (Chopard, 1991; Couder, 1990). Glicksman has pioneered the study of dendritic growth and structure over a number of years (1976-1987). The growth direction and morphology of a dendrite can be influenced by concentration and fluid flow if such growth is in melting solution. Dendrites growing independently of a solid substrate always grow in well-defined crystallographic directions whether it is a free or
enforced growth. But recent studies have shown the existence of non-crystallographic
dendritic growth (Fabietti, 1992). This is a newly found growth habit under certain
experimental conditions of restricted growth. Dendritic crystal growth is traditionally
assumed to be a signature of diffusion-controlled growth (Chan, 1976). However,
mineral dendrites are formed by an irreversible chemical reaction and hence have an
appearance similar to the clusters of diffusion-limited aggregation rather than to the
branched form of the dendrite growth. The fractal properties of mineral dendrites have
been frequently reported (Chopard, 1991).

1.5.3 Spherulitic Structures

Spherulites are polycrystalline aggregates with approximately radial symmetry.
They are commonly formed by minerals crystallizing from viscous magma and
devitrifying phase (Goldenfeld, 1987), but can also form in solution under conditions of
high supersaturation. Close inspection of those spherulites reveals that they are
actually comprised of a radiating array of primary crystalline branches with small,
non-crystallographic angles. Secondary branches build up with different
crystallographic orientations from the primary branches. Many-order branching often
occurs to form a final space-filling structure as large as a few microns or more in
diameter.

As reported earlier, growth environments such as crystalline anisotropy arising
from the presence of a crystal lattice play an essential role in spherulitic dynamics.
Goldenfeld (1987) assumed that in the absence of anisotropy, surface tension and
diffusion can give a qualitative account for the formation of spherulites, because non-equilibrium kinetic effects can cause the radius of the growing crystal to be linear in time. The structure expected for weak or zero anisotropy is characterized by multiple tip-splitting. This accounts for the non-crystallographic branching. Nucleation-controlled growth is a dominant feature of spherulitic growth for both two and three dimensions. Many experiments have already proved this point. That is, the final morphologies can result from the growth dynamics of the interface and are dependent on driving force and anisotropy strength. It is concluded that spherulitic growth is the stage reached from dendritic growth at even higher concentration (Ben-Jacob, 1986-1990). This is due to the well-observed Dense Branching Morphology [many more branches outside of a nucleus]. The progression of the most commonly observed diffusion controlled crystal growth under increasingly nonequilibrium conditions is as follows:

**Dendritic Growth ===> Dense Branching Growth ===> Spherulitic Growth**

1.5.4 Self-organization

The processes in an open system by which structure evolves from physical chaos [defined as irregular motion stemming from deterministic equations], so that the system arrives at a state of higher order, are called self-organized processes. Self-organization is the autonomously sorting out of a system, even an initially uniform one, into regions that are patterned relative to a physical or chemical property. The key factor is that this sorting out comes from the internal dynamics of the system, not
from an outside force. Self-organization is the spontaneous and autonomous passage of a system from a more or less uniform state into a pattern. Self-organized pattern formation is common in geology. Wind blowing across the desert, creating evenly spaced ripples in sand, is an example. And many rocks contain mineral patterns produced by a mechanism of self-organization in nonequilibrium systems (Nicolis, 1977).

The fundamental theories of self-organization have been developed mainly by the Brussels School of Ilya Prigogine and the German School of Hermann Haken (Prigogine, 1984). Briefly, as a chemical description, self-organization requires both far-from-equilibrium conditions and an autocatalytic step (Haken, 1983). An autocatalytic step is a chemical reaction in which a molecule of kind A reacts with a molecule of kind U to produce an additional molecule U. Since the molecule U is produced by the same molecule U as catalyzer, such a step is normally called an autocatalytic step (Soltzberg, 1989). It can be expressed as: $A + U \rightarrow 2U$.

1.5.5 Periodic Pattern Formations

Periodic pattern formation has two categories. One is the permanent pattern formation in space. The other is the temporal pattern formation in time. Based on recent scientific studies, it is suggested that Liesegang rings are pattern formation in space, whereas the ordered pattern formation out of chaos is a temporal one in the B-Z (Belousov-Zhabotinsky) reaction.

Liesegang rings are named for the German physical scientist Raphael Eduard
Liesegang, who, in 1896, observed and studied the concentric ring of silver dichromate which formed when he added a drop of concentrated silver nitrate solution to a glass plate coated with moist gelatin gel impregnated with potassium dichromate. Since then, this phenomenon has been investigated widely and intensively. Many theories and explanations have been proposed for Liesegang ring formation. Basically, it is believed that diffusion processes predominantly control the formation of Liesegang rings. Henisch's new book focuses on periodic precipitation by using computer modelling to solve and produce excellent results (1991). He uses Fick's second law as a core and solves the diffusion equation numerically in terms of some critical parameters such as the solubility constant, the diffusion constant, etc. (Hedges, 1932).

Liesegang rings can be found in almost all types of chemical reactions, from substitution to reduction - oxidation, and in all three normal states, i.e. gases, liquids, and solids. Figure 1.4 is a photomicrograph of typical Liesegang ring formation by CaCl$_2$ diffusing into agarose gel loaded by Na$_2$HPO$_4$ at pH =10.0 at constant room temperature in a supercassette. Patterns formed in this way are extremely sensitive to many variables and parameters, including temperature, external electric field, light, X-ray radiations, UV light, initial chemical concentrations (Baird, 1988), pH, and pressure. These variables can affect Liesegang-ring formation individually or in combination (Stern, 1954, 1967). The macro structure of Liesegang rings is suggested to be mainly a post-nucleation process but subject to the experimental conditions (Ross, 1984). Therefore, particle formation and/or nuclei distribution remains a crucial factor in the ring formation. In these studies, temperature was strictly controlled to
Belousov oscillating reactions, on the other hand, are quite remarkable chemical reactions with oscillating chemical and physical properties. These properties reflect the variations in terms of concentration of some chemical intermediates undergoing oscillations in time. The most important thing is that these reactions do present distinctive spatial patterns in time. It was first reported by the Russian natural scientist B. P. Belousov in 1951 for the cerium ion catalyzed oxidation of organic acids by bromate ion showed oscillatory behavior (1958). A decade later, Zhabotinsky continued the study of these unique reactions (1964; Zaikin, 1970). Such oscillating reactions change physical and chemical properties periodically and also lead to the formation of spatial patterns. Those extraordinary but widespread characteristics have encouraged other scientists to continue the investigations. And pioneer theoretical works by Ilya Prigogine have been recognized (Field, 1985). B-Z reactions are good models for symmetry-breaking pattern formation and they also have very wide range potential applications.

B-Z reactions are typical examples exhibiting not only oscillating behavior, but also very important temporal pattern formation during chemical reactions. Those spatial pattern formations are closely related to the system chaotic behaviors which are critically important to modern science. B-Z reactions as part of chemical chaos already exhibit rich structures in nonlinear dynamics. Very recent computer simulations of spiral waves are in full agreement with experimental results (Markus, 1992). And some precipitates system have oscillating behaviors (Chapter IV).
Chemical oscillation behavior may be driven by an overall decrease in the Gibbs free energy in the reaction system when reactants are converted into the final products. Such systems are far from thermodynamic equilibrium and should treated by the laws of irreversible thermodynamics or other chaotic theories. Nevertheless, the minimum requirements have been determined and applied to all reactions with oscillatory behaviors. First, chemical reactions must be far from the equilibria as previous mentioned. Second, chemical reactions must have an autocatalytic step. And finally, chemical reactions must be able to exist in at least two steady states (Dee, 1988).
1.6 Perspective of Pattern Formation

Other than ordinary crystalline microstructure, the quasi crystal structure has been brought to attention recently due to its unique scientific curiosity (Senechal, 1990). Meanwhile, crystalline pattern formation from a very different perspective has been explored as the stationary spatial pattern formation (Winfree, Ouyang, 1991). Universal pattern development in nature, such as tree shapes, pattern of leaves, animal leather pattern and some biological patterns, as well as many others, could someday be predicted. Partial explanations may be based on the symmetry breaking instabilities of a uniform state of precipitation, and in particular, of the particle size distribution (Melton, 1991).
CHAPTER II

ANALYTICAL TECHNIQUES

2.1 Conventional Polarized Light Microscopy

The optical microscope is used to provide a magnified image of an object which allows one to visualize very fine details of both the texture and internal structure of an object with a selected degree of resolution (Determann, 1982). Modern light microscopy can now be combined with laser, electronic camera and digital image analysis techniques to provide the most advanced instrument with innovative ways of seeing the microscopic world (Taylor, 1992).

2.1.1 Conventional Light Microscopy

The Conventional Light Microscope (CLM) is a primary optical instrument with a very long history. The Wild Leitz LABORLUX 12 POL microscope was used for these studies. Figure 2.1 is a diagram of a typical optical microscope; its working principle is easy to understand. Illumination from the source (e.g. a strong halogen lamp) is reflected by a 45 degree mirror, then controlled by a field diaphragm and aperture iris, and finally passed through the condenser to generate a very uniform, strong light. The light transmitted to the sample reaches the object lens to form the intermediate image, which is then magnified further by a eyepiece to appear as the
magnified final virtual image; this can be detected by any device including human vision (right half of Figure 2.1).

CLM is exceptionally easy and quick and can handle all sort of samples for study without any sample damage (Smith, R., 1990). It takes from 30 minutes to several hours per specimen (including preparation). Satisfactory resolution of topographic or microstructural features or texture at magnifications ranging from 1 to 1500X can be obtained (40 to 1000X is most common, Simpson, D., 1988). CLM was used on almost all the samples studied in this work, particularly for in situ observations which provide invaluable information. When a camera or image caption system was attached to the CLM, a hard copy was obtained. Some black and white micrographs were taken with this type of microscope with a 35 mm camera attached.

Figure 2.1. Diagrammatic Conventional Light Microscope (from Abramowitz, p.2).
A weakness of the CLM is the resolution limitation. Approximately one micron or less for CLM will be the best result in practice. The minimum distance, $d$ or Rayleigh distance by which two points must be separated to be distinguished when illumination is incoherent can be written for a microscope of standard dimensions as:

$$d = \frac{0.61\lambda}{\sin \theta}$$

where: $\lambda$ is the light wavelength, and $\theta$ is the numerical aperture. To calculate the range resolution $d_z$ of an optical microscope, an approximate formula is (Corle, 1986):

$$d_z = 0.45\lambda/[1 - \cos \theta].$$

A typical range resolution is 0.5$\mu$m for an object lens of numerical aperture 0.90 at $\lambda$ = 633 nm. Also the limited depth of field is another limitation: CLM cannot focus on rough surfaces; but this can be overcome with the new generation Tandem Scanning Confocal Microscope (TSM). In addition, CLM does not provide any direct chemical or crystallographic information about the microstructural features of samples (Abramowitz, 1985).

2.1.2 Polarized Light Microscopy

The Polarized Light Microscope (PLM) essentially is the same as the conventional optical microscope. Only two additional key parts are located above and below the sample. One is the polarizer which is located below the sample. Its function is to generate a uniform polarized light which then passes through the sample and is observed by the analyzer located above the sample (Figure 2.2).

The Wild Leitz LABORLUX 12 POL microscope was used for these studies.
Many color micrographs were obtained with this instrument. An Olympus OM-4 TTL (Through The Lens) auto exposure SLR camera body was used with special cross hairs-clear field type focus screen (I-12). The camera body was directly mounted to the microscope by an Olympus mount tube. Also, the Olympus "Recordata Back 4" facility was used for recording time, date, year and series numbers. Film exposures were controlled by two different built-in silicon exposure meters:

1]. Average light measurement: TTL direct "off-the-film" light measuring with aperture-preferred electronic shutter exposure control at speeds from about 1 minute to 1/2000 seconds.

2]. Spot light measurement: TTL spot metering memory system. The exposure control range required was at about 4 minutes to 1/2000 seconds. Measured area is about 10% of entire view finder.

The crystallinity of materials studied were observed by PLM. The texture of crystal aggregates as well as internal structure were examined by transmitted polarized light (Figure 2.2). A wavelength plate (called compensator) was inserted to compensate for color variance observations. The principle behind their use is relatively simple to understand. When the direction of light vibration of the object and inserted wavelength plate (compensator) corresponding to the higher refractive index are parallel to each other, the total phase difference observed will be increased. However, if the two vibration directions corresponding to the higher refractive index are vertical to each other, the complete phase difference observed will decrease. The operation manual provides further details (Bradbury, 1989).
Figure 2.2. Diagram of Polarized Light Microscope (Determann, 1982, p.24).

2.2 Tandem Scanning Confocal Microscopy (TSM)

This new generation optical microscope emphasizes the resolution, accuracy and sharpness of the image both for internal and surface structure. The thickness of a sample can be precisely measured by TSM on a sub-micron scale directly and quickly, and without any damage to the sample. Also, very clear internal structures can be recorded by a camera with film or a CCD (Charge Coupled Device) TV camera head.
equipped with an image processor and dedicated computer software. The image can be captured and stored in the computer, and then processed further. Although the idea of confocal optical scanning microscopy is about forty years old, due to the technological restrictions (Boyde, 1988, 1989), only a few confocal optical scanning microscopes could be found worldwide before 1987, when the new generation of confocal optical microscopes became commercially available.

The Tandem Scanning Confocal microscope was first constructed twenty years ago. The Nipkow disk is now made of semiconductor quality silicon wafer, which can be precisely designed and constructed, and mounted on smooth bearings to reduce vibration and other types of noise (Petran, 1985). The Nipkow disk, which is the simplest linear device for mechanical scanning purposes, was invented by Nipkow over 100 years ago (1884). It is a rotating, opaque disc carrying extremely small holes arranged on an Archimedean spiral. The heart of the Tandem Scanning Reflected Light Microscope device is the aperture disk. The modern Nipkow disk is well designed and carefully manufactured by using semiconducting materials such as a silicon wafer which has deposited on it a low reflectivity black chrome mask to reduce the possible light reflected from the top of the disk. The Nipkow disk was invented by Paul Nipkow in Germany in 1884 (Pawley, 1990). Figure 2.3 is a top view of a typical Nipkow disk, in which a large number (few thousands to 200,000) of pinholes has been well arranged to allow the entire image to be scanned (tandem scanning) and constructed continuously point by point. A large silicon wafer is etched by chemicals in a spiral pattern to offer pinholes in conjugate sets, that is, arranged in a precise
pattern which is symmetrical about any diameter. The size of each pinhole is about 20-25 micron in diameter and they are spaced approximately ten pinhole radii apart. Normally, 1% or 2% of the area of Nipkow disk is transparent to light. Therefore, a very strong illumination source is necessary. The TSM is a very powerful research tool in many fields of contemporary science, typically in biology, chemistry, geology, mineralogy, semiconductor research & development, industrial inspections, physiology and other medical applications as well as general materials research (Shuman, 1989).

2.2.1 Principle of Confocal Imaging

The principle of the confocal microscope utilizes a spiral arranged pinhole silicon disk as the aperture disk to collect light only from the focal plane, in which it can be observed. The major difference is that the out-of-focus image disappears instead of blurring as in the conventional light microscope (Kino, 1989). Light passes through the pinhole to an objective lens and forms a diffraction-limited spot on the object that is on the sample stage. Light reflected from the object passes through the objective lens and then back through a conjugate pinhole. The objective lens is used twice, once for illumination, and again for imaging. If the object is out of focus, the reflected light is defocused and cannot pass through the conjugate pinhole, or the intensity of reflected light placed behind the pinhole drops off rapidly when the light reflected from the object is defocused, therefore causing the image to disappear. The resolution of the confocal scanning optical microscope is approximately in a sub-micron level due to the limitation of wavelength of a source of light. Detailed
calculations are readily found in the literature (Wilson, 1984).

Figure 2.4 is a schematic diagram of the working principle of the Tandem Scanning Reflected Light Confocal Microscope. The model used in this work is Tracor Northern Mark II TSM with a 200W mercury lamp as the light source, and a choice of the filters (UV, green, blue, neutral, etc.). The Nipkow disk speed is continuously adjustable between 500 and 1500 RPM. The fine control objective positioners are piezoelectric elements with closed-looped feedback to position objective lens along the X and Z axes; their range is 50 microns with a resolution of 0.05 microns per step digitally displayed. Mechanical control of the Z axis is by screw adjustment of the sample height, over a 50mm range, with 2 micron graduations. The mechanical X, Y stage has 102mm ranges in each direction. The aperture disk is rotated at high speed, normally at approximately 1500 RPM; this can produce approximately 700 frames of high quality images per minute. More elaborate instruments use a scanning laser spot and optoacoustically controlled mirror in place of the Nipkow disk.

Figure 2.3. Top view of Nipkow disk.
2.2.2 Applications of TSM

TSM greatly extended the application of optical microscopy. It provides an impressive reconstructed 3-dimensional profile of the structure (internal and surface) at very high resolution, and measurement of the height of the surface of the object remains very easy. Also, it can be used to examine the internal structure by totally non-destructive means on various samples (isolated or in situ) in a short amount of time. The thickness of the transparent sample can also be determined. Many examples can be obtained with this superior resolution, such as extended focus images,
stereoscopic images, and 3-dimensional modeling (McCarthy, 1988).

When TSM is coupled with an image processor/accumulator as hardware and a dedicated computer software system, the power of TSM can be further unveiled. The high quality and sharper edge of the image can be dramatically improved and easily analyzed. A Cohu 4810 monochrome solid-state CCD camera head was used for these studies. It can detect a 8.8x6.6 mm image area with 565x650 lines resolutions. An image can be captured with the final 480x640 resolution as 8 bits per pixel (~300K bytes per frame). To deal with low contrast, a real time digital contrast and low light enhancement system ARGUS-10 image processor (analog enhancement) was employed to acquire a high quality image with total number of effective scanning 483x525 lines (as 8 bit converter). The ARGUS-10 also performed simultaneous background subtraction with averaging and digital contrast manipulation. Improved images were printed out by a Sony UP-850 Video Graphic Printer in 9 seconds with resolution 472 lines x 700 dots. The following is a summary of the major advantages of the TSM as used, coupled with a Cohu CCD TV camera head, processed by Jandel Video Analysis software "JAVA" (version 1.40) and operated by an IBM PS/2 70A computer:

*Improved signal to noise ratio;
*Increased effective resolution;
*No more blurring image;
*X-Z scan electronically controlled;
*Three-D image reconstruction;
*Electronically adjustable magnification;
*Contrast enhancement;
*Spatial convolution filters (designed or user defined);
*Quick thermal hard print out;
*Precision measurements;
*Both for light transparent and scattering samples;
*All range of normal optical objective lenses;
*Non destructive to samples;
*Time efficiency;

Other potential or actual applications can be summarized as follows:

* Suppression of stray contrast;
* Measurement of topography;
* Inspection of semi-transparent or transparent coatings and samples;
* 3D measurement of particle orientations;
* Microscopy and measurement of porosities in ceramics and metals;
* Examination of fracture & wear zones with extended depth of focus;
* Investigation of defects in single crystals;
* Microscopy of liquid & emulsions;
* Examination of sensors.
* Determination of fractal dimension.

2.3 Scanning Electron Microscopy (SEM)

The scanning electron microscope was first constructed by M. Von Ardenne in 1938 though the idea and principle of operation were suggested by M. Knoll in 1935. Since then enormous improvements have been achieved. The device can now be used to observe solid surface features at 10 to 100,000X magnification with very high resolution down to 10 nm depending on the nature of a sample. SEM improves the depth of field more dramatically than do other types of microscopes, since the depth of focus is large, thereby enabling three dimensional observations. The SEM instrument used in this work was a JEOL SEM-300II, with resolution 50nm.

SEM uses a focused electron beam to scan the sample surface in a vacuum. The image is most commonly obtained by collecting secondary or backscattered electrons from the source on which the focused and scanned beam impinge. Normally, it is used to examine the prepared sample at magnifications well above the useful magnification of the optical microscope; it also provides the detailed
examination of feature surfaces and deeply curved surfaces requiring depth of field well beyond that possible with the optical microscope. Equipped with an X-ray detector, it can be used to identify chemicals with features down to micron sizes on surfaces of bulk samples (Wells, 1974).

Although a fairly flat sample is commonly required for SEM, the shapes on the surface still can be observed with substantial high resolution. Since the number of electrons collected depends on the nature of the material and its geometry, excellent imaging of geometrical features can be obtained with high resolution (Hayat, 1976). When SEM is equipped with a backscattered electron detector, it provides more detailed surface information, such as grain boundaries, different phases with different compositions, etc. (Hearle, 1972). The limitations of SEM are its inability to provide internal information for the specimen and lack of the very highest resolution. In addition, it also lacks color response and requires a vacuum environment. Figure 2.5 shows a diagrammatic representation of the working principles of SEM. Four major basic components of a typical scanning electron microscope are listed below:

1. The electron column provides the electron source and focus system.
2. The specimen chamber contains the sample support and various detector supports.
3. The vacuum pumping systems provide vacuum for the entire SEM system.
4. The electronic control and imaging systems provide detector controls, scanning coil controls, magnification controls and imaging amplifier controls.
The electron beam is produced with high energy by the electron gun. The electron source comes directly from a heated (approximately 2500°C) tungsten filament by a thermionic emission process. The electrons are then accelerated by a high voltage to form a beam. The high voltage usually ranges from 5 to 30 kV depending on requirements and can be controlled and adjusted by the user. The beam is focused subsequently by condenser and objective lenses and finally reaches the top of the sample surface. The electromagnetic condenser lenses regularly have two stages, a primary condenser lens and secondary one. Typical objective lenses also have two stages. These condenser lenses regulate the final beam spot which controls
the magnification and resolution of the SEM. The spot over the sample surface formed by the electron beam has to be scanned. The scanned electron beam is regulated and controlled by a scan coils component (the scanning generator) which performs the scanning function. When the electron beam bombards the sample surface, many interactions occur simultaneously. Actually, it destroys the sample surface to some degree (Chapter IV). Figure 2.6 shows many possible interaction variations that can occur with a sample, among them, secondary electrons, characteristic X-rays, backscattered electrons were commonly collected.

![Figure 2.6. Interactions between electron beam and sample surface.](image)

In the scanning electron microscope, the surface of the specimen is bombarded by a well controlled electron beam to provide information for producing an image. The image formation is generated by collecting either the secondary electrons or
backscattering electrons through a electron detector in the specimen chamber. The secondary electron detector has a screen surface; detected electrons pass through the screen and are accelerated by high voltage into a quartz light tube coated with a scintillator material. The photons generated by the scintillator pass through the light tube to the photomultiplier tube, where a significant amplification is achieved. The beam reaching the CRT (Cathode Ray Tube) is modulated proportionally to the magnitude of the signal from the secondary electron detector. Scanning is accumulated spot by spot, and therefore, the full picture of scanned areas is accumulated on the CRT. The same principle is involved, namely the backscattered electron image can be constructed by the collection of backscattered electrons. X-ray images can also be generated by an X-ray detector and further treated by computer image mapping techniques to obtain color-coded photo maps.

The SEM instrument used in this work was a JEOL SEM-300II equipped with a secondary electron detector, a Robinson backscattered electron detector, and a solid state silicon X-ray detector with beryllium window, cooled by liquid nitrogen. The sample was prepared (Section 3.4.1) and coated prior to use with either a carbon or gold thin layer in order to improve the image quality by reducing electron surface charging of insulator samples. The acceleration voltage usually ranged from 10 to 25 KeV depending on the nature of the sample and the information required. Normally, the higher the acceleration voltage, the better the image, because of the better resolution. But the electron bombarded area of some samples can be damaged and even destroyed if a higher acceleration voltage is applied.
2.3.1 Backscattered Electron Image (BEI)

Another very important application of SEM is the backscattered electron imaging (BEI) mode. This exhibits atomic number contrast of samples. Recent developments in detectors, especially solid state detectors such as the Robinson detector series, have made possible more efficient detection of backscattered electrons, and hence better resolution of BEI. The major use of BEI is to observe the different elemental distribution of the sample through contrast difference. The heavier the element, the brighter the contrast displayed in BEI mode (Czanderna, 1975).

The principle of backscattered electron imaging is based on the interaction between the electron and nucleus of an atom (Figure 2.6), which gives rise to backscattered electrons containing chemical composition information. The backscattered electrons undergo a Rutherford scattering which can be approximated by a dependence on the atomic number \( Z \) raised to the second power. This produces contrast in the final electronic image if a sample has regions with different elements. For materials containing more than one element such as IMCAs, composites, and so on, the average atomic number determines the backscattered electron coefficient. Backscattered electron imaging was extremely useful in obtaining high quality micrographs throughout these studies.

In comparing the quality of secondary electron imaging (SEI) with backscattered electron imaging (BEI), SEI was superior to BEI, since it has a higher resolution power due to backscattered electrons having a higher energy than secondary electrons coming from very near the surface of the sample. Backscattered electrons
were produced and escape from fairly deep within the sample, depending on the initial acceleration voltage used. When the energy of the finely focused electron beam is increased, i.e. a higher acceleration voltage is applied, the electrons penetrate deeper into the sample and the resultant backscattered electrons escape from deeper within the sample. This increases the volume of backscattered electrons and also that of background electrons (S/N is decreased). All BEI micrographs were taken with the JEOL SEM-300II equipped with a Robinson backscattered electron detector under BEI mode operation and 25~30 kV acceleration voltage (for SEI, 15~20kV).

2.3.2 Energy Dispersive X-ray Analysis (EDX)

X-ray microanalysis provides an in situ means of identifying elements within microvolumes of a tiny sample (a few micron in size) to a very high degree of sensitivity and with precise localization of the regions being analyzed. It was first combined with SEM by Castaing and Guinier in 1949. Since then, many different instruments with facilities for X-ray microanalysis have been produced and used in such diverse scientific investigations and applications as: metallurgy, semiconductor and electronics, mineralogy, geology, biology, and environmental pollution.

In general, microanalysis by EDX is the easiest method, and sometimes is the only available method, for analyzing microscopic areas of samples, because it is a practically nondestructive technique in most cases, and sample preparation requirements are minimal. Energy dispersive microanalysis involves detecting the X-ray emissions induced by an electron beam. It is moderately sensitive to low
concentrations--minimum detection limits (MDL) are below 0.1% in the best cases and typically less than 1% depending on the detecting systems. The dynamic range of EDX can run from 0.1% to 100% with a relative precision of 1% to 5% throughout the range.

The process of X-ray emission is induced by the electron beam of the scanning electron microscope. When an electron beam bombards the sample in a vacuum, an electron is ejected from an inner shell of the sample atom (Figure 2.9). The resulting vacancy is then filled by an electron from a higher energy shell of the atom. This vacancy-filling electron must release a specific energy which is converted to a form of electromagnetic radiation, equal to the energy difference between the two electronic levels involved. This energy is fairly large for inner shells of atom and appears as X-rays. Obviously, many possibilities remain, but the principle and selection rule are very simple: when excited by electrons with sufficient energy, each element in the sample will emit unique and characteristic patterns of X-rays, and the number of X-ray photons emitted by each element bears a more or less direct relationship to the concentration of that element. The position and intensity of the spectral peaks provide qualitative and quantitative information.

The characteristic X-ray can be detected by two different detecting techniques, Wavelength Dispersive Spectrometry (WDS) and Energy Dispersive Spectrometry (EDX) (Fiori, 1976). But only EDX was used in the studies.

In the energy dispersive detection system (EDX), a solid state semiconductor detector is used. The detector is placed very close to the sample (source of X-rays)
and can accept a wide angle of radiations. This clearly increases the detecting sensitivity enormously and thus provides better statistical data. Since the energy discrimination takes place within the detector, the exact position of the X-ray source is not extremely critical. The first solid state semiconductor detector was developed in the mid-sixties at the Lawrence Berkeley Laboratory in California. A single silicon crystal is the complete X-ray dispersing element of a typical energy dispersive detection system such as that used here. Together with appropriate electronic amplifiers and signal processors, it physically disperses the spectra of the characteristic X-rays, then collects emitted X-rays of all wavelengths and sorts them electronically. Since the solid state detector crystals must be operated in a very clean environment and in a very high vacuum, there are two types of solid state detectors, windowless and those with windows. The detector in this work is equipped with a Be window. The detector crystal is maintained in a separate vacuum system to avoid contamination. This is achieved by enclosing the crystal within a tube, then sealing the end of the tube with the window. Since beryllium is relatively transparent to the characteristic X-rays and also withstands the pressure between crystal and sample environments, it is a practical choice as a material for windows. Beryllium windows can transmit X-rays for elements with atomic numbers greater than 11 (X-rays with energies greater than 2 KeV are transmitted with 100% efficiency), but will absorb X-rays of lighter elements with atomic numbers less than 11, which are therefore undetected; as a direct consequence, C, O, F were not detected. Windowless detectors are not similarly restricted, but other physical limitations restrict the resolution of EDX
operating above 100 eV.

The X-ray photon first creates a change pulse in the semiconductor detector; the change pulse is then converted into a voltage pulse whose amplitude reflects the energy of the detected X-rays. Finally, this voltage pulse is converted into a digital signal which causes one count to be added to the corresponding channel of a multichannel analyzer. However, absorption within the window limits the sensitivity of the X-ray solid state detector to low energy X-rays. A limit to the detection efficiency for high energy X-rays also exists, because these high energy X-rays completely pass through the detector crystal, escaping with at least a fraction of their original energy. Normally, this limit is up to 20 KeV. After a period of time, the accumulated counts from a sample produce an X-ray spectrum. A few thousand counts were required to obtain a reliable spectrum.

For SEM samples with rough surfaces and low signal strengths, the EDX system is significantly better than WDS and it has the other advantages of quickness and convenience. For light elements, however, it may be necessary to move to the WDS (signal/noise ratio is ten time higher than that for EDX, 500:50) or other microanalysis techniques such as Auger spectroscopy (for very low fluorescent yield), since EDX systems cannot detect energies lower than 1 KeV.

In short, both energy and wavelength dispersive techniques are fundamentally the same in terms of the Planck relation; the same physical phenomenon is measured. A detailed comparison can be found in Chandler’s book (1977). EDX was widely used throughout the studies to analyze various elements such as Cr, Sr, Ba, P, Ca, Si.
2.3.2.1 Qualitative Analysis by EDX

Extensive chemical information can be qualitatively obtained by EDX except for lighter elements such as carbon, fluorine, oxygen, etc. Qualitative Analysis proceeds by determining the energy of the peaks present in the spectra and comparing them with those in a chart listing the standard energies of characteristic X-rays. Highly sophisticated EDX system software such as IDENT Automatically Peak Identification Program from Northern Instruments was used. These software routines detect ejected electron energy values (position and intensity), check for inconsistencies, and then print out a list of the elements present in the sample. However, for complicated samples, the user can operate the instrument manually to evaluate the elemental compositions.

Characteristic X-rays are emitted when an inner shell electron is sufficiently excited to leave an atom or to go to a higher unoccupied orbital. This electron is then replaced by one from the outer shells conserving energy by emitting an X-ray photon. When an electron is removed from the K shell (1s orbital) to create a vacancy, such vacancy can be filled by one from the 2p or 3p, or any higher occupied state. Only certain transitions are allowed because of quantum mechanical restrictions called selection rules. Hence the emission lines are characteristic and also vary in intensity. The energy released from the transition $E_L$ to $E_K$ (energy of K shell) is emitted as X-rays, and the emission lines are called K lines. When an electron is removed from L shell (transition $E_M$ to $E_L$), it leads to the characteristic L emission lines. Usually, the K lines are most intense, with L lines and M lines having progressively less intensity.
An X-ray spectrum is unique for each element; therefore, an analysis of X-ray emissions for any sample can give an analysis of the constituent elements in the sample. This is the principle behind using EDX to qualitatively identify each element in the sample. The K lines contain the highest energy X-ray photons from each atom. This energy is almost equal to the binding energy of the 1s electron, which in turn is proportional to the atomic number squared ($Z^2$), as first proposed by Moseley in 1914. That is: $[hv] = A Z^2$ or $[hv]^{1/2} = A^{1/2} Z$, where $A$ is a constant, $h$ is Planck’s constant, and $v$ is the frequency of the X-rays. Since then, all the elements of the periodic table have been characterized by the Moseley expression and their X-ray emission spectra tabulated by Bearden in 1964 (Hayat, 1976).

To carry out analysis by means of the characteristic X-rays emitted in the SEM, it is necessary to have an incident electron beam voltage at least twice as large as that for emitted X-rays. Also the analyzer must be calibrated prior to data acquisition. Normally, Cu Kα X-ray (8.047 KeV) radiation was used for calibration purposes. To acquire high intensity K radiation for atoms up to $Z = 30$ (for example, Cr, Sr, Si, P), an acceleration voltage of 30 KeV was used. For heavier atoms of $Z > 65$, K radiation cannot be excited due to its exceptionally high energy, but L radiation was used to determine the composition of the sample instead (such as Ba, Au), since K electrons require greater excitation than L electrons. For elements with atomic number $Z < 11$, the L radiation does not exist because in the ground state these elements do not have any L shell electron. For elements with $Z < 45$, L radiation is too low in energy to be dispersed by any available X-ray detecting system. Since the
lighter elements produce fewer lines and heavier atoms have more complex spectra, the most appropriate elements for accurate EDX analysis are actually those with atomic numbers between 20 and 40.

Dead-time is the period when the detector is receiving X-rays but is "dead" to other incoming X-ray photons. The higher the intensity of the X-ray signal, the longer will be the dead-time. In general experiments, dead-time was not allowed to extend beyond 25%; otherwise, it would have directly affected the results as broadening and overlapping EDX spectral peaks. Dead-time is a function of the X-ray signal intensity entering the detector, and is thus determined by the electron beam current irradiating the sample and can be well controlled by adjusting bias current.

2.3.2.2 Quantitative Analysis by EDX

Energy measurements of the characteristic X-ray emissions from an element allow it to be identified. The intensity measurement of the characteristic X-rays provides a method for quantitative analysis. First, the background needs to be removed from the spectrum. Background contains the electron noise and the useful signal, but contains predominantly white radiation which is continuous radiation. White radiation occurs when the incident electron beam interacts with the nucleus of an atom. In any typical X-ray spectrum, each element will contribute to the total emitted continuous radiation and each will simultaneously produce characteristic X-ray emissions as spectral lines which are superimposed with white radiation. The intensity of white radiation is a function of the total numbers of atoms of all kinds in the
Two types of quantitative analysis methods were used, quantitative analysis for Scanning Electron Microscope Series II X-ray Analyzer and SSQ Standardless semi-quantitative program, both built into the system software. With a precision of about 1%, quantitative analysis was done for the majority of samples. Standardless semi-quantitative analysis also provides good results. However, since most samples are not always homogeneous, certain corrections need to be made. Three important parameters affect the detected intensity of characteristic X-rays dramatically; these are atomic number (Z), absorption (A) and secondary fluorescence (F). ZAF is a theoretical procedure to correct for these factors (Chandler, 1977). The ZAF correction method is most frequently used for quantitative correction of the matrix in electron beam excited X-ray spectra and was used throughout the work described here. Z refers to the effect of atomic number, in which the cross section, and the fluorescent yield of the atom are most important. A refers to the absorption which is related to the interactions of the photon and sample. And F refers to secondary fluorescence induced by X-rays, which depends on the sample matrix (matrix effect). ZAF corrections are applied to the K ratio of X-rays. The K ratio is that between the number of X-rays counted for the same element, under the same operating conditions in a sample of known concentration compared with samples of unknown concentration. The assumption for the K ratio provides a good first approximation of elemental concentrations of a experimental sample in practice. The ZAF Matrix Correction Program from Northern Instruments was used for the most complicated samples.
Standardless semi-quantitative analysis is a good alternative to the traditional ZAF method and was used for some samples. It uses the computed pure element intensity as the basis for all theoretical K ratios. When the collected X-rays stored in computer memory are compared with these internal standards, the computer quickly calculates the K ratios, thus readily providing the elemental concentrations of the sample in minutes.

2.4 Transmission Electron Microscopy (TEM)

TEM is a unique technique which enables the essentially simultaneous examination of microstructural features through high resolution imaging and acquisition of chemical and crystallographic information from small regions of the sample. It uses a standard electron optical instrument. The instrument has two principal assemblies: the electron gun as the high energy electron source, and the electromagnetic lenses which are used to control the electron beam and thus generate an image (Figure 2.7). The condenser lenses I and II are used to focus the initial electron beam to reach certain high level energies. The high energy electrons pass through the sample as transmitted electrons, and are then controlled by objective lens and projector lens to generate the final image on the fluorescent screen by absorption of these electrons.

Although the electron beam cannot penetrate far into a sample, selected area electron diffraction (SAD) does provide valuable information about the crystal internal structure. One special study was done on sheet-like inorganic samples isolated from
gels, strontium carbonate flake Induced Morphology Crystal Aggregates (IMCA). This
IMCA has a unique structure as shown by SEM. The dark field SAD patterns were
obtained. The patterns show the IMCA to be polycrystalline. The d-spacings were
calculated through standard procedures and compared with those of many known
relevant inorganic chemicals (Chapter IV).

TEM cannot actually provide surface information. Therefore, it is not
practically useful for morphological studies. Only SAD (Selected Area Diffraction) is
useful for this study since it can provide internal structure as well as structural
confirmation by diffraction pattern. The model used for the current study was the
JEOL TEM-100CXII. TEM consists of passing a beam of electrons through a very
thin specimen and analyzing the transmitted beam for structural information.
However, there are many limitations: the sample preparation is tedious, and to prepare
a suitable specimen may take days since it must be thin enough to allow electrons to
pass through. For electron diffraction, the minimum size of the region analyzed is
approximately 30 nm in diameter. Crystal structural identification is limited to phases
or compounds tabulated in powder diffraction files (40,000 phases or compounds).
Determination of full space and point groups is possible only by using specialized
microdiffraction techniques. Overall, TEM gives a very high magnification (imaging
resolution is approximately 0.12 nm) and characterization of the microstructure of any
suitable materials, and identification of inorganic phases, precipitates, and
contaminants.
Figure 2.7. Diagrammatic of Transmission Electron Microscope (TEM).

2.5 Electron Spectroscopy for Chemical Analysis (ESCA)

The acronym, ESCA, was assigned by a Swedish research group in 1958 since the chemical environment was observed to affect core level binding energies (Wagner, 1979). The binding energy as measured in ESCA is the difference in the total energy
between the initial and final states of the system in which one electron has been removed. ESCA is a straightforward and valuable technique for the characterization of both elemental and chemical compositions of the surface (4-8 nm) of any solid from metal oxide to organic polymers through the determination of the chemical binding energy of atoms on the surface of a solid. Some of the advantages of ESCA relative to other surface analysis techniques currently available are:

* Nondestructive nature.
* The ability to study plastic and organic surfaces.
* Can be used for all elements with z≥3.

However, some limitations for ESCA also should be mentioned here: data collection is slow compared with other surface analysis techniques such as EDX. Relatively larger sample sizes are required (1 sq-mm). Charging effects can be a problem with insulating samples since most instruments are not well equipped with charge-compensation devices, and finally, the accuracy of quantitative analysis is limited.

Fundamental solid surface analysis by ESCA combined with Auger plays a unique role in materials science. Mechanical properties of metals, surface chemistry of ceramics, kinetics of diffusion and phase transformation as well as oxidation and corrosion of metals can be analyzed by ESCA. ESCA also can be applied in catalysis research, as in catalysts surface composition, adsorption and reaction properties and deactivation. Electronic materials such as semiconductors, metallic films, and substrate processes also use ESCA. These are useful applications since ESCA is a surface sensitive analytical technique which is capable of providing elemental compositions of the outermost atomic layer of solid surfaces through analysis of the
chemical bonding. It involve precise systematic measurements of the number of emitted secondary electrons as a function of kinetic energy in a reliable ultra-high vacuum (UHV, $10^9$ torr is necessary) by an electron energy analyzer. Surface analysis by ESCA is accomplished by irradiating a sample with mono energetic soft X-rays and analyzing the energy of the electrons emitted. X-ray sources used are usually the Magnesium Kα line with an energy of 1253.6 eV. Those X-rays are not powerful enough to penetrate very deeply into the sample. Normally they can penetrate 1 to 10 microns only. The sample thickness for ESCA is approximately 10 nm and is strongly dependent on sample differences (Czanderna, 1975).

ESCA is also called X-Ray Photo Electron Spectroscopy (XPE) because of the X-rays acting as an original energy source. Figure 2.8 shows the production of characteristic electrons by an incident electron or X-ray beam as an incoming energy source. The ejected characteristic electron is normally called a photo-electron and its energy is related to the chemical binding energy which reflects elemental configurations. The initial event is the ejection of an electron from one of the core electronic levels (K shell) by an incident X-ray photon with energy of $h\nu$ (step 1 in Figure 2.8; $h$ is Planck’s constant and $\nu$ is the frequency). The kinetic energy $KE$ of the photo emitted core electron (step 2 in Figure 2.8) is:

$$KE = h\nu - BE - W$$

where $BE$ is the binding energy of the emitted electron in the solid, and the $W$ is the spectrometer work function. After a core hole is generated, two possibilities remain for other analysis. It can be filled by an outer shell electron (step 3 and 4 in Figure
2.8); when this happens, energy is conserved by the emission of a photon with energy of $h\nu_f$, which is related to the X-ray microanalysis techniques, or it will continue to emit an Auger electron (step 5 in Figure 2.8) from a different shell which is a three electron process (Ziebold, 1967).

![Energy level diagram illustrating photo electron and Auger process.](image)

**Figure 2.8.** Energy level diagram illustrating photo electron and Auger process.

ESCA provides chemical state identification of surface species for all elements heavier than helium and in-depth composition profiles of elemental distribution in thin films by using the ion beam milling. Composition analysis of samples by ESCA is specially valuable when destructive effects of electron beam techniques such as EDX must be avoided. Determination of oxidation states of atoms in the sample surface can be done by ESCA; identification of surface carbon as carbonate or carbon dioxide
is a typical example. Each element has its own unique elemental spectrum, and the
spectral peaks from a mixture are approximately the sum of the elemental peaks from
the individual constituents. Since the mean free path (MFP) of the electrons is very
small, the electrons which are detected originate from only the top few atomic layers.

Adjacent elements throughout the periodic chart can be distinguished simply
by their spectrum through ESCA qualitative analysis. Because each element's
electronic configuration in the periodic chart is unique, measurement of the positions
of one or more photoelectron peaks allows the instantaneous identification of an
element present at the sample surface. In addition, different chemical states of the
same element can be resolved by small differences in their binding energies.

Chemical shifts could be used to interpret the detailed structural information of
surfaces, using published data as the basis. Chemicals shifts are a characteristic of
ESCA that distinguish it from other well known surface characteristic techniques; the
idea is based on the fact that the inner electron experiences a small energy alteration
due to a change in the valence shell contribution to the potential based on the outer
shell electron chemical binding. Generally, the greater the electronegativity of the
surrounding atoms, the more the displacement of electronic charge from the atom and
the higher the observed binding energy of the core electrons (Ziebold, 1967).

Continuous X-ray irradiation on nonconductive samples (IMCA, e.g.) can
create a positive surface charge. The potential due to this surface charge decreases the
photoelectron kinetic energy and results in higher apparent binding energies than the
true values and therefore restricts the amount of chemical information obtained. To
correct for surface charge, internal standards such as indium foil or carbon corrections were used.

Quantitative data could be obtained from the peak heights or areas and identification of chemical states often can be made from the exact positions and separations of the peaks, as well as from certain spectral contours. For quantitative analysis, since the intensity of an observed signal is a function of the concentration of materials present in the surface, the collected intensities of the signals in the ESCA spectrum can provide quantitative analysis of surface materials. But some conditions must be met. The sample should be flat and homogeneous so that the photoelectrons are emitted isotropically. The sample surface should be clean without a layer of surface contamination. The features of interest are the photoelectron peaks in the spectrum which form the base for quantitative determination. Some corrections have to be used in practice, such as the Wagner sensitivity factor (Czanderna, 1975). This important factor indicates the efficiency with which X-rays are absorbed by sample (Wagner, 1979). If X-ray absorption of a particular atomic subshell from which an electron is being observed is high, then the sensitivity for this element will be high. Wagner has systematically studied the variation of elemental sensitivity throughout the periodic table (1972).

Complete surface analyses of the IMCAs were done by ESCA. Sample preparation was not complicated. The sample must be free of fingerprints, oils, or any other surface contamination. The sample holder was made of indium foil for single use only. Both carbon and carbonate were analyzed. Experiments were carried out
with a VG ESCALAB MK.II ESCA/Auger surface analysis system. The VG
ESCALAB MK.II has a high resolution hemispherical analyzer and uses magnesium
Kα radiation as an energy source. The electron energy analyzer was calibrated from
the Ag 3d5/2 line at 368.2 eV. The elemental carbon 1s binding energy of 284.6 eV
was used as an internal standard for manual charge compensation. Multiplexed Ba
(3d5/2), Si (2p), O (1s), and C (1s) spectra were collected by using Mg Kα excitation
for 30 scans of each region with the electron energy analyzer set for a constant
analyzer energy of 50 eV, a 0.05 eV spectral step size, and a pass energy of 50 eV.
Small spot ESCA settings were employed such that the analysis area was 0.75-sq mm,
the transfer lens potential was 4.72 V, and the iris solid angle was 10 degrees. The
respective multiplexed elemental photoelectron peaks were integrated and then
normalized using the appropriate Wagner sensitivity factors of the VG ESCALAB
MK.II microcomputer quantification software routine to yield the reported atomic
ratios (Chapter IV).

2.6 X-Ray Powder Diffraction (XRD)

XRD is a very useful technique to obtain structural information for crystalline
materials. General usages include: identification of crystalline phases contained in
unknown samples; quantitative determination of weight fraction of crystalline phases
in multiphase materials; characterization of solid-state phase transformations; lattice-
parameter and lattice-type determinations; orientation of single crystals. Some
limitations of XRD are: the sample must be crystalline for phase identification, and
identification requires the existence of standard patterns (e.g. JCPDS powder
diffraction file of inorganic and organic phases, NBS crystal data (contains lattice
constants for inorganic and organic phases). Qualitative analysis requires less than 1
hour for major phases, and up to 16 hours for trace phase confirmation (Anderson,
1989).

XRD techniques are used to characterize samples in the form of loose powders
or aggregates of finely divided material. These techniques cover various
investigations, including qualitative and quantitative phase identification and analysis,
determination of crystallinity, micro identification, lattice-parameter determinations,
high temperature studies, thin film characterization, and, in some cases, crystal
structure analysis (Ladd, 1985). The powder method (Mirkin, 1964), is perhaps best
known for its use as a phase characterization tool partly because it can routinely
differentiate between phases having the same chemical composition but different
crystal structures (polymorphous). Although chemical analysis can provide the
empirical formula for a given sample, it cannot determine whether the sample is a
mixture of two phases or a single-phase mineral material (Cracknell, 1969). XRD is
able to perform such identifications more simply, conveniently, and routinely than any
other analytical method (Glusker, 1985). XRD can also be used to identify specific
crystalline chemical compounds with a high degree of certainty. It is based on the
fact that the atoms within a crystal are arranged in a regular lattice formation which
acts as a diffraction grating for X-rays (Pendry, 1974).

The sample takes the form of a mass of finely divided crystals in a random
orientation (Lipson, 1970). The Bragg equation indicates the relations between the d-spacing and the angle of incident X-rays as following:

\[ n\lambda = 2d \sin \theta \]

where \( n = 1, 2, \ldots \) is the order of reflection.

\[ \lambda = \text{x-ray wavelength.} \]

\[ d = \text{inter-planar spacing} \]

\[ \theta = \text{angle of incidence}. \]

Since a fixed wavelength \( \lambda \) is used, the angle \( 2\theta \) is directly related to the inter-planer spacing \( d \) by the Bragg relation. Each crystalline compound has its own set of d-spacings and thus gives a characteristic diffraction pattern from which it may be identified using JCPDS files of previously recorded diffraction pattern data in conjunction with search manuals. XRD offers an easy way to determine chemical formulas and crystal lattice structures, especially for studies of complicated systems, such as barium phosphate. XRD was used in this study only for phase identification.

All X-ray diffraction patterns for these studies were obtained on a Philips-Norelco model 112045/3 X-ray diffractometer. Copper K\( \alpha \) radiation (35 kV, 18 mA) was used as an X-ray source. A nickel foil filter was employed in order to decrease the intensity of the K\( \beta \) line and other shorter wavelengths. Both entrance and exit slits were set at one degree. A sodium chloride scan for identification purposes employed a scan speed of 2 degree for 2\( \theta \)/min. with a chart speed of 0.5 inch/min. Two types of X-ray specimen holders were used to mount samples. One specimen holder consisted of an aluminum plate 76 x 25 x 3 mm with a 20 x 15 x 1 mm groove milled into the top surface. The aluminum slide was used to hold samples that were prepared in a quantity sufficient to fill the milled groove. An excess of the powder was placed
in the groove and packed down with a spatula. In order to minimize the preferred orientation of the powder, the edge of the spatula was used in a criss-crossing pattern in the compaction process. More frequently, a precleaned glass microscope slide (2 x 1 inch) was used instead for small amounts of samples. To use the glass microscope slide, a small section (1/4 inch) of Scotch brand double sided tape was placed across the middle section of the micro glass slide, followed by a small amount of vacuum grease applied to the top of the micro slide to form a thin layer of grease. The powder sample was then placed on the double stick tape and spread evenly over the surface with a spatula. Since the sample spot size was so small, no special precautions were taken to avoid preferred orientations.

X-ray powder diffraction was used to distinguish amorphous materials from crystalline materials. For crystalline compounds (at least 5% long range order), the positions of the diffracted beams depend upon the size and geometry of the fundamental unit cell of a crystal, and on the wavelength of the incident X-ray beam. The intensities of these diffracted beams depend upon the type of atoms in the crystal and their location within the fundamental unit cell. Amorphous materials, on the other hand, do not have any long range structural order, or well-defined crystal structures, and, as a result, exhibit no distinct reflections. Hence they cannot be identified as they give no clear diffraction patterns or peaks. Samples which did not show any diffraction peak were considered 100% amorphous materials which have typically only a very short range order. No other attempts were made to quantitatively determine the amorphous content of precipitates by X-ray diffraction.
3.1 Gel Techniques

Silica gel is the most widely used inorganic gel and the best and most versatile growth media among gels for general applications (Henisch, 1988). Although the term "gel" has a broad definition, it is generally considered as a two component system of a semi-solid nature which is also liquid rich. Gels are colloidal solids which are porous materials, containing two phases with internal structural networks; both the solid and fluid components are in a highly disperse state (Vold, 1983). The chemical structures of many gels are formed by macromolecules, which are held together in knots and junction points or a group of junction points, respectively, depending upon the types of interaction between the predominant molecules. The gelling forces are either primary molecular interactions or secondary molecular interactions or both. For inorganic gels which contain ionized groups of impurities, such as silica gel, the ionic and covalent bonds are the dominant force contributors. These gel types are extremely rigid, strong and thermally irreversible due to the nature of their chemical bonding. In other gels, especially organic gels such as agarose gel, hydrogen bonding, dispersion forces or other secondary interactions are significant contributors, and most of them are thermally reversible materials. Many other gels such as PVA (polyvinyl alcohol)
hydrogel (Matsuzawa, 1987) are described in various books and literature reviews (Henisch, 1973, 1988; Brinker, 1990).

Many hydrophilic gels can be prepared from natural substances. Agar gel, for example, is a carbohydrate polymer extracted from red seaweed. It is purified from agar gel by repeated fractional precipitation with a concentrated solution of polyethylene glycol (Determann, 1968). Gelatin gel has a higher purity than general silica gel, and excellent stability over a large pH range with high optical clarity and no interfering ions (Banks, 1973). Also, it has a high physical strength and viscosity as a characteristic thermally reversible gel formed by absorbing an amount of water at least ten times its weight of gelatin powder. Carrageenan gel, on the other hand, comes from Irish moss which consists of plant polycarbohydrate fibers. The structure of carrageenan gel is similar to that of cellulose.

Pore dimensions (distribution) are quite distinctive among several typical gels. The gel with the smallest dimension is silica gel, because its networks are based on small molecular aggregates at certain concentrations. In other gels such as agarose gel, the macromolecule fibers entangle each other to produce three dimensional networks (Henisch, 1968). Pore size distribution has an important influence on the nucleation rate as mentioned in Chapter I. The pore dimension normally is at the micron to nano-meter level, depending on gel concentration and other factors (Brice, 1986). These small pores prevent convection, so that mass transport is by diffusion only.

As semi-solid porous materials, almost all types of gel are amorphous. The
diffusion rate for most chemicals in dilute gels is very close to those in liquids. This is advantageous in studying precipitation behavior in great detail since the effects of the gel on the solution are minimal. Thus, gel matrixes provide a wide range of information about particle size, morphology, optical and geometrical perfection, and the interactions of particles with their matrix. The gel method also provides mechanical protection by its matrix for particles grown in gel; this makes it possible to observe the particles' growth history and morphological evolution at room temperature. The most important factor which should be mentioned is that the gel technique can strongly restrict particle aggregation, which often occurs in solution experiments subject to earth's gravitation forces or through Brownian motion. It also allows diffusion to take place and greatly reduces the heterogeneous nucleation previously mentioned (1.4.1.2). Gels also have some excellent physical properties, which allows for easy transfer from one location to another without a large change in room temperature which provides for in situ observation. It is true that different gels are structurally different; hence, the degree of filtering effects would not be expected to be the same for all gels.

Gel techniques were extensively studied by H. K. Henisch at Penn State University beginning in the early 1960s (1973, 1986). However, the earliest work can be traced back to Liesegang who in 1889 observed periodic precipitation in various gels. Marriage was probably the first one who systematically studied crystal growth in gels in 1891 (Brice, 1967). The gel method has been widely used since 1930. The present study used three different classes of gels, silica gel, agarose gel and
agarose-silica mixed gel. These represent hydrophilic and hydrophobic gels matrices and their combinations. Overall, crystal growth and precipitation in gels as special techniques may be able to reproduce as well as to represent natural growth and precipitation processes (Putnis, 1992).

3.1.1 Silica Gel

Silica gel is translucent and has predominantly three dimensional tetrahedral networks, partially because it is derived from molecular condensation (Iler, 1979). It is quite rigid, and is not thermally reversible. Figure 3.1 shows a partial structure of a three dimensional network of a gel. Although other configurations and structures, such as three, four, and even five member ring structures (Cotton, 1985; Brinker, 1990), are already known, their functions are not experimentally valuable to the formation and major structure of the gel. Even more complicated structures can be constructed, but such details are not important to us for the same reasons. Silicic acid is transformed from silicate solutions to silica through the following reactions:

\[
\text{Na}_2\text{SiO}_3 + 3\text{H}_2\text{O} \leftrightarrow \text{H}_4\text{SiO}_4 + 2\text{NaOH}
\]

\[
(n-1) \text{H}_4\text{SiO}_4 + \text{H}_4\text{SiO}_4 \rightarrow (-\text{Si-O-Si-})_n^- + 2n \text{H}_2\text{O} \quad m\neq n
\]

It slowly thickens and eventually gels. Actually, silicic acid polymerizes into discrete particles that, in turn, aggregate into chains and networks as recognized by Carmen and Iler (1979). $^{29}$Si NMR, vibrational spectroscopy (IR and Raman), and small-angle light scattering are various in situ methods that were used to study the structure of silicate gels (Brinker, 1990). The results from these investigations largely support the
chemical theory proposed by Iler. Silicic acid polymerization occurs in three stages:

1. Polymerization to form particles.
2. Growth of particles.
3. Linking of particles into chains, then networks that extend through the liquid medium, thickening it to a gel.

Condensation takes place so as to maximize the number of Si-O-Si bonds and minimize the number of terminal hydroxyl groups through internal condensation. Thus some kinds of rings are quickly formed, creating three-dimensional particles, which further condense to the most terminal OH groups on the outside. These three dimensional particles can serve as nuclei. Then growth occurs by particles which grow in size and decrease in number as highly soluble small particles dissolve and re-precipitate on larger, less soluble nuclei. Growth stops when the difference in solubility between the smallest and largest particles becomes trivial. Silica gelation can be divided into three approximate pH domains: pH = 1-3, pH= 4-7, and pH > 7. pH = 2 appears as one boundary at the isoelectric point, where the electrical mobility of the silica particles is zero because of zero surface charge. pH = 7 appears as another boundary because both the silica gelation and dissolution rates are maximized. The third domain is at a pH from 7 to 11, where the silica particles are appreciably ionized so that particle growth occurs without aggregation or gelation. The silica gel three-dimensional networks can be further characterized and treated by a surface fractal dimension (Brinker, 1990).

Usually, the active concentration of sodium metasilicate determines the physical properties of a gel. If the concentration is too low, the molecules needed to form
networks are too few in number to set up a recognizable, rigid gel. By contrast, if the concentration is too high, the gel is too dense, and the optical properties cannot be satisfied for \textit{in situ} observation. In our studies, a cation ion exchange resin was used to replace \( \text{Na}^+ \) for \( \text{H}^+ \) and produced gels free of added salts. These were found to be more transparent.

3.1.1.1 Structure and Properties

The real three dimensional structure of the silica gel is shown in Figure 3.1. The gel is thermodynamically unstable with respect to compact silica glass since it has a large interfacial area and lower cross linking density, with terminal OH groups. There is a small energy barrier to prevent the gel from reverting to the glassy state; the structure of the gel is preserved only because the mobility of the atoms is limited at low or room temperatures. The physical and chemical properties gradually change with time over a long period (several months) at room temperature. These changes are dependent on temperature, the concentration and pH of the gel according to recent studies (Brinker, 1990). During this time, any perturbation, such as temperature variation or pressure variation could induce gel phase transformation.

The polymerization of sodium silicate is very complicated. It involves an increase in connectivity of the network, produced by condensation reactions. This classic gelation behavior was outlined by Iler in 1979. Apparently, the silica gelation is either an acid- or base-catalyzed bimolecular nucleophilic substitution reaction; under these conditions, condensation occurs and bond formation continues even after
gelation has occurred. The segments of the gel networks can still move significantly close together to allow further condensation and hydrogen bond formation. The segments produced are about 10 nm in dimension. The change that occurs after gelation and during the ageing process is termed syneresis. Syneresis is the spontaneous shrinkage of the gel network resulting in expulsion of liquid from the pores. It is believed to occur by condensation of terminal OH groups, such as in:

$$\text{Si-OH} + \text{HO-Si} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O}$$

Not only does the ageing process engender syneresis; it also results in the strengthening and stiffening of the gel network. The extent of these effects depends on the pH, temperature, size, concentration and composition of the gel media.

The gelation process is also sensitive to the ionic strength. The addition of salts reduces the electric strength of the environment (by reducing double electric layers etc.), dramatically reducing the gelation period. This is a very important effect for gel preparation at high pH. The choice of cation exchange resin used for neutralization is at least partially based on this effect. An external salt such as sodium chloride was often added to speed up the gelation purposes.

Halberstadt and Henisch (1968) have physically examined the structure of silica gel under the scanning electron microscope. It is characteristically different from those organic gels with less regular structures (segmentation); compare Figure 3.3, a micrograph of agarose gel, with Figure 3.1 which is the widely accepted structure of silica gel as a solid network with continuous porosity.
3.1.1.2 Gel Preparation

Sodium metasilicate solutions were purchased from the Aldrich Chemical Company. As received from the manufacturer, the solution had a density $d=1.390$, and a component of about 27% $\text{SiO}_2$ and 7% $\text{Na}_2\text{O}$. These solutions were then diluted to about 4.5% to 4.0% $\text{SiO}_2$ before gel preparation. To 100 ml of concentrated sodium metasilicate solution were added 700 ml of fresh ultra pure quality water (prepared from Ultrapure Water System, Lab Five by Technic Central Systems; resistivity = 18 Megohm-cm) and mixed well. The solutions were then flushed with $\text{N}_2$ for 20 minutes before using. The pH meter used was a JENCO Model 672 Digital pH/MV/Temp meter equipped with ORION Combination pH Electrode (model 91-06). The general procedure used to prepare the silica gel containing other materials was as
follows (Bates, 1973):

1. Measure out 100 ml 4.5% or 4.0% Sodium Silicate solution.
2. Add certain amounts of additives, such as NaCl, Na₂CrO₄.
3. Stir until all chemicals are dissolved completely.
4. Calibrate the pH meter twice with basic buffer solution (pH = 10.0); wash with ultra pure water.
5. Titrate the solution by carefully adding the strongly acid cation exchange resin (DOWEX 50W Hydrogen Form, Dry Mesh 50-100, 8% Cross-Linked; SIGMA Chemical Company) to give the desired pH.
6. Stop stirring, wait for ten seconds, transfer appropriate amount of the solution to a clean, labeled reaction vessel or a cassette as quickly as possible. Record pH again.
7. Continue to titrate the solution to the lower desired pH, and repeat procedure 6 until the lowest desired pH in the experiment is reached.

The gel solution should be kept at room temperature and in a relatively static area to let it polymerize and further condense to form a three dimensional network.

After gelation, the ageing process may be needed for further stabilizing purposes, because it may involve deep condensation, dissolution and re-precipitation of monomers, or phase transformations within the liquid or solid phases. Ageing of silica gel could reduce the pore size of the gel and consequently the rate of diffusion of ions into the gel (Patel, 1978). Generally, ageing 24 hours was considered sufficient enough for the silica gel after it has been formed.

3.1.2 Agarose Gel

Agarose gel is an excellent thermally reversible gel. The primary material is a linear polysaccharide of D-galactose and 3,6-anhydro-L-galactose which is free of ionizable groups. The gel used during the experiments were of three types, each one of which can produce a very reliable stiff gel with a high degree of purity:
1. Sigma type I-A Agarose (Sigma Chemical Company).
2. Kodak Agarose ME with formula \((C_6H_{10}O_5-C_6H_8O_4)_n\) (Eastman Kodak Company).
3. Boehringer Mannheim Biochemicals Agarose for Pulsed Field Gel Electrophoresis, PFGE Agarose from Division of Boehringer Mannheim Corp.

These three kinds of agarose gels did not differ in their growth progression throughout the experiments since they all have highly similar chemical structure compositions. The concentration of agarose gel can be varied from 0.25% to 5.0% by weight. The ideal concentrations for the experiments are either 1.0% or 0.5% based on the desired stiffness of the gel.

3.1.2.1 Structure and Properties

The primary chemical structure of agarose gel is shown on Figure 3.2. It is a chemically stable gel with an empirical formula of \((C_6H_{10}O_5-C_6H_8O_4)_n\), which is a linear macromolecule with a molecular mass of around a few thousands \((n > 8)\) (Araki, 1956). When gel solutions are cooled to around 45°C, the poly-carbohydrate fibers entangle each other to make random three dimensional networks. Hydrogen bonding interactions contribute significantly to the linkage between fibers. Those fibers can be observed by scanning electron microscopy (Figure 3.3 shows some entangled agarose fibers).

![Chemical structure of agarose gel](image)

Figure 3.2. Chemical structure of agarose gel.
3.1.2.2 Preparation

Preparing the agarose hydrogel is exceptionally easy, although it is difficult to make the cassette gel layer uniform. The cassettes or any reaction vessel must be warmed to around 60°C before the gel solution is poured in. Generally a 0.5% agarose solution was used throughout the experiments. Higher concentrations can be used, but less than 0.5% agarose is not recommended because the gel is too soft. The normal procedure is:

1. Measure out 100 ml ultra pure water.
2. Add 0.5 g agarose.
3. Stir while adding stoichiometric amounts of the chemicals to the solution.
4. Heat gently in the hot water bath while stirring until the solution becomes clear.
5. Transfer a sufficient amount of gel solution to the pre-warmed cassette or other reaction vessel.
6. Place the cassette or vessel in a large desiccator with a wet environment to prevent the top layer of gel from drying.
7. Leave overnight for the gel to stabilize.
Syneresis is less serious than with silica gel, but agarose gel was regularly aged for 24 hours before use in this work.

3.1.3 Agarose-Silica Mixed Gel

Silica hydrogel and agarose hydrogel each have their own stable properties, but they also have some disadvantages as described before. A new type of gel has been successfully developed. This particular mixed gel has greater advantages for separation, observation, and preparation. Specifically, at higher pH, those silica gels are very difficult to solidify; for example, it can require from one day to a whole week for the gel to solidify. At extremely high pH (pH > 10.5), gelation of silica gel from sodium metasilicate aqueous solution does not occur. In contrast, near pH = 7.0, the silica gelation process is extremely fast; the time required ranges from a few seconds to a few minutes. However; the mixed gel can be prepared very easily at virtually any pH, whether basic or acidic. For instance, solutions of pH = 13 were used effectively in some experiments. The optical properties of the mixed gel are remarkable. Transparency is much better than for silica hydrogel which is always cloudy when the pH is higher than 10.3.

3.1.3.1 Structure and Properties

Agarose-silica mixed gel still has the same general characteristics as the pure agarose gel, because the silica percentage is extremely low, never higher than 0.8%. Therefore, in this so-called mixed gel especially at high pH, the silica component may
be not acting as a gel, because the concentration of sodium metasilicate is too low. In this work, it was found that sodium metasilicate itself cannot form a recognizable gel under these conditions unless the concentration of sodium metasilicate is higher than 1%. The mixed gel was examined by SEM. The region examined had a three-dimensional network of entangled fibers, similar to that found in agarose gel. However, this study was confined to a small region of the hydrogel. It was observed that the processing of silica enhanced the stiffness of the gel, consistent with Si(OH)-agarose hydrogen bonding.

3.1.3.2 Preparation

Two hydrogel precursor solutions of agarose and silica were prepared, using the following procedure:

In a beaker with a magnetic stirrer, first prepare a solution which has an exact concentration of some chemical such as Na$_2$CO$_3$, NaCl etc. Then, add sufficient agarose powder to make a 0.5% agarose chemical solution. Titrate the solution to the desired pH value with either 1.00 M hydrochloric acid or sodium hydroxide. Finally, heat the solution in a water bath (60°C) until it becomes clear.

The silica gel preparation is as follows. In a small beaker, titrate sodium metasilicate solution that has exactly the same concentration of added reagents as in the agarose gel solution with 1.00 M hydrochloric acid to reach the same desired pH as that of agarose gel solution with no more than 0.05 unit pH difference. Transfer the correct amount of this solution accurately with a transfer pipet into the already
prepared, heated agarose gel solution. Actively stir for 45 seconds. Then pour into the pre-warmed micro cassette, provide a temporary seal with parafilm or plastic tape, and allow to stabilize overnight for solidification. This well-behaved mixed gel should look clear, homogenous and firm. A simpler procedure which was usually used to prepare agarose-silica mixed gel is to mix the precisely measured amount of sodium metasilicate solutions. Titrate to the desired pH, add agarose powder and heat with stirring until the solution is clear. Then pour into the reaction vessel. Allow to cool to room temperature until the gel is firm. This procedure is a much better technique for making the mixed gel; it is an easy, quick, and accurate preparation method.

3.2 Reaction Vessel Design

Four different types of reaction vessels were used during the study. For the primary experiments, clean test tubes were used. For large quantities, a supercassette was designed and used. However, the micro slide cassettes were more widely used for microscopic investigations of very fine particles. To observe these in situ at extreme conditions (such as very small particle formation), the fourth type of reaction vessel, a modified micro slide cassette, was used. This modified micro slide cassette used a standard microscope cover slip as the upper face of the covering to make a cassette, since most of the high quality objective optical lenses used were designed on this basis. The thickness of the modified micro slide cassette clearly was within this limit.
3.2.1 Conventional Test Tubes

Figure 3.4 illustrates how conventional test tubes were used in experiments with different gel layers. Layer A is a source layer; it normally contains a higher concentration reagent in the agarose gel layer. Layer B is a base layer which contains very dilute reagents solutions such as sodium carbonate, sodium chromate, etc. Layer B can be any type gel, e.g. silica gel, agar gel, or agarose-silica mixed gel. The size of the test tube is not crucial. The only requirement is that all test tubes must be extremely clean and the interior wall of tube must be as smooth as possible. New test tubes were usually examined for this purpose. The cleaning process is simple. Liquid detergent was used to clean the interior without using a brush. The tube was then flushed several times with plain water, then rinsed a few times with distilled water and allowed to dry without any physical contact.

![Gel Layers Illustration](image)

Figure 3.4. Illustration of test tube with gel layers (not to scale).

Observing particles growing inside the tube \textit{in situ} under the optical microscopes is difficult, because the thickness and the geometry of the gel in the test
Ordinarily, test tubes were used only for duplicating experiments or for preparative purposes.

3.2.2 Micro Slide Cassettes

The micro slide cassette was designed for use for a variety of gels, but is particularly suited for gels with medium size particles. The micro slide cassette dimensions are 3" x 2"; it is shown in Figure 3.5. The micro slide cassette has unique advantages for \textit{in situ} observations by either confocal TSM or polarized optical microscopes, also as well for photomicrography and time elapsed photomicrography.

Glass requirements:

1. 3" x 2" microscope slide from Baxter, thickness 1.1 to 1.3 mm, or precleaned plain microscope slide from Labcraft with the thickness approx 1.2 mm.
2. Prewash: immersion in a liquid detergent (e.g., Palmolive dishwashing liquid or Liqui-Nox phosphate free liquid detergent) for 30 minutes. Then use a soft towel to clean both sides of a slide followed by flushing with plain water until no adhesive is visible.
3. Rinsing: twice with de-ionized water.
4. Drying: allow to dry at room temperature for at least 12 hours in the low dust area. These slides are ready to use.

Rubber gasket requirements:

Rubber sheet approx 3 mm thickness purchased from special order as normal red color with semi-soft natural rubber materials (Ever Brand).

1. Precisely cut off 3" x 2" rectangle.
2. Use edge of glass to clean the surface of rubber in order to remove the wax-like substance and other grease materials as much as possible.
3. Wash with liquid detergent and flush until it becomes clean.
4. Allow to dry at room temperature.
5. Cut with a very sharp knife to keep the three edges 8 mm wide,
remove the rest, to avoid any possible rough edges.

Procedure to assemble a cassette:

1. Selection of cleaned microscope slide: only those slides with no visible defect or scratch can be used.
2. Never touch the surface of the cleaned slides.
3. Very carefully put the cleaned rubber gasket in the middle of the lower slide; adding upper slide, then use finger force to slightly tighten the cassette.
4. Finally fix in place with small size bind clips.
5. Remove the metal handles from bind clips.
6. Put into the clean box to avoid any dust. Ready for use.

The calculated volume of the cassette is approx 2.5 ml. Most of the experiments (except those specifically mentioned) use 80% of the base layer (layer B), only 20% is for the source layer (layer A, see Figure 3.6). Figure 3.7 shows the real standard micro slide cassette.

![Illustration of micro slide cassette, not to scale.](image-url)
3.2.3 Modified Micro Slide Cassettes

These were assembled in exactly the same way as the standard micro slide cassettes, except that a 0.2mm cover slip (3"x2", baxter) was used as the upper slide.
3.2.4 Super Cassettes

The super cassette was designed to examine the stabilities of precipitation systems in hydrogel at room temperature and the influence of physical boundary conditions and external perturbations. Figure 3.8 is a diagrammatic design of a super cassette (drawing is not to scale). To make an experiment reproducible, the following requirements should be met. The glass requirements are the same as for the micro slide cassette. It is essential to wash several times in liquid detergent followed by a complete rinsing. The glass dimensions are 8 x 10 inches (200 x 260 mm) with a thickness of 3 mm. The rubber gasket is 20 mm wide at each side. The total volume of a super cassette inside is 120 ml. Ordinarily, 24 ml is for the source layer (layer A) (see Figure 3.8). 96 ml is for the base layer gel layer (layer B) which is charged with a specific concentration of experimental chemicals. All super cassettes were set up inside a large polystyrofoam container. This was to ensure minimum temperature perturbation and gel solidification without stress by very slow and uniform cooling. The gel layer should appear very uniform in a well prepared supercassette. Figure 1.4 shows a typical super cassette in operation.

![Figure 3.8. Illustration of super cassette, not to scale.](image-url)
3.3 Specimen Removal Techniques

Separation from gels is often necessary to examine morphologies of the particles or crystals and to determine their chemical compositions. Separating the precipitated particles is not easy, since these are often small, with sizes ranging from 0.1 - 1 mm, and have complicated shapes. Two major techniques have been used, depending upon which porous media were used in the investigations. In addition, for very regular, fairly large size objects or particles, physical separation procedures can be directly applied to them rather easily.

3.3.1 Chemical Isolation

This technique (Reid, 1992, Garcia-Ruiz, 1982) is very suitable for a few objects, grown under silica gel media. The objects in the cassette were first examined under the optical microscope; then, the cassette was disassembled, and the selected area of gel carefully removed by a spatula and immersed in 2 or 3 ml 0.1 M NaOH solution on a watch glass. After about 2 hours the solution dissolved the silica gel or at least loosened the gel network. The gel was lightly stirred with a fine, very soft brush, to speed up separation. The gel was flushed off with pure water several times. The isolated objects or particles were transferred to a new, clean watch glass, and then washed ten times with pure water in order to completely remove the sodium hydroxide and other impurities. Finally, these objects or particles were picked out one by one and placed in a clean, dry watch glass, and allowed to dry at room temperature under the cover of a Petri dish.
During the separation, the three dimensional networked silica gel is broken by the alkaline solution, and at the same time, the surface of objects or particles (in the study, most precipitates contain silica) is also polished or etched to some extent by the same strong basic solution, depending on length of treatment. Therefore, the actual layer thickness may be reduced and the original surface texture may not be retained. Silica can possibly be dissolved completely in some cases if the concentration of the alkaline solution is too strong. Such disadvantages can be bypassed by physical isolation, a nondestructive technique.

3.3.2 Physical Isolation

As new agarose-silica mixed gel techniques were developed in the laboratory, the appropriate separation techniques were also developed. These techniques are very suitable for large amounts of precipitate separation as well as for a single object or particle isolation. The leading advantage is that the surface, shape and chemical component are not altered by this separation procedure. This gives a way to examine the real surface texture and morphology as in the original gel with minimum alteration.

The procedures for collecting samples are quite similar to those for the destructive technique. The cassette was disassembled and the selected area of hydrogel is carefully removed by a spatula, then put in a watch glass with a small amount of pure water on top of it which is then heated by a hot water bath. Overheating should be avoided. Then, the hydrogel is flushed with pure warm water.
(around 65°C) about ten times, or more often if necessary. Objects or particles are then picked up with a very fine brush and placed on a new, clean watch glass. This is covered with a Petri dish, and allowed to dry at room temperature. Such handling allows the samples to maintain a nearly perfect original surface condition. The morphology of the objects was inspected using the light microscope before and after physical separation from the cassette, and was found to be unaltered. Subsequent morphology examination by SEM showed that a few agarose fibers were sometimes found to adhere to the surface of the isolated objects, which in turn further demonstrates the essentially nondestructive nature of this isolation technique.

3.4 Specimen Preparation for Electron Microscopy

Specimen preparation proved critical for electron microscopy. In order to obtain the original morphology and elemental compositions of all samples, no chemical treatment was applied. Samples were stored at room temperature and in a dust free area for a period of time in order to allow the water to evaporate. Some individual specimens which had been stored at room temperature for a long time experienced a natural breakdown or crack of the surface after they were dried. These distinctive samples proved individually useful for further examination by SEM. Although chemical treatment methods are available for any special study, they are not recommended unless absolutely necessary, because all sample preparation work for microanalysis and imaging in the electron microscope should maintain the integrity of the original sample and maximally preserve the ultrastructure and surface texture of
the sample as well as its elemental composition.

3.4.1 Specimen Preparation for SEM Examination

All samples isolated from the gel should be as clean as possible. Drying at room temperature for at least one day is essential. Sample supports used were aluminum, graphite and zinc containing-copper alloy. Carbon low resistant paste or colloidal graphite (Bio-Rad colloidal graphite with iso-propanol) or silver paint (colloidal silver from Ted Pella, Inc., and silver paint from Fullam) were used for better electrical contact with the support in order to allow the surface charge to leak away. Double-sided Scotch tape was used for conveniently fixing the sample, since it has a strong adhesive ability to make sample orientation (for objects) and dispersion (for particles) quickly fixed (Figure 3.9). The purposes are to capture the detailed three dimensional image and to avoid roughening the surface of the specimen which causes absorption of the characteristic X-rays. These absorptions of X-rays by asperity can cause large errors and sometimes it is impossible to acquire these X-rays in local microanalysis, especially if the X-ray collecting angle is shallow.

Nonconducting samples on stubs were coated to produce a thin conductive layer in order to avoid surface electron charge. Coaters used were of two types: Polaron Instruments Inc. SEM Coating Unit E5100 Cool Sputter Gold Coater, and JEOL JEE-4X Vacuum Evaporator Carbon Sputtering Coater using carbon rods (5mm x 100mm). Coating layers, in addition, will reduce damage to the sample during electron bombardment. All the samples studied here are electronically nonconductive
materials, which tend to give poor quality images due to the surface charging. Therefore, all sample were coated either by carbon for less expensive or gold for high quality imaging. The thickness of the coating layers can be calculated according to the operation manual. For Polaron Instruments Inc. SEM Coating Unit E5100 Cool Sputter Gold Coater, thickness of coating can be calculated at 2.5kV according to:

\[
\text{thickness} = 0.75 \times I \times t \, (\text{nm}) \quad \text{[} V = 2.5 \text{kV, target to specimen distance 50mm]} \\
\text{t} = \text{time in minutes} \\
I = \text{current in mA}
\]

Average coating times were of the order 2 minutes using \( V = 2.5 \text{ kV} \) and \( I = 20 \text{mA} \), hence, thickness will be around 30 nm.

For EDX microanalysis, a coating material that does not interfere with the analysis must be chosen. Carbon coating was acceptable for EDX microanalysis since the model used would not detect carbon anyway. Specimens were examined as soon as possible after coating; coated specimens were kept desiccated and shielded from dust and vapors after use. If charging was intractable after coating, the specimens were normally re-coated. For backscattering electron imaging purposes, coating layers were controlled to be very thin or absent, since charging is not going to affect the quality of the BEI image and the yield of Rutherford backscattered electrons is low.

Figure 3.9. Diagram of specimen mounted on Scotch double sided tape.
3.4.2 Specimen Preparation for Examination by TEM

Transmission electron microscopy copper grids were coated with either gold or carbon film prior to use (3.4.1). The thinnest possible sample which requires no further chemical or physical modification should be chosen first by using transmitted light microscopy. Samples were prepared by placing a water droplet containing the particles in suspension onto a copper grid followed by blotting with a piece of filter paper and drying at room temperature in a dust free area for at least a day.

3.5 Specimen Examination

All specimens for electron microscope examination were used immediately after preparation and coating. Some specimens changed during observation under vacuum and electron beam heating which caused these specimen to crack or even break. Specimens were labeled with a series number to indicate the original experimental conditions, with one sample stub for each specimen.

The conditions for in situ optical observation were recorded, including film used, shutter speed, developing chemicals used, temperature and time, and any other important details. For confocal microscopy, the higher speed black and white film was preferred for image recording (Tmax is recommended for higher sharpness, high contrast). Technical Pan was used in cases where superior image quality with satisfactory contrast is desired, particularly for those specimens with low contrast.
3.6 Chemicals and Materials Used

Chemicals Used

All chemicals were used as purchased without further purification.

Agarose:
A. Sigma type I-A Agarose, from Sigma Chemical Company.
B. Kodak Agarose ME with formula \((\text{C}_{6}\text{H}_{10}\text{O}_{5}\cdot\text{C}_{6}\text{H}_{5}\text{O}_{4})_x\), from Eastman Kodak Company.
C. Boehringer Mannheim Biochemicals, Agarose for Pulsed Field Gel Electrophoresis, PFGE Agarose, from Division of Boehringer Mannheim Corp.

\(\text{BaCl}_2 \cdot 2\text{H}_2\text{O}\) Barium Chloride (Crystal, f.w. = 244.28), Fisher Scientific, Certified A.C.S. reagent, provided by Fisher Scientific Company.

Buffer Solution (pH=10.00±0.02 at 25 °C, pH=7.00±0.02 at 25°C, Certified. Mold inhibitor added. Potassium Carbonate-Potassium Borate-Potassium Hydroxide Buffer 0.05 Molar), purchased from Fisher Scientific Company.

Cation Exchange Resin DOWEX 50W Hydrogen Form, Dry Mesh 50-100 with 8% Cross-Linked from SIGMA Chemical Company.

\(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}\) Calcium Chloride (Fine Granulated, White, f.w. = 147.02).USP/FCC specifications, purchased from Fisher Scientific Company.

\(\text{HCl}\) Hydrochloric Acid (f.w. =36.46), GR grade, by EM Science, EM Industries, Inc.

\(\text{Na}_2\text{CO}_3\) Sodium Carbonate Anhydrous (Granular, f.w. =105.99), Analytical Reagent(AR). Purchased from Mallinckrodt Inc.

\(\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}\) Sodium Chromate (Crystal, f.w. = 234.068), provided by Baker Analyzed Reagent, J. T. Baker.

\(\text{Na}_2\text{HPO}_4\) Sodium Phosphate Dibasic GR (Anhydrous, f.w. = 141.96), purchased from EM Science, West Germany.

\(\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}\) Sodium Metasilicate Pentahydrate (f.w. = 212.1), Sigma chemical.

\(\text{Na}_4\text{P}_2\text{O}_7\) Sodium Pyrophosphate Decahydrate (A.C.S. reagent, f.w. = 446.06, d=1.820), purchased from Aldrich Chemical Company, Inc.

\(\text{NaCl}\) Sodium Chloride (Crystal, f.w. = 58.44), Baker Analyzed Reagent, provided by J. T. Baker.

NaOH Sodium Hydroxide (Pellets, low in Carbonate, f.w.= 40.00), provided by Baker Analyzed Reagent, J. T. Baker.

Sodium Silicate Solution (d=1.390), contains ~14% NaOH, ~27% SiO₂, purchased from Aldrich Chemical Company, Inc.

Sr(NO₃)₂ Strontium Nitrate (f.w.= 211.65), Fisher Certified Reagent. Provided by Fisher Scientific Company.

Photographic Materials Used

Black & White 35mm Print Films (Negative Films):

Kodak TMAX T-100 (ISO 100), T-400 (ISO 400), and P3200 (ISO 800-3200). Processed by D-76 Kodak developer at suitable temperature conditions; if necessary, push process can be applied according to the instructions provided. Fixed by Kodak Fixer.

Kodak Technical Pan ESTAR-AH Base, ISO 25 or set at other desirable speed (e.g. ISO 50, ISO 64), Developed by Kodak Technidol Liquid Developer, D-76, and Kodak HC-110 Developer. Fixed by Kodak Fixer.

Color 35mm Print Films (Negative Film):

Kodak VRG 100 (ISO 100), Kodak GOLD (100), Kodak EKTAR 25 (ISO 25), all developed by C-41 process by commercial services.

Color 35 mm Reversal Films: w/o color filter correction, the color saturation and correctness are virtually the same as Kodak VRG and the equivalent category.

Kodak Kodachrome 25 (ISO 25), 64 (ISO 64), developed by commercial services.

Kodak Ektachrome 100HC (ISO 100), P800/1600, Daytime, developed by commercial services.

Black & White Print Papers: Polycontrast III RC Professional FM type, 8x10 and 8.5x11.5 inches.

All Kodak Photographic Products including chemicals were provided by EASTMAN KODAK COMPANY, Rochester, NY 14650.
Electron Microscopy Films for SEM:

Polaroid 4x5 Black & White, Type 55 (ISO 50), Positive & Negative Instant Sheet Film.

Polaroid 4x5 Black & White, Type 52 (ISO 400), Positive Instant Sheet Film. Provided by Polaroid Corporation, Cambridge, MA 02139.

Electron Microscopy Film for TEM:

Kodak Electron Image Film (B & W Negative Film), ESTAR Thick Base SO-163.
CHAPTER IV

RESULTS AND DISCUSSION

4.0 Overview

Three sets of systems were studied. They were: barium-containing systems (barium carbonate, barium chromate, barium phosphate), strontium-containing systems (strontium sulfate, strontium carbonate), and calcium phosphate systems with additives in gels which were investigated over a wide pH range.

The spiral or helical growth behaviors, and their morphologies, are extremely sensitive to system pH values. After detailed study, three distinguishable classes of induced morphologies were found which are called monsters, spirals and sheets (Figure 4.1 to 4.3). More diversity exists among the sheets. Flakes, disks, and flowers are varieties of the sheet morphology. Not only do they all have laminate structure, but also they are all formed at the same pH range. Normally, a flower is built up from more than one sheet and each sheet is quite beautifully curved. The flake looks like corn cereal with a curved sheet. The disk is basically a single sheet with more rounded edges and beauty; some of the disks appear heart-shaped. Figure 4.1 shows a BaCrO$_4$ monster in silica gel at pH=10.5. Figure 4.2 shows a BaCrO$_4$ spiral in silica gel at pH=10.3. Figure 4.3 shows a BaCrO$_4$ flower in silica gel at pH=10.1.
Some crystalline phases of these unique IMCA (Induced Morphology Crystals Aggregates) were investigated and compared. Secondary crystallizations were observed and studied. Figure 4.4 is a photomicrograph of a BaCO$_3$ disk with small needle-shaped euhedral secondary BaCO$_3$ crystals in agarose-silica mixed at pH=10.0. Figure 4.5 is another photomicrograph of a BaCO$_3$ heart-shaped sheet BaCO$_3$ in silica gel at pH=9.9; The extinction pattern from such objects remains stationary in the laboratory frame work when the object is rotated, consistent with a structure in which crystallites radiate outward from the original nucleus. Notice also the development of spirals from this nucleus and from the tip of the heart shape; these are both very common feature in sheets.

Figure 4.1. SEM micrograph, BaCrO$_4$ monster from silica gel at pH=10.4, scale bar 0.1mm.
Figure 4.2. Detail of BaCrO$_4$ spiral from silica gel at pH=10.3, SEM micrograph, scale bar 0.01mm.

Figure 4.3. BaCrO$_4$ flower from silica gel at pH=10.1, SEM micrograph, scale bar 0.1mm.
Figure 4.4. Secondary crystal growth of BaCO₃ at pH=10.0 in mixed gel, scale bar 0.1mm.

Figure 4.5. BaCO₃ heart-shaped sheet from silica gel at pH=9.9, photomicrograph, crossed polarizer; gypsum plate, scale bar 0.1mm.
Pattern formation and Liesegang ring formation were explored as well. Figure 4.6 is a unique structured, three dimensional Liesegang ring formation in the standard micro slide cassette (section 3.2.3) at pH = 9.0 of CaCl₂–Na₂HPO₄ with addition of Na₄P₄O₁₇ in agarose gel at room temperature.

Figure 4.6. Liesegang ring of CaCl₂–Na₂HPO₄–Na₄P₄O₁₇ in agarose gel at pH = 9.0, Scale bar 0.5mm.

4.1 Barium-containing Precipitates

Barium carbonate precipitates in gel are among the most extensively studied (Garcia-Ruiz, 1978-1985; Reid, 1992). The name Induced Morphology Crystal Aggregates (IMCA) was suggested by Garcia-Ruiz. His group studied group II A, or alkaline earth metals, as carbonates. In this work, it was found that the IMCA formation depends strongly on the cation, and only weakly on the anion. Very brief experiments with rare earth metals such as La³⁺, were carried out, but they showed no tendency to give IMCAs instead of a normal crystal growth. Other metal cations were
also tried and gave normal precipitates only.

Three classes of IMCAs have been categorized, and merge into each other. They are: Monsters or highly twisted spirals; well behaved Spirals and twisted ribbons, Sheets, including disks, flowers or/and flakes. The disk shapes and heart shapes are common forms of sheets with more symmetry. More curved sheets with the greatest irregularities are commonly called flakes (like corn flakes cereal) or flowers which look like Texas yellow rose blooming (Figure 4.2) and, in fact, BaCrO$_4$ flower IMCA are yellow in color. Monsters and sheets cannot be produced under the same experimental conditions. Monsters are formed under very high pH conditions (pH > 10.3 in silica hydrogel) while sheets are formed in moderately high pH conditions (pH ~ 10.0). They are never formed in the same gel area or even in the same cassette. In contrast, spirals do not have such a clear boundary to distinguish them from sheets and monsters, and some poorly defined spirals even have sheets on the end of an arm.

The formation of IMCA can in principle be explained by overall membrane controlled growth and aggregation under far-from-equilibrium conditions. Only for a few kinds of sheet morphology, such as heart shaped disks, do they show any overall symmetry. The rest were totally unconventional.

Chemical equilibrium data and all solubility product constants were obtained from CRC Handbook of Chemistry & Physics (Weast, 1990) and Iler’s book (1979). These data can be used to generate graphical representations of equilibrium data, and such that facilitates the assessment of the relative importance of a large number of species under a prescribed set of conditions and the shift in equilibrium that follows a
perturbation of those conditions. In a distribution diagram, the ratio or percentage
collection of the activity (or concentration) of a species to the total activity of that
constituent was plotted as a function of pH variable at fixed temperature.

The meta-silicic acid distribution behavior in aqueous solution is almost the
same as in gel, because the gel has a continuous phase of liquid. Active SiO$_4^{4-}$ anion
would remain trivial as long as the system pH is not higher than 13.0 (Iler, 1979).
Figure 4.7 showed the much simplified treatment of the SiO$_3^{2-}$ anion distribution
coefficient verses pH. It should be clear that there is no such thing as free SiO$_3^{2-}$,
instead, extremely complicated species such as polysilicate [(SiO$_3^{2-}$)$_n$] may be real
(Iler, 1979). Anyway, SiO$_3^{2-}$ only makes a significant concentration to the silicate
distribution when the pH is higher than 10 (Figure 4.7).

![Figure 4.7. SiO$_3^{2-}$ distribution coefficient versus pH at 25°C.](image)
4.1.1 Precipitation in Silica Gel

The selected experiments were carried out mainly at pH between 9.5 and 10.5 in standard micro cassettes, although some experiments were also conducted at pH as low as 7.3. The silica gel used contained 4.0 to 4.5% SiO$_2$; the SiO$_2$ concentration did not have a significant effect on the morphology of precipitates, but higher percentages of SiO$_2$ produced a very thick gel which was very difficult for in situ observation. 4% SiO$_2$ was the most preferred concentration as determined through preliminary experiments. The concentration of sodium carbonate in silicate solution was 0.05 M for all experiments except where mentioned otherwise. This solution was titrated with cation hydrogen exchange resin (DOWEX 50W Hydrogen Form, Dry Mesh 50-100, 8% Cross-Linked, from SIGMA Chemical Company) to reach the desired pH value, and then poured into the cassette (Section 3.1.1). The solution transformed to a gel in times ranging from a few minutes to a week, depending on pH, external ionic strength, loaded concentration of chemicals and temperature. Then a warm solution of 0.5 M barium chloride with 0.5% agarose (about 50°C) was slowly poured into the top of the cassette and allowed to cool and stiffen. The cassette was then sealed with regular office tape or with silicone rubber sealer gel. Table 4.1 lists some experiments which were carried out. It was found that IMCA formation was most sensitive to system pH with or without an external ionic strength that was varied by adjusting the concentration of NaCl. The concentration of carbonate affects the size of IMCA slightly, but it does not change the trend governing IMCA formation. This is: from very high pH to relative high pH, the overall trend is from monsters to spirals, then
flakes. However, at pH=8, the diffusion controlled dendrite crystal growth is affected by the concentration of carbonate, in which the dendritic became more branched (Baird, 1992).

<table>
<thead>
<tr>
<th>Table 4.1 Barium Carbonate Precipitates in Silica Gel</th>
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<tr>
<td><strong>Diffuse Layer</strong></td>
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<tr>
<td>[BaCl₂] (M)</td>
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<tr>
<td>0.50</td>
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Figure 4.8 is the X-ray energy dispersive (EDX) spectrum of a typical sheet of BaCO₃ IMCA from silica gel at pH=10.1. It shows that the actual IMCA shell
contains barium and silicate as chemical components of the membrane. Figure 4.9 is the EDX spectrum of the interior of the same single BaCO₃ sheet sample collected under the same experimental conditions. Silicon was not detected.

Figure 4.8. EDX spectrum of the sheet BaCO₃, exterior shell analysis.

Figure 4.9. EDX spectrum of the same BaCO₃ sheet, interior spot analysis.
ESCA analysis provides further valuable data. Figure 4.10 shows the complete elemental binding energy analysis for the external surface of bulk spiral IMCAs on indium foil. Figure 4.11 is a similar elemental binding energy analysis for a single sheet IMCA, also on indium foil. Figure 4.12 is a detailed comparison between the spirals and the single sheet IMCA for elemental Si(IV) and Ba(II) only. The barium peaks had almost the same intensity for both spiral and sheet samples, but the silicon peaks had a quite different intensity. It is clearly seen that the silicon peak of the spiral sample was higher than that of the sheet. This can be interpreted as evidence that the spirals contain more silicon on the surface, or that the spiral membrane are richer in silicon than that of the sheet. Figure 4.13 is a detailed carbon (C 1s) comparison between the spirals and the single sheet IMCA. These data indicated that surface membrane contained carbonate; therefore, barium-silicate-carbonate should be the overall chemical components.

ESCA results are complementary to EDX analysis since carbon cannot be detected by EDX. Results for the quantitative ESCA analysis of the spiral sample are shown in Table 4.2. The chemical formula may be expressed as: BaO2SiO2·0.5CO2. Results for the quantitative analysis on the large individual sheet IMCA surface are given in Table 4.3; its chemical composition can be written as: BaO·SiO2·CO2. Thus there is twice as much silica for each barium in the spiral sample as in the sheet. In addition, the shell of the spiral is much thicker than the sheet. These results are expected at higher pH since more active silicate is available for the spiral growth due to the distribution coefficient of silicate anion (Figure 4.6). These results are fully
consistent with EDX qualitative data as well as numerous SEM observations.

Figure 4.10. XPS total elemental analysis of spiral BaCO$_3$.

Figure 4.11. XPS total elemental analysis of sheet BaCO$_3$. 
Figure 4.12. XPS carbon analysis of BaCO₃ IMCA.

Figure 4.13. XPS silicon analysis of barium carbonate IMCA
Table 4.2 ESCA quantitative analysis of spirals BaCO₃ IMCA (data as collected).

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<tbody>
<tr>
<td>Ba 3d5</td>
<td>10.712</td>
<td>1.000</td>
<td>0.021</td>
<td>11.193</td>
<td>24.75</td>
<td>785.55</td>
</tr>
<tr>
<td>Si 2p</td>
<td>20.748</td>
<td>1.937</td>
<td>0.040</td>
<td>1.185</td>
<td>0.865</td>
<td>107.95</td>
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<tr>
<td>O 1s</td>
<td>62.534</td>
<td>5.838</td>
<td>0.122</td>
<td>9.309</td>
<td>2.950</td>
<td>537.05</td>
</tr>
<tr>
<td>C 1s</td>
<td>6.006</td>
<td>0.561</td>
<td>0.012</td>
<td>0.363</td>
<td>1.000</td>
<td>295.00</td>
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</table>

Table 4.3 ESCA quantitative analysis of a sheet BaCO₃ IMCA (data as collected).

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<tbody>
<tr>
<td>Ba 3d5</td>
<td>14.428</td>
<td>1.000</td>
<td>0.010</td>
<td>5.241</td>
<td>24.75</td>
<td>785.35</td>
</tr>
<tr>
<td>Si 2p</td>
<td>15.137</td>
<td>1.049</td>
<td>0.010</td>
<td>0.301</td>
<td>0.865</td>
<td>108.35</td>
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<tr>
<td>O 1s</td>
<td>55.945</td>
<td>3.878</td>
<td>0.038</td>
<td>2.896</td>
<td>2.850</td>
<td>536.85</td>
</tr>
<tr>
<td>C 1s</td>
<td>14.490</td>
<td>1.004</td>
<td>0.010</td>
<td>0.304</td>
<td>1.000</td>
<td>294.95</td>
</tr>
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</table>

Monsters and spirals can be only separated chemically due to the silica gel matrix (Section 3.3.1). The SEM backscattering micrograph of the isolated spiral BaCO₃ (Figure 4.14) clearly shows the formation of the barium silicate membrane from silica gel at pH=10.2. The thickness of membrane is roughly around a few microns for monster IMCA formed by chemical separation (Section 3.3.1). Figure 4.15 is same as Figure 4.14 except the fractures were created by the SEM hot electron beam. This set of micrograph were never seen before and such fractures may signify that: both exterior shell and internal spiral were not coherent when they grew, spiral was force to grow, therefore, physical stress might generate; internal spiral grew fast
than exterior did. Spot EDX analysis of the inside position of the spiral showed the barium peak only, while the exterior shell membrane displayed both barium and silicon peaks (Figure 4.8 and Figure 4.9).

The membrane could be directly observed by adding 0.1M aqueous HCl to the IMCA (either spiral or sheet, but sheet was too thin after treatment with acid.). The carbon dioxide bubbling quickly formed. The hollow membrane kept the original morphology.

Figure 4.14. BEI micrograph of an isolated $\text{BaCO}_3$ from silica gel at pH=10.2, scale bar 0.01mm.

Figure 4.15. Same as in Figure 4.13, taken later, scale bar 0.01mm.
To produce barium chromate IMCA, a BaCl₂ solution was allowed to diffuse into silica gel which contained Na₂CrO₄ in a cassette. The yellowish precipitates formed were clearly BaCrO₄, since there are no other possible solid products. Many different morphologies of IMCA were retrieved from the silica gel by destructive techniques (Section 3.3.1). Basically, BaCrO₄ precipitates have similarities with BaCO₃ in terms of induced morphology crystal aggregates (IMCA). Monster morphology (pH > 10.3, Figure 4.16), spiral morphology (pH = 10.2 - 10.1), and flakes (pH = 10.0 - 9.9) all can be observed at pH between 10.4 and 9.9 in silica gel. IMCA separated by chemical or physical techniques are yellowish in color. Their sizes were also similar to those of the BaCO₃ IMCA and can be as large as 2 mm. Chemical compositions were determined by EDX. Figure 4.17 is a superposition of the EDX spectrum of BaCrO₄ IMCA; it indicates that monsters are far richer in silica than are flakes.

The total growth time for an IMCA was observed to be around 80 hours. The size of the IMCA can be influenced by the degree of supersaturation which develops when diffusion occurs. Lower concentration ratio can grow a larger IMCA. This can be observed at the end of the diffusion front. Table 4.4 lists some experiments in different initial concentrations. The last three experiments had the same Ba²⁺ : CrO₄²⁻ ratio (10 : 1), but a smaller amount of reagents.

As well as IMCA formation, there were some "X" shaped polycrystals and their transitions, such as Figures 4.18 and 4.19. "X" shaped objects can be considered as dendritic growth under the influence of silica if the pH is lower than 9.5. The
angle of the "X" shape decreased when the system pH was increased and a transitional morphology between dendrite and sheet was developed. Figure 4.19 was recorded at lower reagent concentration in the standard micro slide cassette at pH=10.1 (end of the diffusion).

Table 4.4 Barium Chromate Precipitates in Silica Gel.

<table>
<thead>
<tr>
<th>Diffuse Layer</th>
<th>Loaded in Silica Gel</th>
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<tbody>
<tr>
<td>[BaCl₂] (M)</td>
<td>SiO₂ (%)</td>
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<tr>
<td>0.50</td>
<td>4.0</td>
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</tr>
<tr>
<td>0.125</td>
<td>4.0</td>
</tr>
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</table>

Figure 4.16. Photomicrograph of Monster BaCrO₄ in silica gel at pH=10.4, scale bar 0.05mm.
Figure 4.17. Comparison of EDX spectrum between monster and sheet BaCrO$_4$.

Figure 4.18. Dendritic growth of BaCrO$_4$ in silica gel at pH=9.5, scale bar 0.05mm.

Figure 4.19. Dendritic growth of BaCrO$_4$ in silica gel at pH=10.1, scale bar 0.05mm.
In situ photomicrographs show the sheet BaCO$_3$ surface texture. With a polarizer, the crossed pattern can be observed clearly as seen in Figure 4.20. Figure 4.21 shows surface texture. IMCA could only be separated from the silica gel by destructive techniques (Section 3.3.1). Isolated IMCA were then coated by either carbon or gold for further detailed examination by SEM (Sections 3.4.1 and 3.4.2). Flakes were uniformly found to have a laminar structure, with a membrane thickness of around one micron and total thickness of around ten microns, as shown in Figures 4.22 to 4.25.

Figure 4.20. In situ photomicrograph of heart-shaped BaCO$_3$ in silica gel at pH=10.0, crossed polarizer, scale bar 0.2mm.

Figure 4.21. Photomicrograph of heart-shaped BaCO$_3$ in silica gel at pH=10.0, unpolarized light.
Figure 4.22. BEI micrograph of sheet BaCO₃ from silica gel at pH=10.0, scale bar 0.1mm.

Figure 4.23. BEI micrograph of sheet BaCO₃ from silica gel at pH=10.0, scale bar 0.1mm.

Figure 4.24. BEI micrograph of sheet BaCO₃ from silica gel at pH=10.1, scale bar 0.1mm.
When the pH is increased to 10.2, well formed spiral IMCA can be observed easily. These spirals were arranged in all directions in the gel, with no sign of a preferred orientation. Some spirals were physically separated from the gel with a small fine hair brush. Figure 4.26 shows part of a typical well formed spiral. In situ scanning confocal microscopy (Figure 4.27) also shows three dimensional free growth in all directions in the gel, within the limits of the vessel boundaries. In confocal microscopy, the signal is caused by reflectance, which depends on surface characteristics and refractive index differences at the interfaces (Section 2.2.2).

EDX analysis suggests that both barium silicate and barium carbonate are in the membrane. ESCA analysis disclosed more valuable information as discussed earlier. In this analysis, the carbon peak was assigned to the carbonate carbon. Also, it has been found that the silica peak in the spirals is much stronger than in flakes. Quantitative analysis indicated that there is more silica in spiral membrane than in flakes. These data suggest that spirals were substantially controlled by the diffuse
membrane which appears to be a barium carbonate silicate.

The conventional mechanisms of spiral crystal growth were investigated by Verma (1953). A dislocation is the essential factor in such growth. Dislocation-controlled spiral growth does not rotate the crystal axes, and cannot help explain the spiral IMCA studied here.

Figure 4.26. SEM micrograph of spiral BaCO$_3$ from silica gel at pH=10.3, scale bar 0.01mm.

Figure 4.27. In situ confocal micrograph of spiral BaCO$_3$ in silica gel at pH=10.3, scale bar 0.1mm.
Barium phosphate precipitating systems were much more intricate to deal with. Two different chemical structures (Ba$_3$(PO$_4$)$_2$ and BaHPO$_4$) have been reported (Denk, 1961; Banks, 1976). Ba$_3$(PO$_4$)$_2$ was formed with a high Ba:P ratio at pH higher than 8 and grew at pH 10-10.5 as hexagonal plates up to 0.1mm (Banks, 1976). BaHPO$_4$ was formed and grew at pH 4-7 as plates and prism up to 0.4mm (Banks, 1976).

Since barium phosphate growth is very sensitive to the growth conditions, the Ba:P ratio and pH must be controlled carefully. As a direct consequence, more than 60 experiments were actually carried out from low to high pH with variation of other factors (SiO$_2$%, initial concentration, external ionic strength, etc.). Although some of them were done for screening purposes only, they already displayed that the tendency of barium phosphate to give detectable crystals is weak. A distinctive behavior of barium phosphate grown in silica gel at high pH was the length of time required for growth. It took more than 48 hours to complete the entire development. The three categories of IMCA were observed although the difficulty of growing IMCA for this system is apparent; the sheet was the most difficult to grow. Extreme conditions were explored with unusually high external ionic strength ([NaCl]=0.60M), higher pH and longer times being needed to grow IMCA effectively. Some experimental results are tabulated in Table 4.5. The characteristic monster could found at pH=10.6 in silica gel with very high ionic strength as tested. Such conditions make the silica gel extremely cloudy and not suitable for in situ observations at all. Therefore, IMCA has to be isolated chemically (Section 3.3.1).
Barium phosphate IMCA were hard to separate, too, even by chemical separation techniques; only fragments of a whole IMCA were usually obtained. Figure 4.28 is an SEM micrograph showing a monster separated from silica gel at pH=10.6.

Table 4.5  Barium Phosphate Precipitates in Silica Gel.

<table>
<thead>
<tr>
<th>Diffuse Layer</th>
<th>Loaded in Silica Gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BaCl₂] (M)</td>
<td>SiO₂ (%)</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
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<tr>
<td>0.50</td>
<td>4.0</td>
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<td>0.50</td>
<td>4.0</td>
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<tr>
<td>0.50</td>
<td>4.0</td>
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<tr>
<td>0.50</td>
<td>4.0</td>
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<td>0.50</td>
<td>4.0</td>
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<td>0.50</td>
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<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.75</td>
<td>4.0</td>
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<tr>
<td>0.50</td>
<td>4.0</td>
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<tr>
<td>0.20</td>
<td>4.0</td>
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<td>0.75</td>
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<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.10</td>
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</tr>
<tr>
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<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
<td>7.0</td>
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<tr>
<td>0.50</td>
<td>7.0</td>
</tr>
<tr>
<td>0.50</td>
<td>2.0</td>
</tr>
<tr>
<td>0.50</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Figure 4.29 is SEM micrograph of the spiral separated from silica gel at pH=10.5 without external ions; some silica is still bound to the spiral. Figure 4.30 to 4.33 are BEI micrographs of some junctions isolated from silica gel at pH=10.3. That IMCA grows in different directions can be seen. The spiral growth is with a very thick barium silicate shell. A few flakes of barium phosphate were isolated from the silica gel at pH=10.3 without NaCl. Figure 4.34 is a photomicrograph of a typical isolated sheet; the characteristic cross pattern can be observed. Figure 4.35 is an unique in situ photomicrograph of the sheet in silica gel at pH=10.3. Figure 4.36 is the SEM micrograph of a flake separated under the same experimental condition; notice that the rough surface nature of the flake is somewhat different than barium carbonate flakes.

Figure 4.28. SEM micrograph of monster from silica gel at pH=10.6, scale bar 0.1mm.
Figure 4.29. SEM micrograph of spiral from silica gel at pH=10.5, without NaCl, scale bar 0.1mm.

Figure 4.30. BEI micrograph of a junction from silica gel at pH=10.3, scale bar 0.01mm.

Figure 4.31. BEI micrograph of a spiral from silica gel at pH=10.3, scale bar 0.01mm.
Figure 4.32. BEI cross-sectioned micrograph of a spiral from silica gel at pH=10.3, scale bar 0.01mm.

Figure 4.33. BEI cross-sectioned micrograph of a spiral from silica gel at pH=10.3, scale bar 0.01mm.

Figure 4.34. Photomicrograph of the sheet from silica gel at pH=10.3, scale bar 0.1mm.
Figure 4.35. Unique *in situ* photomicrograph of the sheet in silica gel at pH=10.3 scale bar 0.1mm.

Figure 4.36. SEM micrograph of flake from silica gel at pH=10.3, scale bar 0.1mm.

Cross sectional EDX analysis of the isolated monsters indicated that the chemical composition was actual $\text{Ba}_3(\text{PO}_4)_2$ when compared with a range of standard samples of $\text{Ba}_3(\text{PO}_4)_2$, as produced from the reaction between $\text{BaCl}_2$ and $\text{NaH}_2\text{PO}_4$ in aqueous solutions at $\text{pH}=10$ and at high $\text{Ba}:\text{P}$ ratio (Denk, 1961). Since barium phosphate is among the most complicated of barium-containing systems, the effect of additives was explored experimentally, typically by adding small amounts of
pyrophosphate (Davey, 1991) to the loaded silica gel. Table 4.6 lists some of these experiments.

Table 4.6 Barium Phosphate Precipitates in Silica Gel with the Addition of Na₄P₂O₇.

<table>
<thead>
<tr>
<th>Diffuse Layer Loaded in Silica Gel (M)</th>
<th>[BaCl₂] (M)</th>
<th>SiO₂ (%)</th>
<th>[NaH₂PO₄]</th>
<th>[Na₄P₂O₇]</th>
<th>[NaCl]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
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<td>0.0025</td>
<td>0.20</td>
<td>10.4</td>
</tr>
<tr>
<td></td>
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<td>2.0</td>
<td>0.045</td>
<td>0.0025</td>
<td>0.20</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>2.0</td>
<td>0.045</td>
<td>0.0025</td>
<td>0.20</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Pyrophosphate is known to have some effect on controlling barium phosphate crystal growth in the absence of silica (Davey, 1991). This can be explained by chemically controlled crystal growth processes. In the silica gel, no detectable effect to the formation of IMCA was observed.

4.1.2 Precipitation in Agarose Gel

It was decided to probe the barium-containing systems in agarose gel over a wide pH range in order to examine the effect of pH in the absence of silicate. As general examinations, the distinct morphologies evolution can be observed. At a very slightly basic pH, the shape is dendritic as sign of diffusion-controlled precipitation; at high pH, the morphologies assume the "X" shape for chromates (4.18). The distribution of carbonate at various pH values might provide some thermodynamic explanations although a environmental pH increase could cause the system to alter to some degree. Table 4.7 below shows the BaCO₃ precipitating experiments carried out.
Barium carbonate precipitation in agarose gel was studied over the entire pH range, from mildly acidic to highly basic, as shown on Table 4.7. When the pH is at or below 6, no visible precipitation can be observed with the optical microscope. This is due to very low carbonate concentration, as shown in Figure 4.30. At pH = 5, the distribution coefficient of carbonate anion is around $2.3 \times 10^{-7}$, or virtually zero. At pH=7, some small crystals can be observed. At pH = 10, the carbonate anion distribution coefficient is increased to 0.36; this is very significant. Barium carbonate dendrite crystals were clearly seen in the whole cassette at this pH. The photomicrographs in Figure 4.37 through Figure 4.39 show this dendritic BaCO$_3$ crystal growth. As the pH is increased, the dense branch morphology was found. At

### Table 4.7 BaCO$_3$ Precipitates in Pure Agarose Gel.

<table>
<thead>
<tr>
<th>[BaCl$_2$] (M)</th>
<th>Agarose (%)</th>
<th>[Na$_2$CO$_3$]</th>
<th>[NaCl]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
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<td>0.50</td>
<td>0.6</td>
<td>0.10</td>
<td>0.10</td>
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<tr>
<td>0.50</td>
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<td>9.8</td>
</tr>
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<tr>
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<td>0.6</td>
<td>0.05</td>
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<tr>
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<td>0.05</td>
<td>0.20</td>
<td>8.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
<td>0.05</td>
<td>0.20</td>
<td>9.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
<td>0.05</td>
<td>0.20</td>
<td>10.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
<td>0.05</td>
<td>0.20</td>
<td>10.3</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
<td>0.05</td>
<td>0.20</td>
<td>11.0</td>
</tr>
</tbody>
</table>
higher pH (10.3), BaCO$_3$ precipitated in the form of spherical spherulites, a change attributable to the greatly increased free carbonate anion concentration.

Figure 4.37. Photomicrograph of BaCO$_3$ in silica gel without NaCl at pH=9.0, scale bar 0.2mm.

Figure 4.38. Photomicrograph of BaCO$_3$ in silica gel without NaCl at pH=9.3, scale bar 0.2mm.
Figure 4.39. Photomicrograph of BaCO$_3$ in silica gel without NaCl at pH=9.6, scale bar 0.2mm.

\[ \text{CO}_3^{2-} \text{ vs pH} \]

Figure 4.40. \text{CO}_3^{2-} \text{ distribution coefficient vs pH.}
Another highly insoluble inorganic precipitate, BaCrO$_4$, was explored at selected pH ranges through the reaction between BaCl$_2$ and Na$_2$CrO$_4$ in agarose hydrogel. Table 4.8 lists some experiments at pH ranging from 5 to 11.0. With increasing pH, the morphologies changed from dendritic structure into dense dendritic and finally developed as spherulitic morphology (at pH>10.3). These morphologies are considered to be formed by a fully diffusion controlled crystal growth process.

<table>
<thead>
<tr>
<th>Diffuse Layer</th>
<th>Loaded in Agarose Gel (M)</th>
<th>[BaCl$_2$] (M)</th>
<th>Agarose (%)</th>
<th>[Na$_2$CrO$_4$]</th>
<th>[NaCl]</th>
<th>pH</th>
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<td>0.20</td>
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<td>0.05</td>
<td>0.20</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50</td>
<td>0.6</td>
<td>0.05</td>
<td>0.20</td>
<td>7.0</td>
</tr>
<tr>
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<td>0.05</td>
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<td>8.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50</td>
<td>0.6</td>
<td>0.05</td>
<td>0.20</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
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<td>0.05</td>
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</tr>
<tr>
<td></td>
<td></td>
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<td>0.6</td>
<td>0.05</td>
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<td>10.3</td>
</tr>
<tr>
<td></td>
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<td>0.50</td>
<td>0.6</td>
<td>0.05</td>
<td>0.20</td>
<td>11.0</td>
</tr>
</tbody>
</table>

BaSO$_4$ precipitates (Lieser, 1977; Prieto, 1990; Heywood, 1992; Putnis, 1992) were also studied in pure agarose gel for purposes of comparison. Table 4.9 lists some results. These were similar to those for BaCrO$_4$ in terms of morphology from acidic to basic pH conditions. Other characteristics such as growth rate and size were also quite similar, except some butterfly shaped morphology as an unique characteristic (Reid, 1992).
Table 4.9  BaSO₄ Precipitates in Pure Agarose Gel.

<table>
<thead>
<tr>
<th>[BaCl₂] (M)</th>
<th>Agarose (%)</th>
<th>[Na₂SO₄]</th>
<th>[NaCl]</th>
<th>pH</th>
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</thead>
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<td>0.05</td>
<td>0.20</td>
<td>5.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>6.0</td>
</tr>
<tr>
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<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>7.0</td>
</tr>
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<td>0.20</td>
<td>8.0</td>
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<tr>
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<td>0.5</td>
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<td>9.0</td>
</tr>
<tr>
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<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>10.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>10.3</td>
</tr>
<tr>
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<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Under basic conditions and in pure agarose gel, the barium phosphate growth behavior was studied as shown in Table 4.10. The agarose hydrogel was used at high density in order to decrease the pore channel size and hence the rate of diffusion, so as to provide more time for the growth of the precipitates. Direct observations were Liesegang banding with very fine white microcrystals at all pH conditions; brushite crystals were later formed as Ostwald ripening effect.

Table 4.10  Barium Phosphate Precipitates in Pure Agarose Gel.

<table>
<thead>
<tr>
<th>[BaCl₂] (M)</th>
<th>Agarose (%)</th>
<th>[NaH₂PO₄]:[NaCl]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.0</td>
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<td>10.0</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.007</td>
<td>10.4</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.007</td>
<td>12.0</td>
</tr>
</tbody>
</table>
4.1.3 Precipitation in Mixed Gel

The newly developed agarose-silica mixed gel can overcome many disadvantages of pure silica gel and make possible the fundamental study of salt effects in gels. Some advantages of the mixed gel are:

* High degree of transparency
* Extended pH range
* High purity of porous media
* Very easy to separate particles/objects
* Very easy to prepare the gel

In the mixed silica-agarose gel, the crystal growth habits are greatly modified in terms of IMCA relative to agarose alone because of the presence of silicate. The influence of the silicate during the growth period is immense. Without silicate in agarose, only tiny spherical objects, dendritic crystals and densely branch dendrites etc. were developed, with no sign of IMCA formation (4.1.2). One other phenomenon was observed only in the silica-agarose mixed gel; secondary crystal growth. When diffusion started, IMCA developed within a week or less, normally four days, depending upon the experimental conditions. After two weeks the diffusion in the cassette was ended. Around the formed IMCAs, small single crystals could be identified by crossed polarized optical microscopy \textit{in situ}. Some of them were isolated from the mixed gel by non-destructive separation techniques (Section 3.3.2). Figure 4.4 shows an optical micrograph of the secondary crystal growth on the surface of BaCO$_3$ IMCA at pH=10.1 \textit{in situ}. EDX showed that the secondary crystals contained Ba but no Si and therefore were BaCO$_3$. This further confirmed the
necessity for silicate in the formation of IMCA, and also suggests that this is a faster growing process, usually called a dynamical controlled process. After the silicate had run out, the precipitation growth went back to the normal crystal growth.

External materials such as added sodium chloride, and atmospheric carbon dioxide also have some important role to play in the formation of IMCA. The influences of NaCl and CO$_2$ were segregated in some degree through the mixed gel experiments. The NaCl concentration can increase the size of the crystal in the gel by possibly reducing the active concentration, therefore, reducing effective supersaturation and slowing nucleation. Also, in silica gel as described earlier (Section 4.1), sodium chloride can be used to accelerate the solidification of silica gel. In the selected systems, the influences of NaCl in the mixed gel were studied further. A change of a fraction of one pH unit (usually, 0.2) was quantitatively determined (to 0.2M NaCl). External ions such as Na$^+$, Cl$^-$, can lower the system’s pH without substantially affecting the formation of IMCA. On the other hand, NaCl can be entirely ignored without affecting the formation of IMCA at all.

The influences of CO$_2$ were not that easy to isolate clearly. Even when carbon dioxide free ultra pure water (up to 18 M ohms) is used, the sodium meta-silicate solution (very basic) still absorbed a lot of CO$_2$. Subsequent experiments showed that the CO$_2$ is necessary for the IMCA formation. These very primary experiments were done in agarose gel with ultra fresh prepared pure water which contained pure sodium meta-silicate pentahydrate, instead of sodium meta-silicate solutions, in studies of the barium chromate system; much more complicated dendritic growth was observed
primarily. Compare the function of CO$_2$ in calcium silicate cement chemistry, which is to accelerate membrane formation as well as cementation (Lea, 1971). More studies may need to be done in future (Chapter V).

Table 4.11 shows that BaCO$_3$ precipitates in agarose-silica mixed gel over a very wide pH range. Variations of percentages of SiO$_2$ and pH are two critical factors influencing the experimental results.

Table 4.11 Barium Carbonate Precipitates in Agarose-Silica Mixed Gel.

<table>
<thead>
<tr>
<th>[BaCl$_2$] (M)</th>
<th>Agarose (%)</th>
<th>SiO$_2$ (%)</th>
<th>[Na$_2$CO$_3$]</th>
<th>[NaCl]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.6</td>
<td>0.22</td>
<td>0.05</td>
<td>0.20</td>
<td>14.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
<td>0.22</td>
<td>0.05</td>
<td>0.20</td>
<td>13.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
<td>0.22</td>
<td>0.05</td>
<td>0.20</td>
<td>12.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
<td>0.22</td>
<td>0.05</td>
<td>0.20</td>
<td>11.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
<td>0.22</td>
<td>0.05</td>
<td>0.20</td>
<td>10.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
<td>0.22</td>
<td>0.05</td>
<td>0.20</td>
<td>9.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
<td>0.22</td>
<td>0.05</td>
<td>0.20</td>
<td>8.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
<td>0.22</td>
<td>0.05</td>
<td>0.20</td>
<td>7.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
<td>0.22</td>
<td>0.05</td>
<td>0.20</td>
<td>5.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
<td>0.22</td>
<td>0.05</td>
<td>0.20</td>
<td>3.0</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.48</td>
<td>0.05</td>
<td>0.20</td>
<td>10.4</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.48</td>
<td>0.05</td>
<td>0.20</td>
<td>10.2</td>
</tr>
</tbody>
</table>

No precipitates were observed at pH<7. Dendritic growth was found in the range 8-9, sheets between 10.2, spiral between 10.4, and monsters at pH>10.4. Thus monsters, spirals, and sheets were all observed under the appropriate pH conditions, at slightly higher pH than in silica gel alone. Figure 4.41 is a photograph of the same sheet as shown in Figure 4.4, but between crossed polarizer; the cross pattern can be clearly seen. Normal crystal growth occurs in agarose gel without silica present.
Nevertheless, in the presence of silicate at high pH, growth habit is dramatically changed and the new branch of crystals was formed above the surface of the IMCA (Figure 4.4 and Figure 4.41). In order to examine these phenomena, some of these secondary crystals were dug out from the mixed gel, and were characterized by EDX and BEI. This secondary crystals were identified from EDX as barium carbonate.

Figure 4.42 is a BEI micrograph of secondary crystal growth at pH=10.2; the thread-like objects are traces of agarose adhering to silicate layer. The secondary crystal growth often happened at least one week after an experiment was set up, although the initial diffusion process was normally complete in about four days. It occurred over the full pH range in which the IMCA formation conditions were satisfied. It did not matter whether the IMCA were sheets or spirals. The reason for this phenomena can be explained by the total amount of active silicate. The growth of IMCA consumed most of the active silicates in the cassette, but the small amounts of barium chloride and sodium carbonate were still accessible. This led naturally to the secondary barium carbonate crystal growth.

By controlling the concentration of original silicate, the properties of the mixed gel can be determined. Too much silicate in the mixed gel means not much difference from pure silica gel in nature, and with too little silicate the mixed gel behaved like agarose gel. The threshold point could be determined experimentally for the each precipitating system. As a good example, a few designed experiments showed that the spiral growth was not the nature of barium carbonate crystal itself. Figure 4.43 to 4.45 are BEI micrographs of the spiral separated from the mixed gel at pH=10.2.
this set of experiments, silicate was deliberately controlled to be deficient (0.48% or less), but there was enough silicate to make the corkscrew develop. A corkscrew growth pattern can be seen and it is basically spirals.

Figure 4.41. Same as Figure 4.4, polarized photomicrograph, scale bar 0.1mm.

Figure 4.42. BEI micrograph of secondary crystal growth at pH=10.2, scale bar 0.001mm.
Figure 4.43. BEI micrograph of spiral from deficient silicate mixed gel at pH=10.4, scale bar 0.01mm.

Figure 4.44. Same as Figure 4.43.

Figure 4.45. Growth tip of spiral BaCO$_3$, top view, scale bar 0.01mm.
Table 4.12 Barium Sulfate Precipitates in Agarose-Silica Mixed Gel.

| Diffuse Layer Loaded in Agarose-Silica Gel (M) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| [BaCl₂] (M)     | Agarose (%)     | SiO₂ (%)        | [Na₂SO₄]        | [NaCl]          | pH              |
| 0.50            | 0.6             | 0.22            | 0.05            | 0.20            | 10.4            |
| 0.50            | 0.6             | 0.22            | 0.05            | 0.20            | 10.3            |
| 0.50            | 0.6             | 0.22            | 0.05            | 0.20            | 10.2            |
| 0.50            | 0.6             | 0.22            | 0.05            | 0.20            | 10.1            |
| 0.50            | 0.6             | 0.22            | 0.05            | 0.20            | 10.0            |
| 0.50            | 0.6             | 0.22            | 0.05            | 0.20            | 9.9             |
| 0.50            | 0.6             | 0.40            | 0.05            | 0.20            | 10.5            |
| 0.50            | 0.6             | 0.40            | 0.05            | 0.20            | 10.3            |
| 0.50            | 0.6             | 0.40            | 0.05            | 0.20            | 10.1            |

Ten different experiments of barium sulfate precipitates in the mixed gel with variations of concentration of silicates were carried out as listed on Table 4.12, one group of experiments for 0.22% SiO₂ by weight, another is 0.40% SiO₂ by weight in basic pH conditions. At lower SiO₂ percentages, more dendritic crystals were found. Monsters, spirals, and sheets were all observed at appropriate pH conditions only at 0.40% SiO₂.

Table 4.13 Barium Chromate Precipitates in Agarose-Silica Mixed Gel.

| Diffuse Layer Loaded in Agarose-Silica Gel (M) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| [BaCl₂] (M)     | Agarose (%)     | SiO₂ (%)        | [Na₂CrO₄]       | [NaCl]          | pH              |
| 0.50            | 0.6             | 0.25            | 0.05            | 0.20            | 10.4            |
| 0.50            | 0.6             | 0.25            | 0.05            | 0.20            | 10.3            |
| 0.50            | 0.6             | 0.25            | 0.05            | 0.20            | 10.2            |
| 0.50            | 0.6             | 0.25            | 0.05            | 0.20            | 10.1            |
| 0.50            | 0.6             | 0.25            | 0.05            | 0.20            | 10.0            |
| 0.50            | 0.6             | 0.25            | 0.05            | 0.20            | 9.9             |
| 0.50            | 0.6             | 0.20            | 0.05            | 0.20            | 10.4            |
| 0.50            | 0.6             | 0.20            | 0.05            | 0.20            | 10.2            |
| 0.50            | 0.6             | 0.40            | 0.05            | 0.20            | 10.4            |
| 0.50            | 0.6             | 0.40            | 0.05            | 0.20            | 10.3            |
Table 4.13 listed three different groups of experiments of barium chromate precipitates with variations of concentration of silicate. One group was 0.25% SiO₂ by weight, another was 0.4% SiO₂ by weight, the last was 0.20% SiO₂ by weight which showed no detectable difference from 0.25% SiO₂ by weight. In this porous medium, there was a saturation point of SiO₂% to grow IMCA, 0.20% was sufficient for growth of IMCA at appropriate pH condition. SiO₂ below 0.20% lead to no formation of IMCA for this system. IMCA has a more smoothed surface at higher percentage of SiO₂ (0.40%).

The experiments with barium phosphate precipitates in mixed gel are listed on Table 4.14. In this system, even at high pH, it is very difficult for the mixed gels with silicate to develop any sizable particles. Liesegang banding formed with high density of tiny spherical objects at pH=11.3; at pH=11.0, these objects were larger while the Liesegang banding was less filled with the objects.

Table 4.14 Barium Phosphate Precipitates in Agarose-Silica Mixed Gel.

<table>
<thead>
<tr>
<th>Diffuse Layer</th>
<th>Loaded in Agarose-Silica Gel (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BaCl₂] (M)</td>
<td>Agarose(%) SiO₂(%)</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5 0.30 0.05 0.20 11.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5 0.30 0.05 0.20 11.3</td>
</tr>
</tbody>
</table>

The highest pH used in agarose-silica mixed gels was 14, as shown on Table 4.11. Pure silica gel dissolves at this pH. There is no evidence that any crystal (for barium carbonate system) was formed in such gels as examined by the optical microscope in transmission light and polarized light in situ. The reason for this
phenomenon may be explained by the high concentration of OH in the gel to prevent any possible diffusion towards the base layer at this special condition.

There is plenty of evidence in this study to support the development of normal crystal morphology under acidic conditions. Some experiments produced the dendrite morphology which are controlled solely by diffusion processes. Other growth patterns are the same as the normal crystal growth. However, one important factor that should be mentioned is the matrix effect, as described in Chapter III, in which the agarose-silica mixed gel may have different diffusion power, simply because its gel matrix network is different from that for silica gel.

4.2 Strontium-containing Precipitates

Growth behavior in strontium systems is basically the same as for barium precipitation systems overall, but there some specific differences. For example, there are more curves in flake morphology than in barium systems. The solubility ranging in this category of precipitates has wider range than in other systems (4.1; 4.3). Strontium carbonate is highly insoluble (solubility products $K_{sp} = 5.6 \times 10^{-10}$ at 25°C) while strontium sulfate (Sohnel, 1981, 1984) is 30 times more soluble (solubility product $K_{sp} = 3.44 \times 10^{-7}$ at 25°C, Weast, 1990). The growth behavior can be influenced by these enormous variations at certain conditions as well as other factors. First, precipitation in agarose gel was very briefly studied.
4.2.1 Precipitation in Agarose Gel

Table 4.15 SrSO$_4$ Precipitates in Pure Agarose Gel.

<table>
<thead>
<tr>
<th>[Sr(NO$_3$)$_2$] (M)</th>
<th>Agarose (%)</th>
<th>[Na$_2$SO$_4$]</th>
<th>[NaCl]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>5.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>6.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>7.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>8.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>9.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>10.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>10.3</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Strontium sulfate precipitates were studied over a wide pH range (5-11); the initial concentration ratio in pure agarose gel was set at 10. The experiments listed in Table 4.15 were carried out. SrSO$_4$ polycrystal growth in pure agarose gel showed little sensitivity to pH, but the size of crystals became bigger when pH was increased. The results were otherwise comparable with those for BaSO$_4$.

Table 4.16 SrCO$_3$ Precipitates in Pure Agarose Gel.

<table>
<thead>
<tr>
<th>[Sr(NO$_3$)$_2$] (M)</th>
<th>Agarose (%)</th>
<th>[Na$_2$CO$_3$]</th>
<th>[NaCl]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>5.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>6.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>7.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>8.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>9.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>10.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>10.3</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.05</td>
<td>0.20</td>
<td>11.0</td>
</tr>
</tbody>
</table>
As listed on Table 4.16, SrCO$_3$ precipitation growth in pure agarose hydrogel were carried out. No particle growth at pH=5 and 6 was ever observed, due to a very low CO$_3^{2-}$ distribution coefficient. At pH=7 and 8, numerous, but very small particles were observed in the first half of the cassette. These particles appeared as spheres. As the system pH was increased to 9, the morphology showed no big change, but the number of particles increased. There was some micro banding observed at pH=10 and 11, but no formation of IMCA. The morphology was modified a little bit and rice-shaped tiny crystals were formed.

4.2.2 Precipitation in Silica Gel

Pattern formation for the strontium phosphate precipitating system including monsters, spirals and flakes in silica gel were observed at high pH. Table 4.17 summarizes some experiments involving the diffusion of Sr(NO$_3$)$_2$ into a NaH$_2$PO$_4$ loaded silica gel at various pH. The pure crystals grown at this condition were probably Sr$_3$(PO$_4$)$_2$ as reported by Banks (1973). Sr$_3$(PO$_4$)$_2$ is formed in the mobile solution at pH 10-10.5 as rhombic plates up to 0.1mm; β-SrHPO$_4$ is formed at pH 4-7 as crystals up to 0.15mm, polycrystalline spherulites up to 0.4mm. The present focussed on pH from 9.0 to 10.3. Figures 4.46 and 4.47 are photomicrograph of strontium phosphate flakes in situ of silica gel at pH=10.1. The cross pattern can be seen, but not as clearly as in the barium phosphate sheet (Figure 4.35). Strontium acted slightly differently than barium in silica gel at high pH. Many IMCA's, particularly flake types as shown on Figures 4.46, have many more curves along the
flakes’ edges. Strontium phosphate precipitates were much more complicated than had previous been expected. Although many spirals and flakes were formed over pH 10.1-10.3, there were many more other fine precipitates formed, too. Their morphologies appear as spherically shaped with Liesegang banding.

**Table 4.17 Strontium Phosphate Precipitates in Silica Gel.**

<table>
<thead>
<tr>
<th>Diffuse Layer</th>
<th>Loaded in Silica Gel (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Sr(NO}_3\text{)}_2] (M))</td>
<td>(\text{SiO}_2 (%))</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Figure 4.46. Photomicrograph of strontium phosphate flake in silica gel at pH=10.1.
For strontium carbonates, the precipitating systems studied are listed in Table 4.18. There were many curved flakes formed at high pH. Selected IMCA were separated from silica gel by chemical methods (Section 3.3.1). An example is shown in Figure 4.48 which is a BEI micrograph of the hollow curved sheet formation from silica gel at pH=10.0. Figure 4.49 is a BEI micrograph of another flake at pH=10.0. The fracture at the edge at top of the micrograph reveals a structure, discussed further in the following section (Note also that the spiral in the background is not part of the sample). Figure 4.50 is a BEI spiral from silica gel at pH=10.2. This is a very well-behaved spiral.
Table 4.18 Strontium Carbonates Precipitates in Silica Gel.

<table>
<thead>
<tr>
<th>Diffuse Layer</th>
<th>Loaded in Silica Gel (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Sr(NO$_3$)$_2$] (M)</td>
<td>SiO$_2$ (%)</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
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<tr>
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<td>4.0</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Figure 4.48. BEI micrographs of the hollow from silica gel at pH=10.0, scale bar 0.1mm.
4.2.3 Precipitation in Agarose-Silica Mixed Gel

Table 4.19 Strontium Carbonate Precipitates in Agarose-Silica Mixed Gel.

<table>
<thead>
<tr>
<th>Diffuse Layer</th>
<th>Loaded in Agarose Gel (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Sr(NO₃)₂] (M)</td>
<td>Agarose (%)</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Figure 4.49. BEI micrographs of flake from silica gel at pH=10.1, scale bar 0.1mm.

Figure 4.50. BEI micrographs of spiral from silica gel at pH=10.2, scale bar 0.1mm.
The strontium-containing systems precipitated in agarose-silica mixture behaved the same as in silica gel. Dendritic crystal growth and IMCA formation were similar in the silica gel. However, the influence of matrix effects of the porous media were apparent. Table 4.19 lists the experiments relating to the strontium carbonate in the mixed gel.

The laminar structure is a regular feature of sheet IMCA. The maximum total thickness for this category is no more than 5 micron in the strontium carbonate system. Because there was no significant damage to those IMCA originated by the physical separation process, the orientation and interface among laminar could be observed directly by BEI. The special laminar structure differs from the barium system. Instead of a three layered sandwich structure, strontium carbonate sheets actually contained four layers, two inner strontium carbonate layers with different texture and two outer layers of strontium silicate. Examples are shown in Figures 4.51 to 4.54. Figure 4.51 is a double hollow separated from the mixed gel at pH=10.3. The double layers that can be seen directly are both strontium carbonate. Figures 4.52 to 4.54 were also from the mixed gel at pH=10.3. This is the most novel finding for the strontium-containing precipitates so far. These double layers imply a total four real layers, because exterior strontium silicate was not counted in. The two major layers were identified by EDX which showed only Sr, with no silicon.
Figure 4.51. BEI micrograph of double hollow from the mixed gel at pH=10.3, scale bar 0.1mm.

Figure 4.52. BEI micrograph of curved sheet from the mixed gel at pH=10.3, scale bar 0.01mm.

Figure 4.53. Enlarged of Figure 4.52, scale bar 0.01mm.
Another important finding was a new crystalline phase of strontium carbonate sheet. The selected area electron diffraction pattern of strontium carbonate sheet specimen shows a richness of polycrystals (Figure 4.55). The calculated d spacings for these did not match any known inorganic substances found in the literature. Calculations were performed according to the TEM instruction manual. Table 4.20 lists the calculated d spacings and comparison with known related inorganics. This suggested that a new lattice phase had been formed, possibly a novel strontium carbonate silicate.
Figure 4.55. SAD pattern of strontium carbonate sheet from the mixed gel at pH=10.3.

Table 4.20 d Spacings of SrCO₃ Precipitate (Dentonite) and d Spacings of some known Inorganic SrCO₃ Phases (NIST 1983).

<table>
<thead>
<tr>
<th>Dentonite</th>
<th>3.49</th>
<th>2.95</th>
<th>2.53</th>
<th>2.02</th>
<th>1.79</th>
<th>1.56</th>
<th>1.47</th>
<th>1.26</th>
<th>1.13</th>
<th>1.03</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCO₃</td>
<td>3.54</td>
<td>3.45</td>
<td>2.05</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrO</td>
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<td>2.48</td>
<td>1.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrO₂</td>
<td>2.52</td>
<td>3.13</td>
<td>2.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr₃SiO₄</td>
<td>3.02</td>
<td>3.14</td>
<td>3.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr₃SiO₅</td>
<td>2.91</td>
<td>3.56</td>
<td>2.06</td>
<td></td>
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<tr>
<td>Sr₂SiO₄</td>
<td>3.28</td>
<td>2.93</td>
<td>3.24</td>
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<tr>
<td>Sr₂SiO₅</td>
<td>2.80</td>
<td>2.29</td>
<td>3.27</td>
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<tr>
<td>Sr₃SiO₃</td>
<td>2.92</td>
<td>2.35</td>
<td>2.98</td>
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<td></td>
<td></td>
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<td></td>
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<tr>
<td>α-Sr₃SiO₃</td>
<td>3.59</td>
<td>3.57</td>
<td>2.93</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Na₂SrSi₂O₆</td>
<td>2.74</td>
<td>2.68</td>
<td>3.45</td>
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</tr>
<tr>
<td>Na₄SrSi₂O₈</td>
<td>3.11</td>
<td>2.72</td>
<td>2.68</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr₃Si₂O₄·2H₂O</td>
<td>2.76</td>
<td>3.73</td>
<td>1.91</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Sr₃Si₂O₅·2H₂O</td>
<td>2.89</td>
<td>3.33</td>
<td>6.73</td>
<td></td>
<td></td>
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<tr>
<td>SrSiO₃·2H₂O</td>
<td>3.23</td>
<td>3.09</td>
<td>2.23</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>SrSiO₃·2H₂O</td>
<td>3.11</td>
<td>2.13</td>
<td>16.1</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>SrSiO₃H₂O</td>
<td>3.44</td>
<td>2.07</td>
<td>3.03</td>
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</tr>
<tr>
<td>Sr₂SiO₄H₂O</td>
<td>3.17</td>
<td>3.58</td>
<td>2.92</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>SrSiO₃H₂O</td>
<td>4.26</td>
<td>3.27</td>
<td>2.96</td>
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<td></td>
<td></td>
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</tr>
</tbody>
</table>
Strontium chromate and sulfate precipitates were also very briefly studied in mixed gels under basic conditions with focus on the formation of IMCA. The concentration of silicate in the mixed gel was explored, to determine how much silicates in the mixed gel was necessary to develop IMCA. Table 4.21 shows the experimental conditions at 0.5% agarose gel with a low silicate percentage (0.23%). No formation of IMCA at this low silicate concentration was observed even at high pH, except for some spherulites. For strontium sulfate precipitates in the mixed gel (Table 4.22), three sets of experiments were carried out with various percentage of silicates (0.20, 0.25, and 0.40%). Some large potato-shaped crystalline masses were observed at pH=9.9. Flakes were observed at pH=10.3. More silicates are needed for further growth of IMCA. The pH is no longer a predominant indicator in silica-agarose mixed gel for this system. Instead, the percentage of sodium silicate is the more important variable.

Table 4.21 Strontium Chromate Precipitates in Agarose-Silica Mixed Gel.

<table>
<thead>
<tr>
<th>[Sr(NO₃)₂] (M)</th>
<th>Agarose (%)</th>
<th>SiO₂ (%)</th>
<th>[Na₂CrO₄]</th>
<th>[NaCl]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.23</td>
<td>0.05</td>
<td>0.20</td>
<td>10.4</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.23</td>
<td>0.05</td>
<td>0.20</td>
<td>10.3</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.23</td>
<td>0.05</td>
<td>0.20</td>
<td>10.2</td>
</tr>
<tr>
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<td>0.5</td>
<td>0.23</td>
<td>0.05</td>
<td>0.20</td>
<td>10.1</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.23</td>
<td>0.05</td>
<td>0.20</td>
<td>10.0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
<td>0.23</td>
<td>0.05</td>
<td>0.20</td>
<td>9.9</td>
</tr>
</tbody>
</table>
Table 4.22 Strontium Sulfate Precipitates in Agarose-Silica Mixed Gel.

<table>
<thead>
<tr>
<th>Diffuse Layer</th>
<th>Loaded in Agarose Gel (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Sr(NO₃)₂] (M)</td>
<td>Agarose (%)</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
</tr>
<tr>
<td>0.50</td>
<td>0.6</td>
</tr>
</tbody>
</table>

4.3 Calcium Phosphate Precipitates

Calcium phosphate precipitates are the most complicated precipitating systems in nature partly because of their multiphase characteristics (Nancollas, 1989) and exceptional difficulty of crystallization. Examples are Ca₅(PO₄)₂, CaHPO₄, Ca₅(PO₄)₂OH, Ca₄H₉(PO₄)₂, etc., and some of these are always amorphous. In addition, calcium phosphate precipitates are easily affected by additives (Damen, 1989). Biphasic phosphates were observed in this system (Figure 4.56). This notable phenomenon exists widely in nature due to the transformation from one phase to another, but such transformations are very slow (Smith, L. 1980; Birchall, 1984).
4.3.1 Precipitation of CaCl$_2$ with NaH$_2$PO$_4$

Experiments in cassettes and supercassettes were carried out for a few weeks. Brushite [CaHPO$_4$] crystallites were found. Various plates of brushite crystals reported by LeGeros (1972; Rubin, 1970) were found over a large pH range from 6.0 to 10.3 (Table 4.23). Among the experimental results was that the number of distinct crystalline objects (whether single or poly crystals) that decreased rapidly when the pH was increased from 6 to 10. In agarose gel, at pH=6.0, more than 10 crystals were found; at pH=7.0, 7 crystals were found; at pH=8.0, 5 crystals were found; at pH=9.0, only one crystal was found; finally at pH=10.0, there were no visible crystallites in agarose gel but Liesegang bands, although some crystalline objects were observed.

Figure 4.56. SEM micrograph of biphasic calcium phosphate; A~Ca$_3$(PO$_4$)$_2$, B~CaHPO$_4$, scale bar 0.01mm.
around the rough edges of the rubber gasket of the micro slide cassette, which is very common in these systems. Those results indicated that acidic conditions favor Brushite crystal growth due to the \( \text{HPO}_4^{2-} \) distribution coefficient in the system. At around \( \text{pH}=7 \), the maximum coefficient of \( \text{HPO}_4^{2-} \) is achieved. Therefore, it is easy to understand these experimental observations. As the acidity decreases, the number of crystals decreases; finally, when \( \text{pH} \) reaches 10.0, no brushite crystal were found inside the gel, since the formation of tricalcium phosphate was much more favorable at this higher \( \text{pH} \). Crystalline tricalcium phosphate is extremely difficult to grow even at a very high \( \text{pH} \) and amorphous (to XRD) \( \text{Ca}_3(\text{PO}_4)_2 \) is often formed instead (Smith, L., 1980).

The fine particles among Liesegang bands were separated from agarose gel at \( \text{pH}=10.3 \). The X-ray powder diffraction of these solids (Figure 4.57) showed them to be largely amorphous, with a small fraction of crystallinity of \( \text{Ca}_3(\text{PO}_4)_2 \) or \( \text{Ca}_9(\text{PO}_4)_6 \) or mixture of both (Montel, 1961). The observed XRD peaks did not exactly match those of the pure calcium phosphates standard XRD files; This may due to instrumental limitations.

<table>
<thead>
<tr>
<th>Diffuse Layer Loaded in Agarose Gel (M)</th>
<th>([\text{CaCl}_2] ) (M)</th>
<th>Agarose (%)</th>
<th>([\text{NaH}_2\text{PO}_4] )</th>
<th>( \text{pH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.50</td>
<td>1.0</td>
<td>0.05</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>1.0</td>
<td>0.05</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>1.0</td>
<td>0.05</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>1.0</td>
<td>0.05</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>1.0</td>
<td>0.05</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>1.0</td>
<td>0.05</td>
<td>10.3</td>
</tr>
</tbody>
</table>
Isolated crystals from agarose gel at pH=9 proved to have two different phases as mentioned early (Figure 4.56). EDX detailed analysis indicated this difference, i.e. the major phase (A as arrow indicated) was close to tricalcium phosphate (Figure 4.59), the minor phase (B as arrow indicated) was calcium phosphate (CaHPO₄) as shown in Figure 4.60.

Twin supercassettes were used for the CaCl₂-NaH₂PO₄ precipitation system at high pH (10.3). The experiments displayed instability as Liesegang bands break out. Time lapse photography recorded the development of this instability at pH=10.3 in a reproducible manner (Twin supercassettes were set up at the same conditions). It can be interpreted as diffusion-reaction controlled processes far-from-equilibrium, in which periodic precipitates (Liesegang banding) developed with less uniformity. Figure 4.58 shows time-lapsed photographs of CaCl₂-NaH₂PO₄ precipitation system at pH=10.3.

Figure 4.57. X-ray diffraction pattern of Ca₃(PO₄)₂, horizontal is 2θ, vertical is relative intensity of reflection %.
<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>10.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCl₂</td>
<td>NaH₂PO₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A, B</td>
<td>clean</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>middle pertur</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1, 3, 5, 7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Perturbation point

Total Time:
1. 6 hrs
2. 12 hrs
3. 24 hrs
4. 29 hrs
5. 36 hrs
6. 47 hrs
7. 55 hrs
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<th>Time</th>
<th>Film</th>
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</thead>
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<tr>
<td>87 hrs</td>
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<tr>
<td>96 hrs</td>
<td>Kodak 5053 TMY</td>
</tr>
<tr>
<td>112 hrs</td>
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</tr>
<tr>
<td>120 hrs</td>
<td>Kodak 5053 TMY</td>
</tr>
<tr>
<td>Time (hrs)</td>
<td>Numbers</td>
</tr>
<tr>
<td>-----------</td>
<td>---------</td>
</tr>
<tr>
<td>185 hrs</td>
<td>12</td>
</tr>
<tr>
<td>193 hrs</td>
<td>13</td>
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<td>203 hrs</td>
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<td>227 hrs</td>
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<tr>
<td>251 hrs</td>
<td>28</td>
</tr>
<tr>
<td>280 hrs</td>
<td>32</td>
</tr>
</tbody>
</table>
Figure 4.58. Time-lapsed photography of Liesegang banding at pH=10.3.
Figure 4.59. EDX spectrum with semi-quantitative analysis of Ca$_3$(PO$_4$)$_2$, layer B.
Figure 4.60. EDX spectrum with semi-quantitative analysis of CaHPO₄, layer A.
4.3.2 Precipitation of CaCl\textsubscript{2} with NaH\textsubscript{2}PO\textsubscript{4} and NaF Additives

The addition of NaF to agarose gel with NaH\textsubscript{2}PO\textsubscript{4} has a dramatic influence on brushite crystal growth. The complete course of brushite crystal growth did not occur at all pH ranges due to the inhibitive behavior of sodium fluoride in this case. Table 4.24 gives a summary of the related experiments carried out. Even after a long period of time, \textit{in situ} observations with the highest magnification optical lens (100x10), showed no sign of crystal formation. But it is still possible that microscopic crystals were formed. Liesegang rings formed with very fine spherical objects with a diameter of around 100 \textmu m.

Table 4.24 CaCl\textsubscript{2} - NaH\textsubscript{2}PO\textsubscript{4} - NaF Precipitates in Agarose Gel.

<table>
<thead>
<tr>
<th>Diffuse Layer</th>
<th>Loaded in Agarose Gel (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CaCl\textsubscript{2}] (M)</td>
<td>Agarose (%)</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
</tr>
</tbody>
</table>

External sodium chloride, on the other hand, had a strong impact on Liesegang ring formation. The variation of phosphates has the least effect on the formation of brushite crystals. Such variations would not affect the growth habits (Rosmalen, 1990) because brushite crystal growth was a slow process and the crystals were certainly not sensitive to initial concentrations. The external NaCl dynamically affects Liesegang ring formation, for example, it prohibited the development of Liesegang rings, at least for the serial experiments tabulated on Table 4.25.
Table 4.25 \( \text{CaCl}_2 - \text{NaH}_2\text{PO}_4 - \text{NaCl} \) Precipitates in Agarose Gel.

<table>
<thead>
<tr>
<th>[CaCl(_2)] (M)</th>
<th>Agarose (%)</th>
<th>[NaH(_2)PO(_4)]</th>
<th>[NaCl]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.007</td>
<td>0.02</td>
<td>10.0</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.007</td>
<td>0.02</td>
<td>10.4</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.007</td>
<td>0.02</td>
<td>12.0</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.05</td>
<td>0.00</td>
<td>10.3</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.05</td>
<td>0.00</td>
<td>9.1</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.05</td>
<td>0.00</td>
<td>7.0</td>
</tr>
</tbody>
</table>

4.3.3 Precipitation of \( \text{CaCl}_2 \) with \( \text{NaH}_2\text{PO}_4 \) in the presence of \( \text{Na}_4\text{P}_2\text{O}_7 \)

Sodium pyrophosphate was added to the \( \text{CaCl}_2-\text{NaH}_2\text{PO}_4 \) precipitating system. Table 4.26 lists the detailed experimental conditions. Minimum temperature fluctuation was maintained for four weeks at room temperature inside of a large polystyrofoam box. Crystal growth was observed at a pH range from 6.0 to 10.0. The morphology of these crystalline objects at lower pH is certainly not the same as at higher pH. Optical examinations and geometrical measurements showed that the crystals' shapes were not those of brushite crystals. Selected crystals at pH = 7.0 were dug out from the gel (Section 3.3.2). Those crystalline objects can be best described as spherulitic structures (Section 1.3.1.3 and Figure 4.61). EDX analysis of these crystals showed that the chemical composition was tricalcium phosphate. This surprising result demonstrated that trivial amounts of pyrophosphate did stabilize and enhance the tricalcium phosphate crystal growth because there was no formation of the crystalline tricalcium phosphate at the same pH without presence of \( \text{Na}_4\text{P}_2\text{O}_7 \).

Moreover, the additive effect had not only an influence on the morphology, but also
had an influence on growth habit (Berner, 1975). Figure 4.62 is EDX with a semi-quantitative analysis of the crystals shown in Figure 4.61. Semi-quantitative analysis determined the ratio of Ca to P as 3:2. As mentioned earlier (see Figure 4.6), Figure 4.63 shows another three dimensional Liesegang ring formation of 

\[ \text{CaCl}_2 \sim \text{Na}_2\text{HPO}_4 \sim \text{Na}_4\text{P}_2\text{O}_7 \] in agarose gel at pH = 9.0. This unusual banding contained continuing and stepped band formation; perhaps it was a transition point to something which is not clear at this moment.

Table 4.26 CaCl$_2$ - NaH$_2$PO$_4$ - Na$_4$P$_2$O$_7$ Precipitates in Agarose Gel.

<table>
<thead>
<tr>
<th>Diffuse Layer</th>
<th>Loaded in Agarose Gel (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[CaCl$_2$] (M)</td>
</tr>
<tr>
<td>0.50</td>
<td>0.045</td>
</tr>
<tr>
<td>0.50</td>
<td>0.045</td>
</tr>
<tr>
<td>0.50</td>
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</tr>
<tr>
<td>0.50</td>
<td>0.045</td>
</tr>
<tr>
<td>0.50</td>
<td>0.045</td>
</tr>
</tbody>
</table>

Figure 4.61. SEM micrograph of spherulitic calcium phosphate at pH=7.0, scale bar 0.1mm.
Figure 4.62. EDX spectrum with semi-quantitative analysis of calcium phosphate.
4.3.4 Precipitation of CaCl$_2$ with Na$_4$P$_2$O$_7$

The role of sodium pyrophosphate alone reacting with calcium ions was examined (Table 4.27). As in the experiments, the number of crystals formed decreased when the system pH was increased. There were no crystalline objects observed at very high pH, perhaps due to the formation of other microcrystals such as calcium hydroxide or carbonate at the diffusion interface, which obstructed and suppressed the target crystal formation. Thus, acidity may be used as a reliable controlling index for this system. Chemical analysis of the isolated crystals showed them to be calcium pyrophosphate. Figure 4.64 provides a comprehensive EDX with semi-quantitative analysis.

Figure 4.63. Liesegang ring of CaCl$_2$–Na$_2$HPO$_4$–Na$_4$P$_2$O$_7$ in agarose gel at pH = 9.0, scale bar 0.5mm.
Table 4.27  CaCl\(_2\) - Na\(_4\)P\(_2\)O\(_7\) Precipitates in Agarose Gel.

<table>
<thead>
<tr>
<th>[CaCl(_2)] (M)</th>
<th>Agarose (%)</th>
<th>[Na(_4)P(_2)O(_7)]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.0025</td>
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</tr>
<tr>
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<td>1.0</td>
<td>0.0025</td>
<td>7.0</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.0025</td>
<td>8.0</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.0025</td>
<td>9.0</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.0025</td>
<td>10.0</td>
</tr>
</tbody>
</table>
**EMI-QUANTITATIVE ANALYSIS: Ca$_2$P$_2$O$_7$ as P$_2$ in Agarose Gel**

NORM, K-RATIO

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-K</td>
<td>0.55713 ± 0.00218</td>
<td>0.44286 ± 0.00140</td>
</tr>
</tbody>
</table>

AF CORRECTION 10.00 KV 50.08 Degr

j. of Iterations 0

--- K [Z] [A] [F] [ZAF] ATOM.% WT.%

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a-K</td>
<td>0.557</td>
<td>1.000</td>
<td>1.026</td>
<td>1.000</td>
<td>1.027</td>
</tr>
<tr>
<td>-K</td>
<td>0.442</td>
<td>1.001</td>
<td>1.032</td>
<td>0.991</td>
<td>1.025</td>
</tr>
</tbody>
</table>

* High Absorbance

Figure 4.64. EDX with semi-quantitative analysis of calcium pyrophosphate.
4.3.5 Precipitation of CaCl$_2$ with NaF

Table 4.28 CaCl$_2$ - NaF Precipitates in Agarose Gel.

<table>
<thead>
<tr>
<th>Diffuse Layer [CaCl$_2$] (M)</th>
<th>Loaded in Agarose Gel (M)</th>
<th>Agarose (%)</th>
<th>[NaF]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.01</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.01</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.01</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.01</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.01</td>
<td>10.0</td>
<td></td>
</tr>
</tbody>
</table>

These experiments were intentionally designed to explore the reaction of NaF with CaCl$_2$. Table 4.28 tabulated the experiments performed under both basic and acidic conditions. No sizable crystalline objects were observed even after a few weeks. Instead, a large quantity of fine, apparently hollow spherical objects (less than 100μm) was observed. The hollow appearance under the light microscope was probably due to the formation of a single crystal CaF$_2$ core (cubic system), followed by more complex processes. Ex situ EDX analysis showed calcium with no anion, consistent with a formation as calcium fluoride (Figure 4.65).

Liesegang banding were observed at an early precipitating period in the interphase at pH=6. More visible banding can be easily observed at the same location of another cassette at pH=7. For the rest of experiments, the observations were almost the same. In short, this system is not very sensitive to pH for particle size and Liesegang banding.
Figure 4.65. EDX spectrum of calcium fluoride from agarose gel at pH=6.0.
4.4 Conclusions

Systematic experimental investigations showed that the following conditions lead to the formation of IMCA:

* Presence of sodium silicate;
* Alkaline earth metal ions;
* Atmospheric exposure (for non-carbonates);
* High pH;
* Highly insoluble precipitates.

The presence of silicates in gel is one of the most critical factors in the formation of IMCA. During the formation of highly insoluble precipitates, metal silicate hydrates are also formed as an overall exterior membrane which control and influence the morphology. Experiments were carried out in three different porous media; pure silica hydrogel (Sections 4.1.1 and 4.2.1); pure agarose hydrogel (Sections 4.1.2 and 4.2.2); and agarose hydrogel in the presence of sodium meta-silicate (Sections 4.1.3 and 4.2.3).

Only alkaline metal cations gave IMCA under the conditions studied; others such as Pb$^{2+}$, Cu$^{2+}$, La$^{3+}$, Fe$^{2+}$, Fe$^{3+}$ etc., did not grow IMCA under the same conditions. Earth’s atmosphere provides abundant carbon dioxide which enhances IMCA growth. This factor is hard to separate from others. A basic pH is essential, because silicate anions are present in significant amounts at high pH only; at less basic pH, gelation removes free silicate.

Crystal growth in gels takes place at lower supersaturation than in mixed mobile solutions, which allows the development of denser structure and more perfect crystals (Henisch, 1973, 1986). This may affect the ease of dissolution and re-
precipitation at the end of the growth process. IMCA growth behaved as a typical irreversible sequence under nonlinear conditions, however. In many cases, there was no re-precipitation even after years. Seeding experiments were carried out at the exact conditions that lead to formation of IMCAs. Such experiments were done at different locations of the cassette which reflect different degrees of supersaturation and concentration gradients. There were no observations indicating re-precipitation or heterogeneous nucleation. In contrast, re-precipitation phenomena were observed in ordinary crystals of brushite \([\text{CaHPO}_4]\) and calcite \([\text{CaCO}_3]\) grown in gels. Thus, some kind of dynamic pathway imposes control over the entire morphology of IMCAs. Such pattern formation can be regarded as a self-organized process (Garcia-Ruiz, 1994).

That the thickness of metal silicate membranes may control the entire morphology of IMCA by self-organized process was proposed based upon experimental data and \textit{in situ} and \textit{ex situ} observations and with considerations of matrix effects of porous media. Controls may be by physical force (e.g. pore size) or a result of co-precipitation throughout the course of IMCA growth.

[1]. For the monsters, the metal silicate membrane reached the greatest thickness, to controlling irregularities of this typical IMCA.

[2]. For the sheet-like IMCAs, which formed as sheets, flowers, or flakes, the metal silicate membrane achieved the least thickness to control the morphology of this type IMCA. It was found that the monster type and sheet IMCAs were never formed together.

[3]. For the well defined spiral IMCAs, an intermediate thickness of metal silicate membrane controls the IMCA morphology.

The construction of metal silicate membrane occurs during the precipitation
reactions and is determined by the effective concentration of sodium silicate in the gels. The pH index is an excellent and adequate indicator for this extremely important control variable. The reason for this can be explained by the following treatment. For any weak acid (such as silicic acid) in aqueous solution:

\[ H_nA \leftrightarrow nH^+ + A_n^a \]

\[ [A_n^a][H^+]^n/[H_nA] = k_1k_2...k_n = \text{constant} = c \quad (k \text{ is dissociation constant}) \]

\[ [A_n^a] = C \cdot 10^{\alpha \text{pH}} \quad (C \text{ is a constant}) \]

\[ x = [A_n^a]_2/[A_n^a]_1 = 10^{\alpha \text{pH}} \]

<table>
<thead>
<tr>
<th>ΔpH</th>
<th>x = ratio of concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 2</td>
<td>n = 3</td>
</tr>
<tr>
<td>0.1</td>
<td>1.6</td>
</tr>
<tr>
<td>0.2</td>
<td>2.5</td>
</tr>
<tr>
<td>0.3</td>
<td>4.0</td>
</tr>
<tr>
<td>0.4</td>
<td>6.3</td>
</tr>
<tr>
<td>0.5</td>
<td>10</td>
</tr>
<tr>
<td>1.0</td>
<td>100</td>
</tr>
</tbody>
</table>

If the pH of silicic acid changes from 9.9 to 10.4 (ΔpH = 0.5), [SiO₄²⁻] will be 100 fold changed, a significant effect. So, the effect on the IMCA is also enormous as many experiments indicated.

IMCA should be considered as one example of self-organized pattern formation (Merino, 1992) rather than of normal crystal growth. Spherical nuclei are formed in gels when precipitation took place; this phenomena was observed again and again. The metal silicate shell forms early in the growth process, perhaps even at the same
time as the nuclei did. Metal silicate shell formation is a feedback process, which in
turn, controls and influences further particle growth. Different pH gives different
strength to this feedback process, so that different morphologies are formed. This is
true at least for the monster type IMCAs. Spiral IMCAs are not even alike to spiral
growths found in nature (Brown, 1956; Andrews, 1961). On the other hand, spirals
might require a more complicated explanation related to the oscillating behavior in
crystal growth observed by Garcia-Ruiz (1979, 1987) and Henisch (1988). Ortoleva
thought this is macroscopic phenomenon and hence should be understood in terms of

For sheet structures of barium systems, the normal laminate structure were
observed with the thickness of about 1 micron. Barium phosphate had a very rougher
surface than others and was hard to grow due to its poor crystallinity.

The strontium system, on the other hand, had more curves than did the barium
system. Double internal layers were observed. A new crystalline phase called
Dentonite was detected in strontium carbonate.

The complicated calcium phosphate system was investigated by examining the
effects of additives and of various pH conditions in agarose gel. Brushite crystals
were found over a wide pH range (6-10), but low pH favored this phase for
thermodynamic reasons. Also, a biphasic structure was found in the crystalline
materials with one phase being $\text{Ca}_2(\text{PO}_4)_2$ and the other $\text{CaHPO}_4$. Ostwald ripening
effects were very strong in these systems. NaF was strongly inhibiting to growth of
large crystals in the calcium phosphate system. Promoted Liesegang banding is
associated with the formation of very fine microspherical aggregates. Pyrophosphate additives had an exceptionally strong influence on the calcium phosphate systems.

Spherulitic crystals of tricalcium phosphates were obtained under the conditions that would otherwise have generated brushite. Moreover, in this system, three dimensional Liesegang bands (Figure 4.6) were observed.
CHAPTER V

SUGGESTED WORK

The nature of pattern formation might be referred to the energy efficiency (Glicksman, 1987), particularly these diffusion-reaction controlled pattern formations. The energy may play a critical role in the formation of IMCA.

Image processing combined with TSM confocal microscopy could be used in the development of other studies in situ. Detailed analyses may be conducted to investigate whether these pattern formations are controlled by diffusion or by other physical-chemical processes or even directly by physical force. Details through the imaging analysis can probably lead to the calculation of surface dimensions (fractal dimension), in which the fractal approximation can be approached experimentally.

Other experimental surface techniques including Scanned-Probe Microscopies (Wickramasinghe, 1989) and WDS (Section 2.3.2) can be very effective in characterizing the surface of IMCA at the atomic level. However, IMCA has many more complicated features than much-studied single crystal structures such as silicon.

Organic matrix enhanced crystallization is potentially important for various inorganic systems (Pach, 1990). It may be worthwhile to design some experiments to study some related precipitates (BaCrO$_4$, etc.) in great detail. The inorganic lattice phase may be studied further. The phase arrangement (lattice to lattice) and the small crystal aggregates (crystal to crystal, or nuclei to nuclei) should be treated separately,
because they do not likely belong to the same category of processes.

One of the experimentally important factors is the salt effect, which can be subsequently explored using other chemicals (KCl, LiCl, e.g.) in order to distinguish between specific ionic effects. At present, the sodium chloride added in the gels is equivalent to a fraction of the pH in the experiments of IMCA formation. That is, when NaCl is added to the gel solution, the IMCA can grow at a relatively lower pH. Without NaCl in the gel solution, the IMCA may grow at a somewhat higher pH. Such salt or ionic strength effects is equivalent to 0.2 pH unit per 0.2 M [NaCl]. Therefore thermodynamic calculations should be considered to provide an explanation of this phenomena.

One series of possible experiments as suggested can be done to review the influence of carbon dioxide on the silica gel (Deju, 1965; Nicholas, 1972; Double, 1976; Bircell, 1980). The experiments may be designed as the blank experiments and comparison experiments which will be carried out under the exact same conditions (Chapter IV). Solid sodium silicate hydrates should be used to prepare the solution; the blank experiments should be carried out using this solution to make hydrogel directly to observe the $\text{CO}_2$ effect; use the same solution, but flush with carbon dioxide for 10 minutes, then prepare the hydrogel. Further quantitative determination of carbon dioxide in the experiments could provide useful information (Fowler, 1989). At this stage, the composition of IMCA may be determined. Alternatively, $\text{Na}_2\text{CO}_3$ could be added as such.

The strontium carbonate unique internal double layers can be studied
sequentially to determine the orientation of the main lattice phase by STM. This might lead to the final resolution of which phases are growing faster than others at certain chemical and physical conditions if such growth obeys lattice with lattice relationships.

Varying cation-anion ratios may be studied further to explore any possible influence on IMCA and other crystal growth under silica, agarose and the mixed hydrogel.

Experiments designed to stop feeding chemicals before diffusion process is completed may provide an opportunity to observe growth under deficiency conditions by using small volume of loaded gel.

A quantitative study of the effect of SiO$_2$ in the mixed gel on IMCA formation and the tightness of spirals should be considered.

Homogeneous reactions (e.g. hydrolysis of urea or of metal ion buffer system) should be utilized to reduce complexities caused by variation in concentration with position and time.

Combined SEM-EDX may used to examine the mixed gel to see whether the silica is uniformly distributed among agarose fibers.
APPENDIX

X-RAY DIFFRACTION FILES


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