

Liesegang Rings

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Abstract

The diffusive mixing of ions that form insoluble compounds can result in elegant striated precipitation patterns known as Liesegang Rings. In a 1-D system the bands of precipitant form reproducibly with a logarithmic spacing at times determined by the diffusion rate of the ion species. At the same time beautiful crystals, rounded spherulites and other dendritic structures can form and dissolve. Ostwald-Liesegang precipitation cycles could be responsible for banding in minerals such as agates although other mechanisms could also give rise to similar patterns.

1 Introduction

In the CA-504 Liesegang Ring kit (described in Appendix B) phosphate ions diffuse through a vertical silica gel doped with manganese and cobalt ions. Over time, regularly spaced rings of precipitant form down the column and amethyst crystals grow. Figure 2 shows the vertical position of each ring while gel columns for two similar precipitant systems are illustrated in Figure 3.

The phenomena of Liesegang rings was first observed by Runge in 1855 during a study of precipitants in blotting paper but Raphael Eduard Liesegang (born 1869) was the first to systematically explore their behaviour in the course of research on colloids and emulsions for photography[6]. Liesegang Rings have interested many scientists including J.J. Thompson and Lord Rayleigh because of their curious nature and resemblance to bandings in natural materials. When grown in a gel Liesegang rings are often accompanied by superb crystals and spherulites.

Sections 2 and 3 focus on the known experimental properties of Liesegang patterns and physical models for periodic precipitation. The nature of the gel environment and its effect on crystal growth is discussed in Sections 4 and 5. Section 6 addresses more disordered precipitant phases such as spherulites while Section 7 discusses the proposal that banding in silicate minerals arises through the Liesegang mechanism.

2 Experimental Knowledge of Liesegang Rings

With over 100 years of experimental study the behaviour of Liesegang Rings has been well characterized. In the majority of experiments an ion is introduced into a medium via diffusion where it forms bands of precipitant by reacting with ions already present in the medium. The time elapsed before the formation of the n -th band, t_n , and the distance to the band, x_n follows the general law

$$x_n \propto \sqrt{t_n} \tag{1}$$

indicating that the phenomena is indeed controlled by diffusion[3]. Studies of band formation influenced by electro-diffusion confirm this[6]. In 1923 Jablyczynski and Laio established a relationship between successive bands,

$$\frac{x^{n+1}}{x^n} = 1 + p \tag{2}$$

which in some systems is obeyed to within a few percent. During the 1950's Matalon and Packter studied the dependence of p on the diffusing ion concentration a_o and inner ion concentration b_o concluding that,

$$p = F(b_o) + \frac{G(b_o)}{a_o} \tag{3}$$

Across a variety of systems the best fits were for $F(b_o) \propto b_o^{-\gamma}$ ($0.2 \leq \gamma \leq 2.7$) and $G(b_o)$ as a monotonic decreasing function. There is less consensus on the band width, w_n , but Droz et al. [3] report

$$w_n \propto x_n^\alpha \tag{4}$$

with $\alpha \approx 1$.

The nature of the precipitant in each ring varies greatly between systems. For calcium tartrate and silver chromate the band material is in the form of distinct crystals[6] but in other systems bands are a sub-micron powder. Particle size can be uniform enough to diffract optically and light exposure can affect particle size (p120 [6]). Figure 4 shows the effects of gravity on ring position for the (KI:Pb(NO₃)₂) precipitant system. The 10% variation in ring spacing for $\pm g$ is intriguing (p129 [6]). Impurities in the gel can strongly alter ring positions but bands formation does not require a gel as shown by Wo. Ostwald in 1926 (p65 [6]) and can form in a gas as demonstrated by Spatz and Hirshfelder in 1951.

More complicated patterns are also possible. Figure 5 shows the “revert rings” of silver chromate where ring spacing diminishes as a function of n . When two precipitants are present in the medium rings may develop independently, cohabit or interleave [14]. Rings may dissolve after other rings have formed further down the column - a common behaviour for cobalt salts[14]. Finally, in 2 dimensional diffusion spiral patterns can form much like the ATP-waves in *Dictyostelium Discoideum* and electrical activity patterns in fibrillating muscle tissue.

3 Theory of Liesegang Rings

Alan Turing made a seminal contribution to pattern formation when he noted that auto-catalytic processes naturally form spatial patterns. Regions of high concentration increase, depleting surrounding areas and spontaneously generating complicated arrangements of active and inactive regions. The intricate and varied patterns on seashells is an elegant illustration of this[11]. Two basic models have been proposed for Liesegang ring formation. The ion product super-saturation model was proposed in 1950 by Wagner [1]. Ion B is distributed throughout the medium while ion A diffuses in the positive x-direction from a semi-infinite reservoir at $x = 0$. Precipitation occurs when the super-saturation equation,

$$q \leq AB \tag{5}$$

is satisfied and where q is the super-saturation constant. When Equation 5 is met at x_n a band of precipitant forms. The ion product AB drops below the precipitation limit in the neighbourhood of x_n . As A continues to diffuse the ion product for $x > x_n$ rises until at x_{n+1} precipitation occurs again.

In intermediate species theories the precipitant forms through a two step process. In the first, A and B combine to form a state C which may be a may be the molecule AB or a sol particle formed from A and B. The intermediate species, C, diffuses until the concentrations of C, A and B cause precipitation to occur. Simultaneous measurements of pH, colloidal particle formation, turbidity and density gradient by Kai et al. support this two step mechanism for the Mg(OH)₂ system.

Calculations for detailed theories inevitably end in numerical simulations because of the non-linear rate of precipitation and large number of parameters. Instead of pursuing such a calculation we illustrate the logarithmic ring spacing law using a limiting case of the ion super-saturation model. Let us suppose that $A \gg B$ so that precipitant formation is always limited by the supply of B. Furthermore, we take the limit $q \gg q_{sol}$ where q_{sol} is the solubility product so that the concentration of B effectively is held at zero in the presence of precipitant. Under these conditions A’s diffusion into the material is unimpeded so its concentration is given by,

$$A(x, t) = a_o f \left(\frac{x^2}{D_a t} \right). \tag{6}$$

where a_o is the concentration of A in the reservoir, D_a the diffusion constant for A and f the standard 1-D semi-infinite boundary condition diffusion profile.

In contrast, after the n -th ring is formed the concentration of B will be locally depleted so for $x > x_n$ and $t > t_n$,

$$B(x, t) = b_o \left(1 - f \left(\frac{(x - x_n)^2}{D_b(t - t_n)} \right) \right). \quad (7)$$

The ion product is given by,

$$q(x, t) = a_o b_o f \left(\frac{x^2}{D_a t} \right) \left(1 - f \left(\frac{(x - x_n)^2}{D_b(t - t_n)} \right) \right) \quad (8)$$

so precipitation occurs when the spatial maximum of $q(x, t) = q$ - a condition that must have a solution if $D_a > D_b$. An obvious ansatz is,

$$x_n = x_0 \exp(\mu n) \quad t_n = t_0 \exp(2\mu n) \quad (9)$$

which establishes the $(1 + p)$ spacing rule and the $x_n \propto \sqrt{t_n}$ laws of Liesegang rings.

Real scenarios are considerably more complicated than this idealized case but requires accurate modeling of precipitation mechanism. The complicated dependence of solubility and nucleation on ion and counter-ion condensation explains competing ion effects and redissolution of rings. Ion and counter-ion motion are also electrostatically coupled. The change in behaviour for a particular interaction can easily be gauged but quantitative results are more challenging.

4 Gel Formation and Characterization

A gel is formally defined as a “two component system of a semi-solid nature, rich in liquid” (Alexander and Johnson 1949, p29 [6]). One component is in a porous solid state and resists shear and tensile forces while the remaining volume is filled by a contiguous liquid component. Gels can be quite stiff with a 1:10 silica gel showing concoidal fracture (p32. [6]) yet the diffusion time for small molecules is comparable to that in bulk liquid ($D = 2 \times 10^{-5} \text{ cm}^2/\text{s}$ ($\pm 10 \times$)). Common materials used for hydrogels are gelatin, agar and polyvinylalcohol. Gels of the biopolymers gelatin and agar are usually formed by cooling a hot solution of the polymer so that cross-links between chains form. PVA gelation is started by the addition of a chemical cross-linker. The characteristics of a gel can vary greatly with preparation and minute impurities and silica gels have been found to give the most reliable results for Liesegang experiments.

In the CA-504 experiment a silica gel was formed using sodium meta-silicate. The initial solution for this is quite alkaline with a dynamic equilibria of (p35, [6]),



By Le Chatelier’s principle, acidification of the solution drives the equilibrium to the right and also favours the dehydration of $\text{Si}(\text{OH})_4$. An Si-O-Si bonded network forms irreversibly as described in the book “Silica and Me” (1967, Alexander). Gel network formation is complicated and shows three phases in silica gels. Upon mixing the solution viscosity rapidly rises as polymeric chains of silica form. With time the solution displays non-Newtonian behaviour and after a considerable period solidification sets in.

The room temperature, low density silica gel forms through the same chemistry as silicate precipitation from igneous rock melts explaining why acidic magma produces silica rich minerals like granite while basic conditions produce basalts and other Fe/Mg rich minerals.

5 Crystal Growth in Gels

Despite the technological importance of crystals and their intrinsic symmetries, crystal growth remains a challenging problem. The chart in Figure 1 attempts to hierarchically organize the battery of growth techniques employed in research and industry. Finding a method of crystallization for new materials remains a fine art and solution growth conditions are particularly finicky. Quite a few materials naturally grow in gels including calcite, gypsum in cement, ice crystals in icecream and uric acid in joints (p5 [6]). However, gel growth has only been successfully used to prepare a few crystal systems.

The requirements for good crystal growth are straightforward. Nucleation should occur infrequently, growth must be slow and steady and the crystal should be supported to prevent strain. For some crystals, gels assist with all three of these requirements and Calcium Tartrate, for example, grows spectacular crystals in gels (p10 [6]).

Gels chief claim over other solution techniques is the suppression of convection. Bulk fluid motion is prevented by the fine, porous structure of the gel ensuring that growth is regulated by the diffusion of material to the crystal face. Under most circumstances the the crystal radius, R , obeys the equation,

$$R^2 \propto Dt \tag{10}$$

where D is the diffusion constant and t the time of growth. Matalon and Packter studied diffusion limited growth by analysing reagent concentration in slices of the gel surrounding crystals. Varying gel density alters the rate of nucleation but it is unknown if crystal nuclei are suppressed by the small pore volume, the adsorption of impurities and nuclei to pore walls or some other mechanism (p105 [6]). A final role of the gel is as a crucible for the growing crystal. Kaimov and Malikov measured the interfacial pressure for growing an aluminium-potassium alum crystal on a silica gel as 1×10^5 Pascals. This pressure rarely applies directly to crystal faces, though, as the gel fragments in front of each face to form cusps. The crystal is then supported only by the corners that intercept the cusps. CaCO_3 is a prominent exception where silica gel includes in the growing crystal - a most unfortunate consequence.

If diffusion regulated growth from solution suits a crystal then a gel may well be a superior medium when compared to regular solution growth media.

6 Crystal Habit

The first crystals to grow in the CA-504 experiment were spherical with a dendritic, fractal surface. Spherulites are quite a common crystal habit and their behaviour is important in the production of cast iron where carbon can form graphitic sheets, dendritic structures as in Damascus Steel or spherulitic balls. Figure 7 shows spherulites of $\text{Zn}(\text{OH})_2$ growing in a gel under similar conditions to the $\text{Mg}(\text{OH})_2$ Liesegang Ring system shown in Figure 6.

Dendritic structures such as spherulites can grow only by virtue of the concentration gradient across each crystal face[10]. The higher concentration at crystal edges allows them to grow faster leading to needle-like edges. These new surfaces in turn develop curved edges so the dendrite grows through a branch and grow, branch and grow mechanism. Figure 9 shows the “wheat-sheaf” nucleus for spherulitic growth. Because radially-directed “branches” grow fastest, the “fast” growth axis at any point on a spherulite should point towards out from the nucleus. Figure 8 from Hutter et al.[9] confirms this prediction for a 2-D liquid crystal.

Spherulitic growth is kinetically stabilized by its great diffusive growth rate but is thermodynamically unstable with regard to a faceted crystal. Just as heating snow-flakes causes them to crystallize [12], spherulites will erode and reshape unless the system is quenched. In the $\text{Zn}(\text{OH})_2:\text{NH}_4\text{OH}$ system spherulites form and grow but when new spherulites form further into the gel spherulites nearer the diffusant shrink and dissolve. The mean location of spherulites x is proportional to \sqrt{t} . Another interesting feature of spherulites is a development of circular banding during their growth as shown in Figure 8. The effect occurs in both pure and mixed systems.

7 Agates

Bands akin to Liesegang rings abound in nature. Figure 10 illustrates some particularly beautiful colourings on an agate sample. Agates correspond to 90% of gems displayed at lapidary fairs [13] and although strictly a sub-class of the broader chalcedony family can run under a variety of names including jasper, sardonx, chalcedony, carrelian, sard and onyx. Agates are banded crypto-crystalline quartz (Hardness=7Moh) bodies, rounded (1cm to 100cm in diameter) and occur in flood basalts [16].

One type of banding in agates is compositional oscillations between chalcedony and quartz. The finest features are shown in Iris agate with sub-micron concentric striations[5] of fine-grained, high-defect chalcedony and coarse-grained low-defect quartz. Microprobe analysis shows concentrations

of Na^+ and Al^{3+} in the chalcedony which also has a different crystallographic orientation. Another modulation of composition between chalcedony and quartz with a length-scale of 200 micrometers is superimposed upon this. Finally, the density of chalcedony is usually higher at the outside of a thunderegg.

In addition to compositional bands, agate is famous for coloured bands with red from iron oxide, green from chlorite and black from manganese dioxide. These also oscillate in intensity although not with the astounding periodicity of the sub-micron compositional striations (8000 times or more)[5]. Dendritic patterns are found in moss agates.

The growth mechanism of agate is still a matter of contention. Several mechanisms by which silica finds its ways into voids in basalt have been proposed but it is agreed that prior to agate forming silica, impurity ions and water are within the void. Certainly agate formation occurs when fibres of quartz and chalcedony grow towards the centre of the void. Lab experiments prove that spherulitic chalcedony forms from polymerized silica solutions and silica gels have been found embedded in rock[6].

Heaney et al. [5] have proposed that the sub-micron striations arise from an Ostwald-Liesegang crystallization cycle. As polymerization of silica proceeds a critical concentration at the solidification front is reached causing the rapid growth of chalcedony fibres. This depletes the concentration of polymeric silica. Monomeric silica then dominates growth while fresh polymeric silica diffuses to the solidification front to start another layer of chalcedony. In a slightly different approach, Wang and Merino [16] focus on impurity ion catalysis of polymerization and solidification. Polymeric silica diffusion remains important but the striations are also regulated by ion diffusion. Although the physical details of the models differ considerably, the non-linear nature of solidification and diffusion limited supply of reagents ensures banding.

Explanations for coloured banding in agates is more complicated. Impurities may have precipitated within the silica gel and entirely precede chalcedony and quartz formation. At the other extreme, it is possible that impurity diffusion occurs well after solidification. Holten et al. [8] have shown the colourations are self-affine over 3 orders of magnitude and suggest that solidification and impurity formation obey a single set of precipitation kinetics.

The incredible regularity of banding on the shortest length scales strongly supports an auto-oscillatory process. However, spontaneous banding occurs even for crystallization in single component systems [9] so ion diffusion/Ostwald-Liesegang precipitation cycles are only one feasible mechanism. There is considerable reason to hope that laboratory experiments will lead to good models for quartz and chalcedony growth from solution. This should confirm the sub-micron banding mechanism and could well eliminate many of the colour impurity models. While it is likely that some of the striations in agates are caused by Liesegang ring phenomena more evidence is required. Not every striped ungulate is a zebra.

8 Conclusion

Liesegang Rings are a beautiful illustration of spontaneous spatio-temporal pattern formation arising in a simple system approaching equilibrium. While the basic phenomena of cyclic precipitation is robust and relatively simply explained, each change to the system exhibits many new and interesting features. Crystal growth within the gel medium is particularly interesting and raises questions about osmotic stress, anisotropic face growth through gel-facet pressure and other puzzling questions. Using a gel to trap the growing crystal and confocal microscopy to measure reagent concentrations throughout the material might yield interesting answers to outstanding puzzles in solution crystal growth. The postulate that Ostwald-Liesegang precipitation cycles cause banding in agates is an exciting link between soft and quite hard condensed matter physics.

A A-Exam Question

Spend no more than approximately seven days in total on this question, replying in the form of a short paper (at most about five pages of text, not including tables, figures and references). Write in the style of Physical Review/Physical Review Letters including a title and abstract. You may use any resources, including conversations. Consider the CA-504 Cobalt Manganese Phosphate Liesegang Rings and Crystals chemical kit from Science and Nature Distributors. Extend and correct as appropriate the discussion provided with the kit along the following lines or in a direction of your own choosing: Describe and/or discuss the growth phenomena that you have observed with the kit or would expect based on the kit's notes: What is the logarithmic law of the rings mentioned in the kit, and how well is it obeyed? Describe the morphology of crystals that are formed. Compare the ring formations to that of agates. Do you agree with the notes that a gel is an ideal environment for growing crystals? Write your answer in a self-contained manner, e.g. so that the committee need not read the kit's notes to follow your paper. Give your answer and a copy of this question to your committee at least three days before your A-exam.

B Crystal Magic Kit Details

Title : CA-504 Cobalt Manganese Phosphate Liesegang Rings and Crystals

Components :

- Vinegar with traces of Cobalt Chloride and Manganese Sulphate. (Approximately 50ml.)
- Sodium Silicate Solution (Approximately 50ml.)
- Ammonium Phosphate solution
- A glass tube approximately 2cm in diameter and 10cm in length.

Instructions :

- Mix vinegar and Sodium Silicate solution in the glass tube. Once mixed, allow the tube to sit vertically for 1-3 days to allow the silica gel to harden. Gel hardness can be tested by tapping the tube. If a ringing sound is heard, the gel has formed nicely.
- Add the Ammonium Phosphate solution on top of the gel. Place the tube vertically in a quiet place. Coloured bands will begin forming within days while crystal growth can extend for up to 1 year.

Supplier Details :

Crystal Magic,

Science and Nature Distributors, PO Box 808.

Yarmouth, Maine 04096

C Protocol for Growing $\text{Mg}(\text{OH})_2$ Liesegang Rings

Materials -

- Knox Unflavoured Original Gelatin
- MgSO_4 powder
- 6M Ammonia solution
- Glass tubes of diameter, $d \approx 5\text{mm}$ and length, ($l \geq 100\text{mm}$). 5ml Glass disposable pipettes with one end sealed are suitable.

Method -

- Each glass tube needs to be filled half-way with 0.3 M MgSO_4 , 9% (w/w) gelatin gel. To make the gel, water should be heated to 60C and stirred vigorously. The MgSO_4 should be completely dissolved before adding the gelatin. Once the hot solution turns completely clear pour into each tube taking care to avoid bubbles. The gel solidifies in minutes. Cover the tube and allow the gel to harden for a day.
- Add 2-3ml of Ammonia solution on top of the gel, cover the tube top and place it vertically in a quiet place. Within the first hour a milky cloud should form at the top of the gel. The first ring should form within 3 hours and subsequent rings follow over a period of days. Ring spacings are of the order of a 2mm and ring thickness of size, 0.7mm.

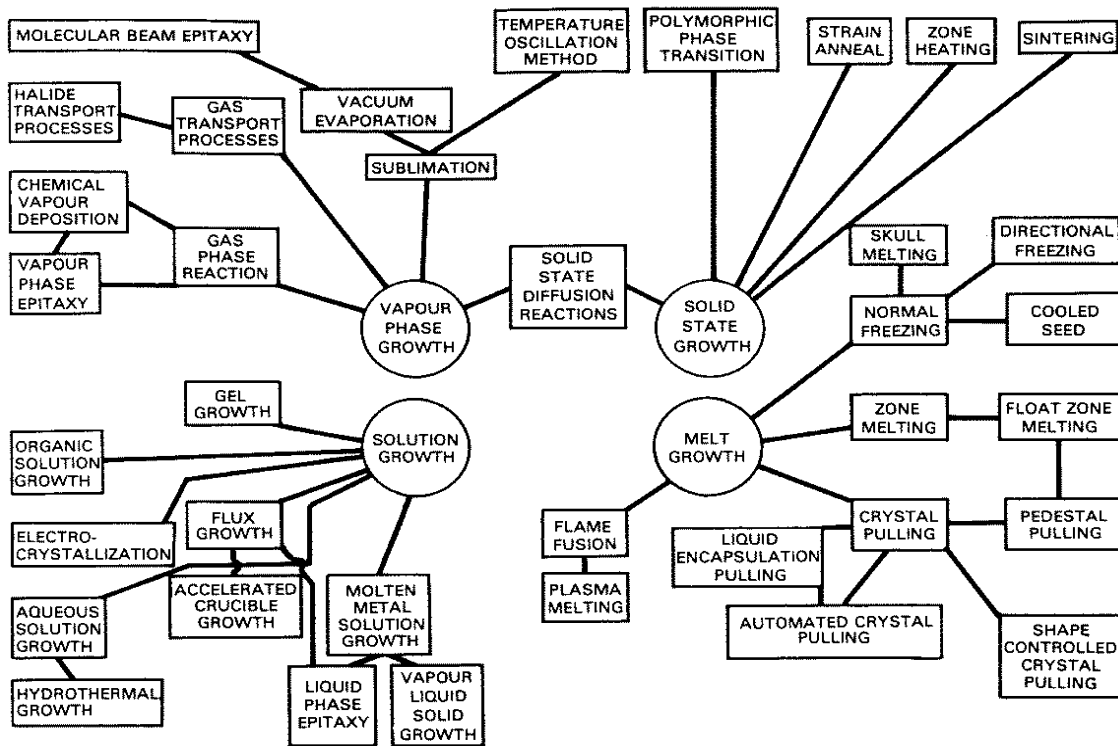


Figure 1: Crystal Growth Method Chart. p2, “Crystal Growth”, Brian Pamplin ed.

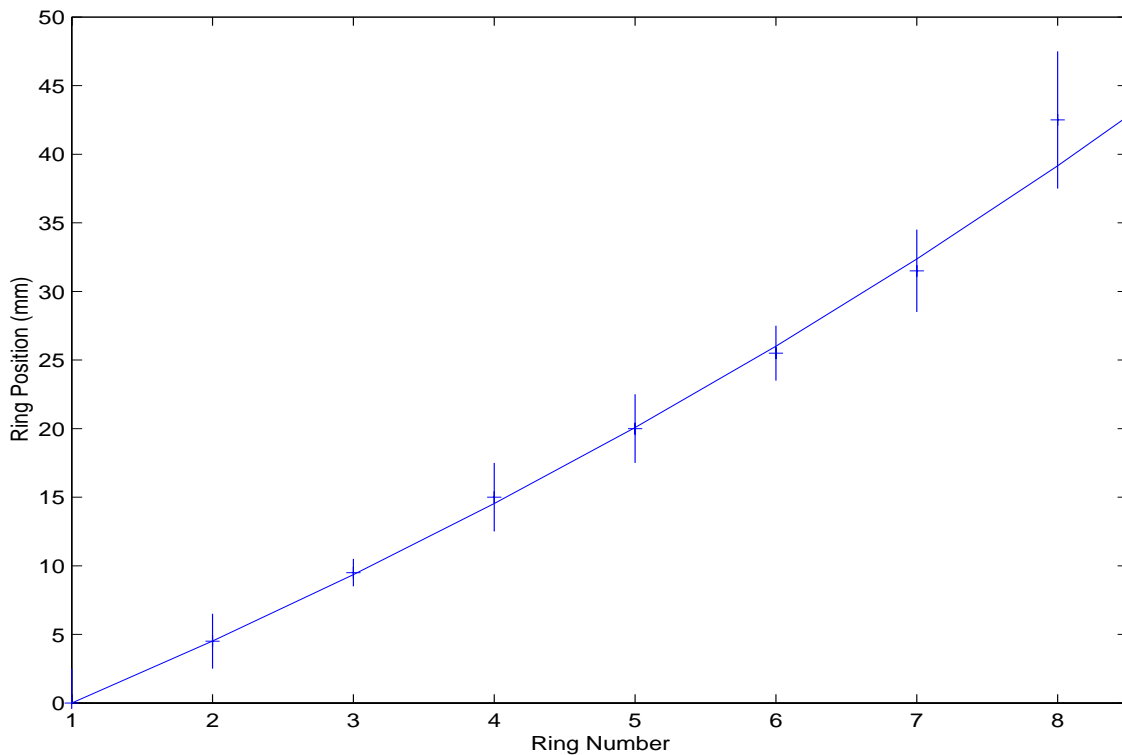


Figure 2: Ring Spacing as observed on Sophie Franck’s Crystal Tube 11 days after ring growth was initiated. Rings 1,2 and 3 were pale blue in colour while rings 6,7 and 8 were purple. Rings 4 and 5 were of intermediate colour. The error bar for each ring represents the ring width. The fitted line is a single exponential for which the initial ring spacing is 4.2mm and ring spacing grows by 7% per ring. Ring 8 deviates considerably but this may be because it is so close to the bottom of the tube. A small, amethyst-coloured crystal had formed between the 6-th and 7-th rings.

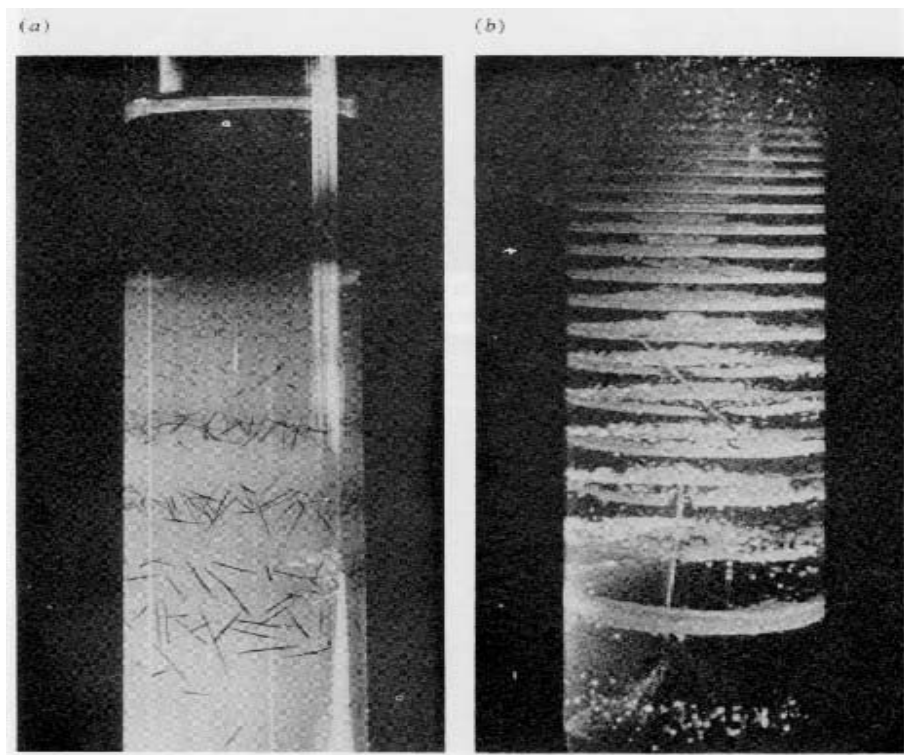


Figure 3: Liesegang Rings in (a) silver chromate and (b) calcium phosphate. (p6. [6])

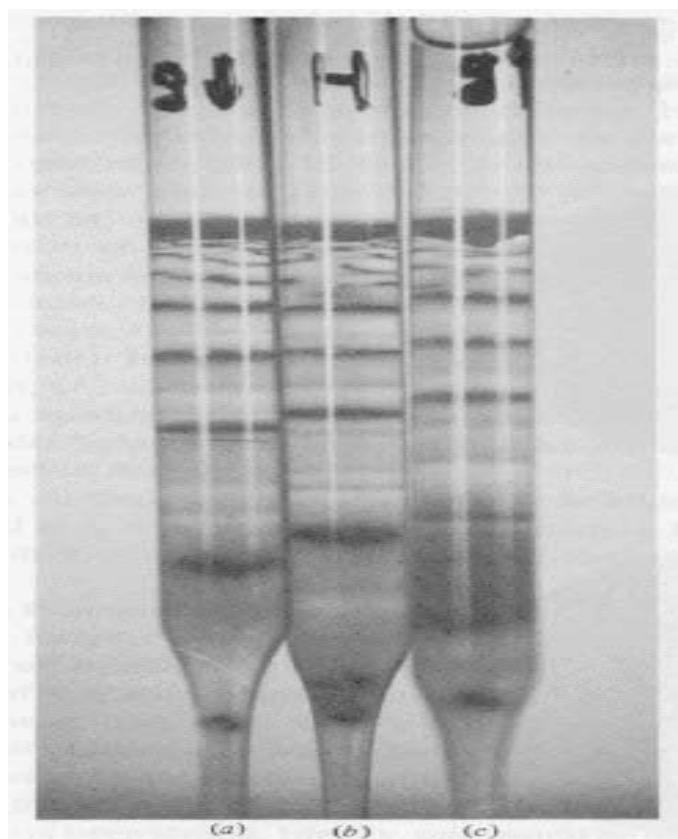
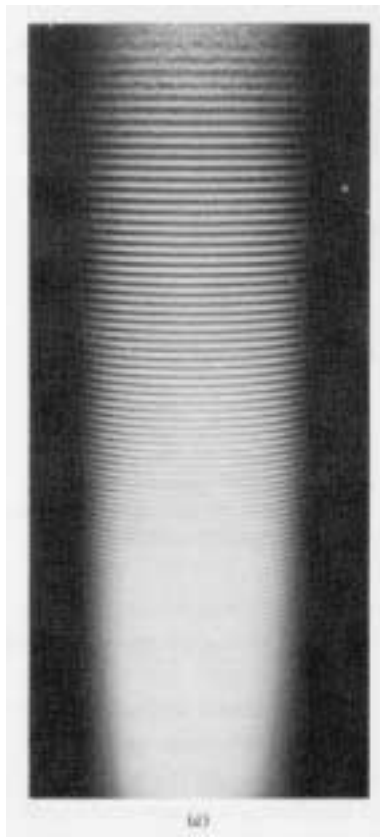


Figure 4: Effect of Gravity on Ring Position. KI diffusion into $\text{Pb}(\text{NO}_3)_2$ from above (a-left), horizontal (b-middle) and below (c-right). (p129 [6])



) Figure 5: Revert Copper Borate Ring System grown in a silica gel. (p135 [6])



Figure 6: $Mg(OH)_2$ ring system grown in gelatin. The ruler shows 1mm markings.



Figure 7: $\text{Zn}(\text{OH})_2$ spherulites growing in gelatin. Individual Spherulites are 2-3mm in diameter. This specimen was prepared with the protocol in Appendix C substituting Zn for Mg.

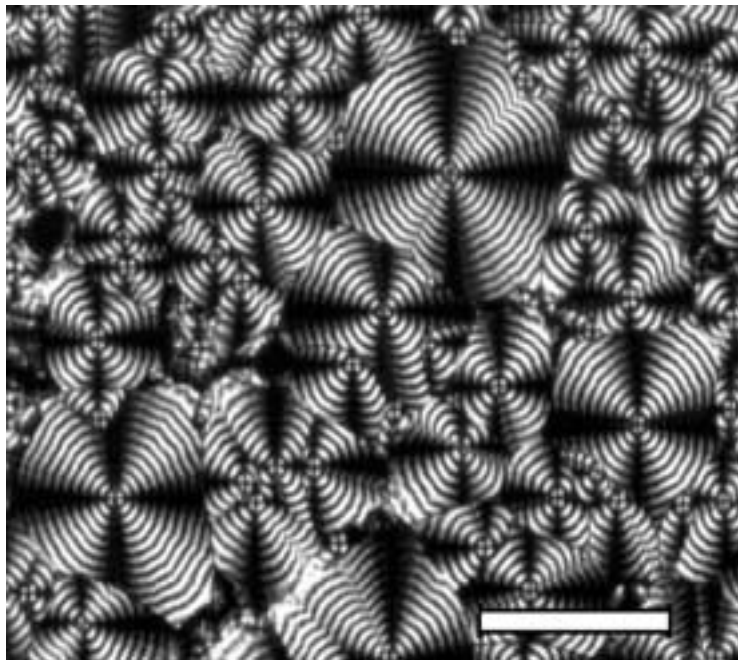


Figure 8: Spherulitic domains of in a $10\mu\text{m}$ thick sample of the liquid crystal 10OCB viewed through crossed polarizers. The scale-bar represents $25\mu\text{m}$. (Fig 2 from Hutter et al. [9])

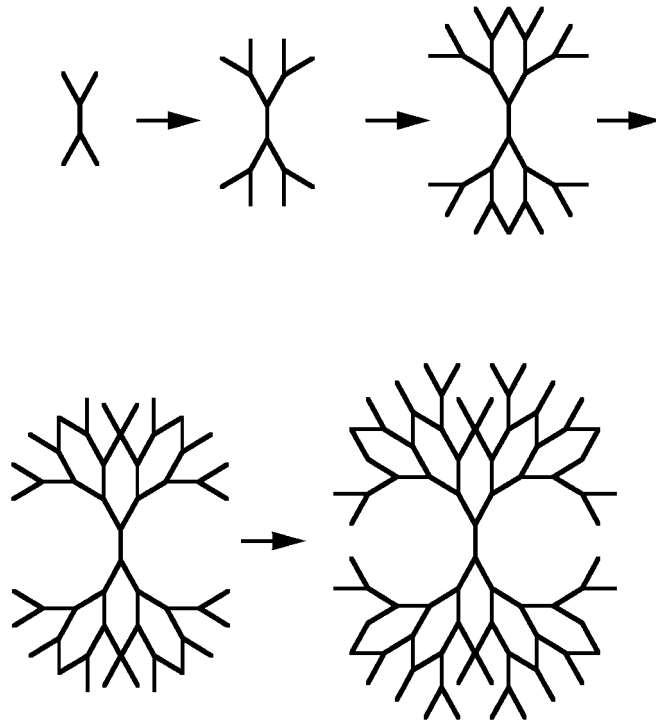


Figure 9: Pictorial Representation of “sheaf-like” spherulite nucleus. (Fig 4 from Hutter et al. [9])



Figure 10: Agate specimen inside a thunderegg/geode found in the Ochoco mountains, Oregon. (<http://orerockon.com/orchoco.htm>)

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