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On dynamic self-organization: examples from magmatic and other geochemical systems

Rabih F. Sultan*, Abdel-Fattah M. Abdel-Rahman†

Departments of Chemistry* and Geology†, American University of Beirut, P.O. Box 11-0236, 1107 2020 Riad El Solh, Beirut, Lebanon. *Email: rsultan@aub.edu.lb

Abstract

Standard Liesegang banding is the display of parallel bands of precipitate formed periodically when co-precipitate ions interdiffuse in a gel medium. The most striking resemblance with Liesegang patterns in Nature lies in the diverse scenery of banded textural features commonly observed in some geological materials, such as geodes, agates, malachites, as well as stratigraphic units of certain rock formations. Here, we explore the possible relationship between the Liesegang banding scenario and magmatic-type pattern formation, such as zonations in km-scale circular zoned plutons and anorogenic ring complexes, cyclic layering in large mafic–ultramafic layered intrusions and orbicular granites, as well as in mm-scale crystal zonations. We also investigate magmatic processes such as fractional crystallization, and the ranges of T and p that are compatible with operating conditions for Liesegang banding. For geochemical self-organization to operate via a Liesegang-type mechanism, a necessary condition is that the system be transiently out of equilibrium, and be described by complex nonlinear kinetic laws. We examine the viability of the development of geochemical patterns, in relation with the various requirements for the growth of Liesegang structures.

Keywords

Liesegang, precipitate patterns, geochemical self-organization, magmatic ring complexes, layered intrusions.

1 INTRODUCTION

One of the fascinating and visually most attractive phenomena, widely studied and documented in the physical chemistry literature, is that of periodic precipitation commonly known as Liesegang banding [1-3]. Liesegang bands of precipitate appear when a solution of a specific ion (say $Cr_2O_7^{2-}$) diffuses in a tubular gel medium containing its co-precipitate ion (such as Ag^+). The sparingly soluble $Ag_2Cr_2O_7$ precipitate forms a set of discotic strata perpendicular to the tube axis. A panorama of banded Liesegang patterns for different precipitate systems is displayed in Fig. 1.

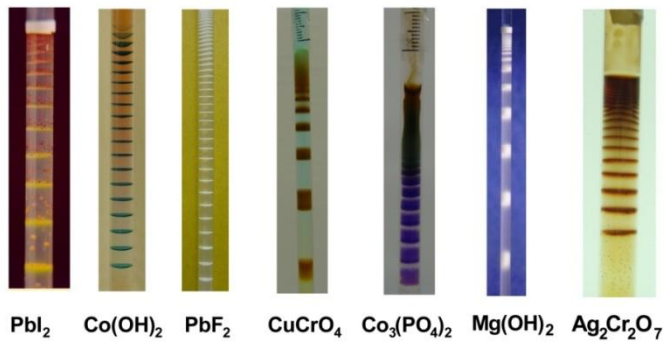

Figure 1: Typical Liesegang patterns grown in gels, for a number of sparingly soluble salts.

The mechanism of the Liesegang banding phenomenon is not one of universal character. Most scientists believe that the first band forms away from the first precipitation region, delayed by diffusion over a zone initially depleted in the diffusing ion, until the concentration product builds up and exceeds the supersaturation and nucleation thresholds. Then this cycle is repeated, and hence causes the formation of the next bands periodically, in a concerted scenario known as the supersaturation-nucleation-depletion cycle, first elucidated by Wilhelm Ostwald [4]. Another group of scientists believe that bands emerge from the break-up of a pre-formed uniform colloidal sol, due to a competitive particle growth mechanism mediated by the surface tensions of the various colloid particles having a broad distribution of sizes [5-7]. Due to larger surface tension, the small particles dissolve and the newly-formed aqueous species diffuse, driven by the concentration gradient toward the lower concentration vicinity of big particles. Thus the big particles grow and aggregate at the expense of the smaller ones, leaving in the middle a zone void of precipitate. The two 'mountains' of big particle aggregates constitute the bands separated by a precipitate-free 'valley'. This so-called 'Ostwald ripening' mechanism [8,9] leads to a state of the system with fewer but larger particles (large particles survive and grow, while small particles disappear). The dynamics of particle size distribution and number of grains per unit volume were conjectured in a detailed kinetic study by Lifshitz and Slyozov [10]. Liesegang strata are not restricted to 1D systems. Concentric rings of precipitate form as the ions diffuse radially from a central source into a 2D gel film [2,11]. Recently, concentric spheres have been obtained and studied in 3D [12].

A striking analogy exists between the Liesegang stratifications and the stripes that are commonly observed in a large variety of rocks and minerals [13-17]. Specimens of such a resemblance are depicted in Fig. 2.

Also, agates and geodes displaying exotic colorful ring periodicities exhibit a great visual similarity with the appearance of Liesegang rings [17,18]. A wide variety of similarities between simple Liesegang bands on a small, laboratory scale and a number of diverse geological features has been exemplified and reported in the literature [13-15,17]. These have been explained via different scenarios and operating mechanisms. Such studies have recently been compiled in a comprehensive review

by Sadek and Sultan [17], which include geological materials and biological systems, along with applications in medicine, physics and engineering.



a) b)

Figure 2: Patterns of concentric rings in a felsic volcanic rock (rhyolite; frame a), and in a malachite mineral specimen (frame b) resembling Liesegang banding. Width of the rhyolite specimen is 10 cm and that of the malachite specimen is 12 cm.

In this contribution, we focus on some magmatic systems with the aim of discussing whether the Liesegang phenomenon can be considered as a viable mechanism to produce patterns in geological materials at small as well as large scales, and to shed light on the relationship between magmatic processes and the Liesegang phenomenon.

2 LIESEGANG PATTERNING IN CRYSTALS AND MAGMA CHAMBERS

We attempt to see whether zonations characteristic of some large-scale circular zoned plutons and anorogenic alkaline ring complexes (such as Wadi Dib alkaline ring complex of Egypt [18], or the Deloro ring complex of Ontario, Canada [19,20]) can be somehow related to a Liesegang – type mechanism operated at a large magma chamber level. Through this study, we will also shed light on questions such as: could cyclic layering observed in mafic–ultramafic layered intrusions represent a natural expression of the Liesegang phenomenon? Do magmatic processes such as the processes of fractional crystallization (versus equilibrium crystallization) be also related to the Liesegang phenomenon? Examples of both rhythmic and cryptic layering in magmatic bodies and lopolithic layered intrusions, and examples of zoned silicate minerals (as garnet and plagioclase) have been presented in the literature. Also, petrographic or textural evidence, as well as chemical evidence exist for the presence of typical features developed in natural geological systems, possibly as a result of a self-organization mechanism. Among these, the following three examples are here presented.

2.1 Disequilibrium crystallization: millimeter- to nanometer-scale crystal zonation

In general, minerals crystallizing from a melt attempt to reach equilibrium for any given set of composition, temperature and pressure conditions. Textures, as well as chemical compositions of various parts (from core to rim) of individual mineral grains can be used to assess the extent to which equilibrium was reached. Compositionally homogeneous and typically non-zoned crystals usually develop as a result of equilibrium crystallization at a very slow rate of cooling. Because of

reaction kinetics, some minerals will approach physical and chemical equilibrium more readily than others, but perfect equilibrium is probably only rarely attained [21]. Certain petrographic features such as quench crystals and zoning observed in some mineral grains are examples of textural evidence of disequilibrium. Normal zoning, reverse zoning, and oscillatory zoning in crystals have been observed in a number of mineral groups, including plagioclase and garnet minerals. Zonation observed in crystals has been interpreted to reflect a failure of the silicate melt to achieve equilibrium with its crystallizing solid phases. This is typically associated with a relatively fast rate of cooling of magmatic bodies, in which crystallization takes place either at shallow crustal levels of magmatic emplacement or due to eruption of silicate lavas at the Earth's surface during volcanism.

The plagioclase feldspar series represents a solid solution series comprising six minerals varying in composition from the Ca-rich end member (anorthite; $CaAl_2Si_2O_8$) to the Na-rich end member (albite; $NaAlSi_3O_8$), developed due to the coupled substitution Ca-Al >> Na-Si. In the binary solid solution phase diagram of plagioclase, it is clear that $CaAl_2Si_2O_8$ or anorthite crystallizes at a much higher temperature (1553°C) compared to $NaAlSi_3O_8$ or albite, which crystallizes at 1118°C. During fast cooling, the process of fractional crystallization commonly produces oscillatory zoning, displaying very thin zones ranging in thickness from 0.l to 100 microns of Ca-rich and Na-rich plagioclase. An example of an oscillatory chemical zoning profile [22] shows the alternations of Ca-Al-rich zones occurring at the core, and Na-Si-rich zones that form later on in the crystallization sequence towards grain margin. Such zonations are highlighted in Fig. 3.a and interpreted in Fig. 3.b.

The origin of oscillatory chemical zonation in plagioclase was linked to the kinetics and the mechanisms of diffusion within the liquid and within the crystals. The absence of homogeneity in the plagioclase that has normal zonation has been interpreted to be related to the high activation energies necessary to break the inter-ionic bonds in the feldspar and accelerate the diffusion of ions, as Si^{+4} and Ca^{+2}, towards the feldspar – liquid interface. Such homogenization difficulty can also be explained by the fact that the substitution Si+Na >> Al+Ca, because the

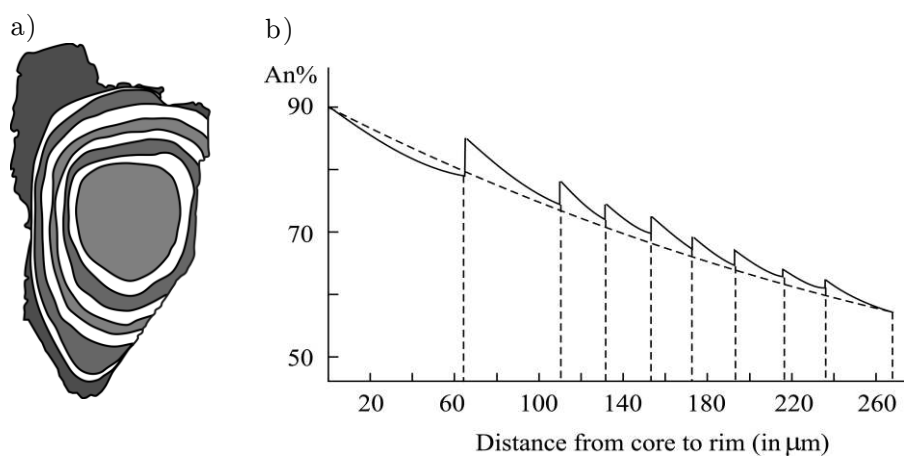

Figure 3: a. Sketch showing oscillatory zoning of plagioclase from Ca-rich core to Na-rich rim. b. variations in the An-content of the plagioclase crystal zonation from core (left) to rim (right). Adopted from [22].

exchange between Si-Al tetrahedral cations is more difficult than that between Ca-Na, with the vibrating large-size cations (Ca-Na) having coordination 8 to 10. Many hypotheses have been put in place to explain the oscillatory zonation. During the process of crystallization, self-organization alone may not be sufficient to produce oscillatory zoning in plagioclase feldspar. A host of other factors also play a major role. These include rhythmic variations in the conditions of temperature T, rate of cooling, fluid pressure p, fluid fugacity, H_2O content in the magma chamber, among other variations in the conditions of crystallization and its dynamical properties. For instance, the influence of the silicate melt and its elemental concentration, the presence of competitor ions and the presence of an electric field, all play a significant role in the formation of oscillatory zoning. These variations undergone by the magma during its crystallization "modify", in an alternating manner, the equilibrium composition of the residual plagioclase-liquid interface, thus resulting in the formation of Ca-Al-rich and Na-Si-rich domains, yielding alternation with periodicities that produces oscillatory zoning. Some authors consider the development of oscillatory zoning in plagioclase to be the result of cyclic combinations that would allow the intervention of diffusion gradients of Ca^{2+} and Na^{+}, interfering in the liquid. The interference of concentration gradients and diffusion of Ca and Na cations in the melt, along with any variable speed of growth of the crystallizing plagioclase also influence the development of oscillatory zoning. In such case of variable growth rates, the surface of the crystallizing mineral will be characterized by alternating strong and weak lattice planes that can explain the growth stages by heterogeneous nucleation along crystal faces. Here, the development of numerous irregularities on the growing crystal surfaces would correspond to rapid growth periods during which the liquid-solid interface would become depleted in Al^{3+} (with constant μ_{Na} and μ_{Ca}); since the relative proportions in Al^{3+} are variable in albite and anorthite, and thus layers rhythmically rich in Na (albite) and Ca (anorthite) can be obtained [22]. Therefore, micrometer-scale oscillatory zonation in plagioclase feldspars reflects clear differentiation from an initially uniform silicate liquid (magma or lava), in which Na-rich and Ca-rich oscillatory zones develop possibly as result of a magmatic self-organization mechanism, controlled in part by some external triggers. Figure 3.b shows both the actual (observed) variations, as well as the expected variations in the An-content in zoned plagioclase from core to rim according to the binary solid solution phase diagram in the system $CaAl_2Si_2O_8$ – $NaAlSi_3O_8$, assuming fractional crystallization conditions. As Ca-rich plagioclase crystallizes at higher temperature compared to Na-rich plagioclase, a gradual decrease in the An-content is expected during crystal growth from core to rim under ideal fractional crystallization conditions. This anticipated behavior is shown by the dashed single curve. However, in this diagram, the actual or observed oscillatory zones are represented by a series of small stepwise curves or hyperbolae developing towards an overall decrease in the An-content from core to rim, but with clear fluctuations (upward jump in the opposite direction) at the zone-zone interface that marks the solid-liquid interface for each of the numerous oscillatory zones developed. This may suggest a possible Liesegang-type mechanism being responsible for their development. It should be noted that the nonlinear nature of the curves may suggest the involvement of the coupling of chemical reaction kinetics to the laws of transport in this system that is clearly transiently out of equilibrium (a necessary condition for geochemical self-organization to operate via a Liesegang-type mechanism). Local perturbations in T and p, as well as mass exchange near the contact zone between the silicate liquid and the neighboring solid crystal face induce changes in the free energy [22]. Oscilla-

tory zoned crystals commonly experience variable growth rates, in which the surface of the crystallizing mineral will be characterized by alternating strong and weak lattice planes that can explain the growth stages by heterogeneous nucleation along crystal faces. Possible minor perturbations in the magmatic system may lead to dissipative structures producing patterns having a range of symmetries. As is usually the case in Liesegang-type patterning, free energy must be constantly dissipated ($\Delta G < 0$) in order to maintain fractional crystallization conditions in which the system must be out of equilibrium. Mass exchange takes place between the fractionally-crystallizing solid plagioclase crystal surface and the silicate liquid occurring immediately in contact with it.

2.2 Large scale disequilibrium crystallization (layered intrusions)

Evidence of disequilibrium (fractional) crystallization has best been observed in layered mafic-ultramafic igneous intrusions or lopoliths. The latter are large funnel-shaped igneous bodies or intrusions such as the Skaergaard Complex of Greenland, the Stillwater Complex of Montana, USA, and the Norite Zone of the Bushveld Complex of South Africa. These large igneous bodies are characterized by cumulate textures, cryptic, rhythmic and cyclic layering, in which sequences of banded magmatic layers reach thousands of meters thick. The question is: could these represent Liesegang-type structures?

The Stillwater complex, which is 5.5 km thick, is divided into three series from bottom to top as follows: the Basal series, the Ultramafic series, and the Banded Series (see Fig. 4, after Raymond [23], and citations therein). Each series is divided into a number of zones. The ultramafic series contains a lower peridotite zone and an upper bronzitite zone. The peridotite zone consists of cyclic, rhythmically and cryptically layered units. The banded series is marked by the first appearance of cumulus plagioclase. The series is characterized both by the abundance of plagioclase and by locally distinctive layering in the gabbros, and is subdivided into three parts, the Lower Banded series, the Middle Banded series, and the Upper Banded series, which are themselves subdivided into 12 to 14 zones. Cyclic and rhythmic layering are obvious, and the cryptic layering (the sequence of chemical change within the minerals) fluctuate with the cycles, rather than changing monotonically towards more iron and alkali-rich compositions [23].

The overall trends and the tholeiitic differentiation nature, on the AFM diagram of the Stillwater rocks, are consistent with an origin by fractional (or disequilibrium) crystallization. Rocks of the Stillwater Complex do not simply change monotonically upward towards more siliceous, alkali-rich, or iron-rich compositions, but instead cyclically repeat compositional types. Because

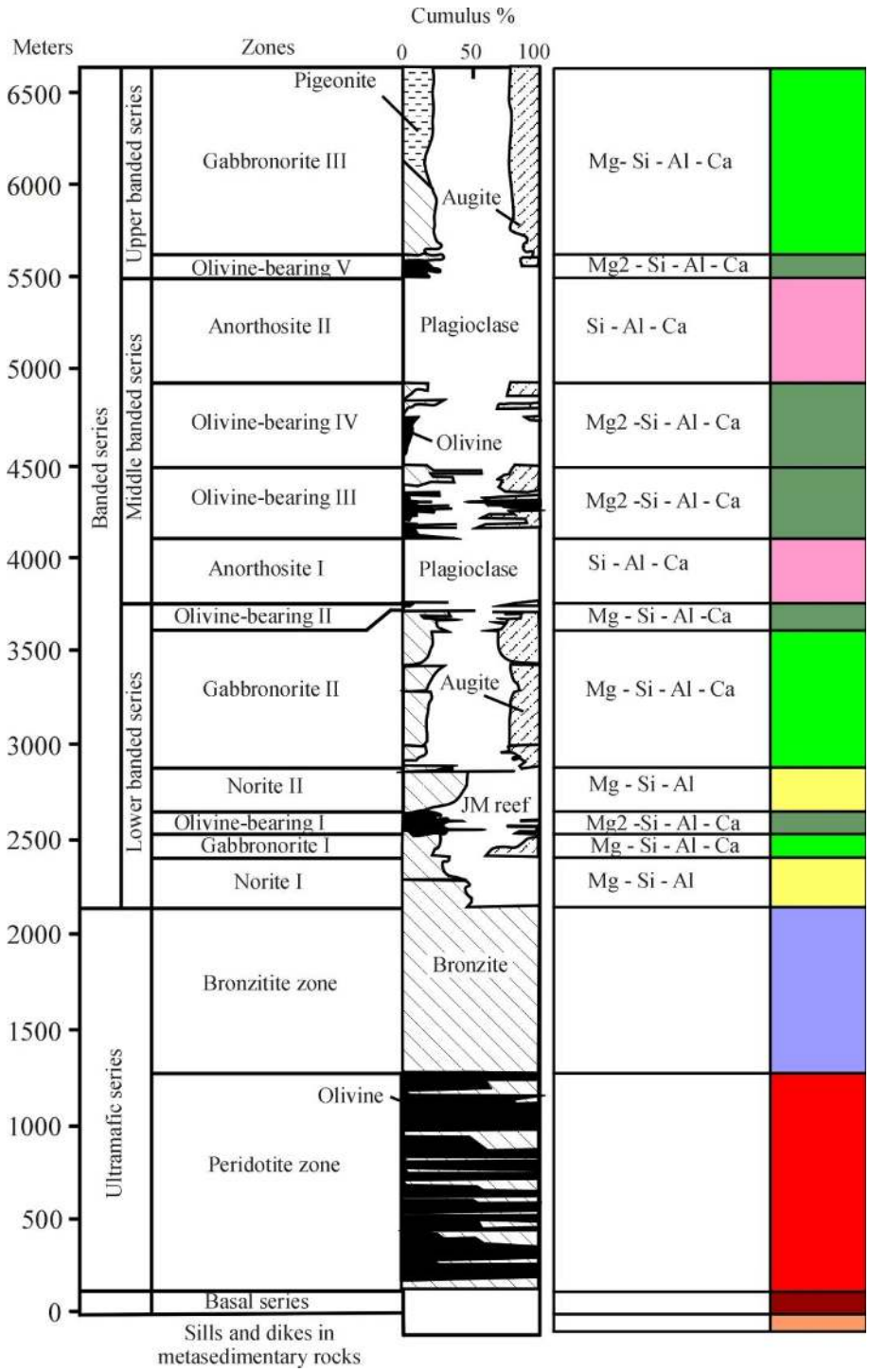

Figure 4. Mineralogical variations in the various ultramafic and banded series of the Stillwater Complex Montana (after Raymond, 2002, and references therein), along with the main chemical elements of the various banded layers, demonstrating and emphasizing the presence of cyclic banding, as clearly depicted by the color cyclicity and alternations in the right column.

of these and other factors, their origin is not yet fully understood. The various hypotheses on the origin of cyclic and rhythmic layering in layered intrusions can be explained by particular combinations of physical and chemical factors, including variations in magma compositions, density, pressure, temperature, current action, and diffusion, to develop particular aspects of those rocks [23]. The multiple chemistries and various rock types of the dike and sill complex of the Basal contact zone represent multiple intrusions of five major magma types (with mantle sources for the parent magmas). Abundant injections of the aluminous parent magma into the chamber initiated and sustained the extensive plagioclase crystallization that characterizes the banded series. Repeated injections of the various mantle-derived magmas, which mixed and experienced fractional crystallization (aided by crystal transport and deposition), crystallized to form the diverse layers of the Stillwater Complex (Raymond [23], and citations therein).

Chemical variations and cyclic banding that characterize the Stillwater complex (depicted in Fig. 4) might be interpreted to reflect Liesegang-type structures, which may have resulted by variations in the relative rates of chemical and thermal diffusion during cooling. Here we suggest that in-situ crystallization with an oscillatory interference of nucleation and crystal growth may be a more acceptable hypothesis than just mere layered sedimentation by simple crystallization and deposition via gravitational settling of early-formed minerals. Dissolution due to surface tension effects is believed to be the dominant factor in crystal aging. On this "Stillwater" layered intrusion, Boudreau [24] has shown that fine-scale layering is mainly mediated by crystal aging, itself being a concerted dissolution-diffusion-precipitation grain coarsening scenario. Boudreau used a Competitive Particle Growth (CPG) model similar to the one developed by Ortoleva [5,6], Ross [7] and their co-workers. The doublet layers in the banded norites were shown to arise from band splitting, rather than the discrete nucleation of each counterpart. Regions of marginally larger crystals grow at the expense of nearby smaller ones, which disappear by dissolution. The overall mechanism causes the band to split through the dissolution of particles at its center and precipitation (coarsening) at its two edges, thus yielding the observed doublets.

In the somewhat similar layered Skaergaard intrusion, McBirney and Noyes [25] distinguished four cooling stages, each governed by one dominant physico-chemical factor with progressively falling temperature: thermal diffusion, reaction rate at liquid-crystal interface and growth of large crystals at the expense of small, disappearing ones respectively. Mass exchange near the liquidus [the surface boundary between the crystallizing solid (crystals) and melt], coupled with some local perturbations in T and p may induce changes in the free energy. Stresses experienced by magmatic bodies in orogenic as well as anorogenic settings could lead to alternations in the free energy of neighboring crystallizing minerals, thus maintaining fractional crystallization conditions in which the system must remain out of equilibrium.

2.3 Medium scale disequilibrium crystallization in zoned ring complexes

Most of the Precambrian shields exposed in various locations worldwide were intruded by ring complexes [18-20]. One of these is the Wadi Dib magmatic ring complex that intruded granodioritic Pan-African host rocks in eastern Egypt. It is a small (2 km in diameter) ring complex, exhibiting a distinct concentric compositional zonation. The Wadi Dib complex is schematically represented in Fig. 5.a.

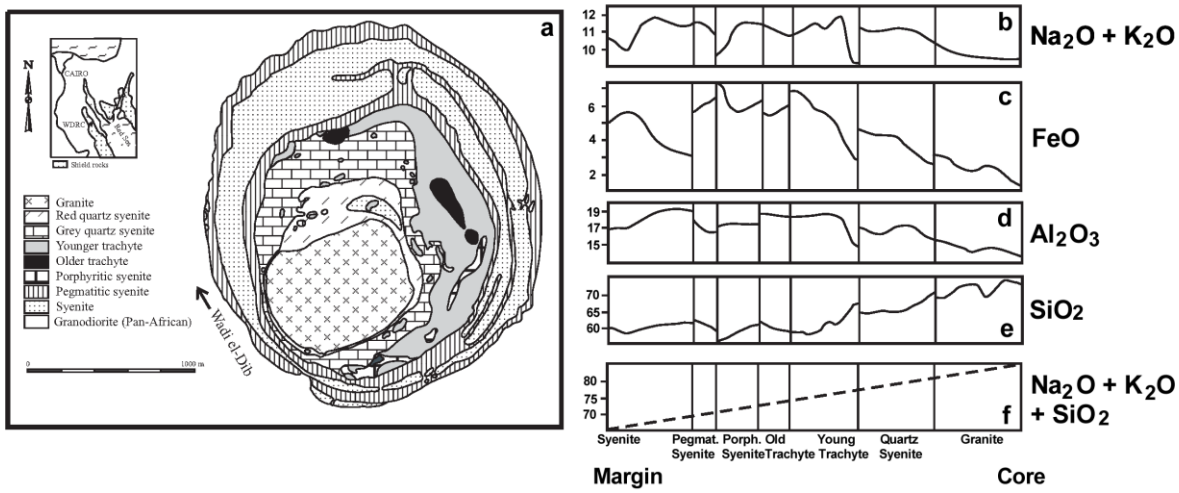

Figure 5. a. Geological map of the Wadi Dib alkaline ring complex, after Ref. [18]. Inset map shows location of the complex in the Eastern Desert of Egypt; (2.b-e) Observed variations of alkalis plus silica from margin to core within the Wadi Dib ring complex; 2.f. Ideal variation.

The complex contains several syenitic outer ring sheets, a mainly trachytic intermediate ring sheet, and a quartz syenite inner ring sheet with a granitic core [18]. Relative ages decrease from margin to core. Major and trace element patterns underline the co-magmatic origin of the suite, but indicate three stages of evolution with several pulses of emplacement. The ring complex was interpreted to have been developed by fractional crystallization from an originally alkali-basaltic parent magma that was emplaced along ring fractures at a subvolcanic level. Amphiboles and Ca-rich feldspar minerals in syenitic rocks at the margin typically crystallize at higher temperature compared to biotite, albite and quartz that are abundant in quartz syenite and granitic rocks in the core of the ring complex. Under ideal fractional crystallization conditions, the expected variation in silica and alkalis from margin to core within this complex is their gradual and continuous increase from margin to core, as reflected in Fig. 5. The dashed line in Fig. 5.f is showing just that. However, in this diagram, the actual or observed variations between the various compositional rings from margin to core are rather represented by a series of small step-wise curves developing towards an overall decrease in total iron (as FeO) and aluminum (Al_2O_3), and an overall increase in silica (SiO_2), but with clear fluctuations (upward jump in the opposite direction) at the ring-ring interface that marks the solid-liquid junction for each of the rock types of the various rings developed. This may suggest a possible Liesegang-type mechanism being responsible for their development. It should be noted that the nonlinear nature of these curves may suggest the involvement of the coupling of chemical reaction kinetics to the laws of transport in this system that is clearly transiently out of equilibrium (a necessary condition for geochemical self-organization to operate via a Liesegang-type mechanism). This may suggest a sequence of supersaturation-nucleation-depletion events occurring during the formation (fractional crystallization) of each ring. Here precipitation is not an equilibrium process, and does not form immediately and continuously upon diffusing of the elements at the solid-liquid interface, but occurs when a critical value of the concentration product, called the nucleation threshold, is reached. Before crystallization or precipitation, the co-precipitate ions are present in an

undersaturated silicate liquid. When exceeding the value of the supersaturation threshold, nucleation is initiated and a precipitate ring forms at this position. After the formation of the first ring, the concentration is rapidly depleted and the nucleation is suppressed. As time proceeds, the diffusion of the ions continues until again it exceeds the threshold value and triggers the formation of a second ring, and in this case, a slightly more Si-Na-K-rich ring. This sequence lies at the heart of the Ostwald supersaturation-nucleation-depletion cycle [4].

3 REACTION-TRANSPORT STEERED BANDING

For a geochemical self-organization process to operate via a Liesegang-type mechanism, a necessary condition is that the system be transiently out of equilibrium as established by the Brussels school led by I. Prigogine [26]. The dynamic equations describing the evolution of the system are nonlinear, and involve the coupling of chemical reaction kinetics to the laws of transport processes. Such an underlying dynamics provides a clearly different scenario from mere seasonal variations, believed to be functional in, say, sedimentary layering. A feature of paramount importance observed in banded rocks, which points in the direction of a novel scenario other than a routine external template, is the difference in length scale within the same rock pattern. Patterns in banded iron formations, as well as marl/limestone alternations were shown to have been developed from an initially uniform sediment. Alternatively, small scale banding may arise from a diagenetic amplification of a larger scale sedimentary pattern [27]. Small local perturbations in the system are eventually amplified, and lead to dissipative structures; and thus unfold into patterns of a wide variety of symmetries. A requirement for maintaining the system out of equilibrium during the formation process is that free energy be constantly dissipated ($\Delta G < 0$). Such conditions are fulfilled in a host of examples in geological processes. Local perturbations in T and p, as well as mass exchange near the contact zone between the magma and a neighboring solid induce changes in the free energy. Stresses experienced by metamorphic and sedimentary rocks drive alterations in the free energy of neighboring grains [16]. In this section, we analyze a wide spectrum of geological patterns and examine the viability of the prevailing conditions of their formation, in relation to the various requirements for the growth of Liesegang structures.

Consider a porous rock aquifer infiltrated by solute reactants from reactive water upstream (inlet), as shown in Fig. 6 [16]. The dissolution of the minerals downstream (outlet) causes the

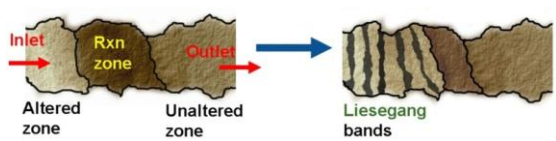

Figure 6: Porous rock aquifer infiltrated by an inlet of ion-rich water, causing the dissolution of parts of the rock (left; reaction zone). The subsequent precipitation in the sink of counter-ions occurs in a way similar to Liesegang banding (right), by coupling of diffusion to reactions. Rxn zone ≡ reaction zone.

release of aqueous ions. The released ions can react with those of the inlet, provoking the precipitation of one or more authigenic minerals upstream.

We thus see that the moving reaction zone can be maintained out of equilibrium just like in a constantly-stirred tank reactor (CSTR). In this context, the banded deposition of the new mineral occurs in the form of Liesegang bands, and arises as a strictly nonequilibrium process. Sultan et al. [28] presented a theoretical model with analytical and bifurcation solutions of a rock system subjected to the flow of an O_2-rich solution causing the dissolution of the pyrite (FeS_2) mineral within this rock. The deposition of goethite (FeO.OH) mineral by precipitation behind the dissolution front was demonstrated. Three different depositional patterns were obtained depending on the choice of a special bifurcation parameter, which is the rate constant (k) of the precipitation reaction. As k is gradually increased, the transition from a steady deposition pulse to a 'wiggle' structure (with hills and valleys) to distinct Liesegang bands was exhibited.

Not all the banded features observed in geological materials and outcrops follow a nonequilibrium self-organization scenario. Oscillations in grain size which appear in sedimentary bedding sequences are established to be due to external factors. They arise from seasonal variations in the feed rate and character of the material when it was originally laid down. On the other hand, pressure solution or stress driven grain transformation can induce several self-organization processes in limestone rocks, leading to the loss of porosity, lamination or band formation during diagenetic processes. The coupling and alternation of dissolution and compaction zones with cementation zones could give rise to the formation of stylolites, clay seams or marl-limestone oscillations. Such various structures are driven by a host of coupled reaction and mass transport processes. Pressure solution adds to other significant factors by altering the rock porosity, thus governing the type and rate of reaction, notably differentiating reactions at grain-grain interface (low porosity) from those on free-face grains (high porosity). The strain free energy on the grain surface plays a primordial role in driving the dynamics of pattern formation. Dewers and Ortoleva [29] proposed a reaction-transport-mechanical model, incorporating elastic matrix-inclusion effects into reaction-transport formalism, adapted to a low porosity calcite-clay rock. They showed that intergranular pressure solution occurs when grain-contact reaction is the rate-determining process. Stylolites are formed when dissolution at grain-contact peripheries is faster than within contacts themselves, whereas cm-scale clay seams and marl-limestone alternations occur when face free reaction is the rate-limiting process. The model accounts for the formation of secondary or "satellite" stylolites induced by initial local textural heterogenetities in the vicinity of primary stylolites.

Most studies treating geochemical self-organization are based on theoretical modeling on the reaction-transport-mechanical stress processes [16]; whereas most experimental simulations of geological banding involve mimicking the supporting medium through diffusion-precipitation experiments of the Liesegang type, in gel media [15]. There exist a few studies however, which address the problem via conducting experiments *in-situ*, i.e. in real rock bed systems. Rodriguez-Navarro et al. [30] observed Liesegang rings by monitoring the slow carbonation of traditional, aged lime mortars. The mortar [portlandite putty embedded in a quartz (SiO_2) sand aggregate] was kept under excess CO_2-rich water. This long-time contact transforms the portlandite into calcite ($CaCO_3$) via the reaction:

$$Ca(OH)_2 \quad + \quad CO_2 \ (aq) \quad \longrightarrow \quad CaCO_3 \quad + \quad H_2O.$$

The carbonation reaction yields 3D Liesgeang patterns consisting of concentric ellipsoids of alternating calcite and calcite-free zones. A sol of colloid-size calcium carbonate nuclei is first formed,

driven by supersaturation inside the small pores of radius < 0.1 μm. This uniform sol then evolves and transforms into well-crytsallized calcite through an Ostwald ripening mechanism [8], mediated by the Lifshitz-Slyozov coarsening instability [10]. The rings exhibit revert spacing [31] instead of direct spacing and obey Jablczynski's spacing law [32]. The decrease in CO_2 uptake and diffusion as the process progresses toward the core may explain the revert nature of the Liesegang pattern. Msharrafieh et al. [33] carried out acidization-precipitation experiments inside a ferruginous limestone rock. When sulfuric acid is used, the sulfate counter-anion causes the precipitation of the acid-insoluble gypsum ($CaSO_4$) and anhydrite ($CaSO_4.2H_2O$) according to:

$$CaCO_3 \quad + \quad H_2SO_4 \quad (aq) \quad \longrightarrow \quad CaSO_4 \quad + \quad CO_2 \quad + \quad H_2O$$

Starting at a central source injected from a syringe of a regulated infusion pump, the acid infiltration causes the precipitation of $CaSO_4$ in concentric zones, with oscillatory composition in gypsum-anhydrite minerals (i.e. $CaSO_4$-rich and $CaSO_4$-poor regions) [34]. Infiltration cracks in rocks were simulated by immersing ion-gel films sandwiched between sealed glass plates in solutions rich in the co-precipitate ions. The plates were then hammer-broken to allow the infiltration of the submerging solution through the imposed crack. Precipitation was observed instantaneously in the form of dendritic ramification structures [35,36].

Banding in rocks can also exhibit a great degree of complexity. As highlighted above, band splitting and fine-scale layering are characteristic features often associated with a nonlinear dynamic scenario. Multiplets of laterally extensive beds exist in marl layers of Jurassic limestone-marl rhythmites, wherein the marl sediment is less resistant to weathering [27]. Using a cellular automaton model, Böhm et al. [27] showed that rhythmic alternations are formed through the coupling of an external pulse trigger to diagenetic self-organization. Bundles of calcite-cemented layers are generated, consisting of cement couplets with increasing number over a finite number of time steps. The ascending number of bands over successive multiplet bundles within the rock was reproduced in the dynamics of a Liesegang pattern involving three precipitates [37]. Such an intriguing pattern is displayed in Fig. 7.

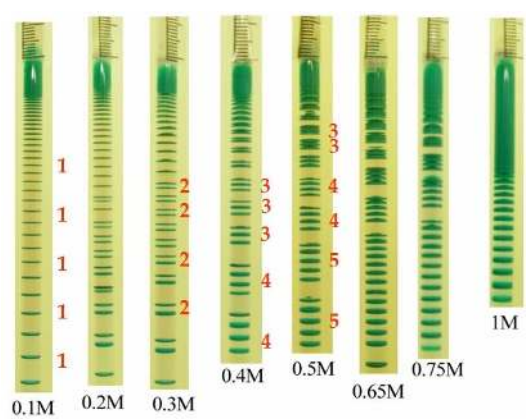

Figure 7: Liesegang pattern involving three cations (Co^{2+}, Ni^{2+} and Mg^{2+}), and displaying intriguing, highly unusual geometric rhythmicity, consisting of multiplet groups with ascending number of bands: 2, 3, 4, 5, etc. The indicated concentrations correspond to $[Mg^{2+}]_0$ used as a control parameter (see Ref. 37).

4 OTHER EXAMPLES: EVOLUTION OF ORBICULES

Orbicular patterns are small structures (cm-scale) with spheroidal geometry wherein mineral content alternates in concentric shells [16]. This alternation is usually between dark shells, rich in phyllosilicate, and lighter ones wherein quartz and feldspars are predominant [16]. The medium hosting the orbicules is predominantly of plutonic nature, while the cores may consist of plutonic or metamorphic rocks, or crystals [38]. The orbicules are essentially composed of plumose K-feldspar around various nuclei. The mechanism of genesis of the orbicules is still under debate, although their magmatic origin is not disputed, the orbicular structure being controlled by adiabatic undercooling. The magma in which orbicules develop has diffusive and rheological properties typical of a paste or gel of mixed hydrosilicates, just like the host medium of a Liesegang pattern. The growth of successive shells is then governed by rapid diffusion-controlled supersaturation and crystallisation of the different components within the melt. This scenario is essentially a nonequlibrium dynamical picture, as opposed to one wherein the shell formation is explained by the rapid crystallization of immiscible supersaturated magmas convecting around the orbicular nuclei. Thus, a Liesegang connection to the formation of orbicular granitic bodies is here envisaged.

5 CONCLUSIONS

a. Oscillatory zoned crystals commonly experience variable growth rates, in which the surface of the crystallizing mineral will be characterized by alternating strong and weak plane lattices that can explain the growth stages by heterogeneous nucleation along crystal faces. Possible minor perturbations in the magmatic system may lead to dissipative structures producing patterns having a range of symmetries. As is usually the case in Liesegang-type patterning, free energy must be constantly dissipated ($\Delta G < 0$) in order to maintain fractional crystallization conditions in which the system must be out of equilibrium. Local perturbations in T and p induce changes in the free energy [22]. Mass exchange takes place between the fractionally-crystallizing solid plagioclase crystal surface and the silicate liquid occurring immediately in contact with it.

b. In layered intrusions such as the Stillwater complex, chemical variations associated with cyclic banding that characterizes this complex may be interpreted to reflect Liesegang-type structures, which could have resulted by variations in the relative rates of chemical and thermal diffusion during cooling. Here we suggest that in-situ crystallization with an oscillatory interference of nucleation and crystal growth may be a more acceptable hypothesis than just mere layered sedimentation by simple crystallization and deposition via gravitational settling of early-formed minerals.

c. In magmatic alkaline ring complexes, a sequence of supersaturation-nucleation-depletion events occurring during the formation (fractional crystallization) of each ring may have been the dominant processes controlling their evolution. Here precipitation is not an equilibrium process, and does not form immediately and continuously upon diffusing of the elements at the solid / liquid interface, but rather occurs when a critical value of concentration product, called the nucleation threshold, is reached. Before crystallization, the co-precipitate ions are present in a supersaturated solution. When exceeding the value of the threshold, nucleation is initiated and a precipitate band forms at this position. After the first band formation the concentration is rapidly depleted and the nucleation is suppressed. As time proceeds, the diffusion of the ions continues until again it exceeds the thresh-

old value and triggers the formation of a second ring. The process continues till all melt fractions crystallize, in a disequilibrium environment, to produce the entire concentric ring structure. d. A number of observed features performed in the laboratory, both in-situ and in Liesegang experiments, sometimes with intriguing dynamical abnormalities, were also presented and discussed.

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