Realtime Observation of Diffusing Elements in a Chemical Garden

Wenyang Zhao†‡ and Kenji Sakurai§†‡

†University of Tsukuba, 1-1-1, Tennodai, Tsukuba, Ibaraki 305-0006, Japan
‡National Institute for Materials Science, 1-2-1, Sengen, Tsukuba, Ibaraki 305-0047, Japan

ABSTRACT: The chemical garden, which has been known as the plant-growth-like diffusion of chemicals since the 17th century, has regained much attention in recent years. Significant progress in research not only promoted the understanding of the phenomenon itself but also suggested a prospective method of synthesizing new materials via the chemical garden route. It is extremely important to introduce new characterization techniques to provide more insights into chemical diffusion and element redistribution during the reaction process. The present article describes some successful applications of the realtime X-ray fluorescence (XRF) movie technique to observe each diffusing element. The protagonist of the movie is a chemical garden reaction growing from a seed of calcium salt and ferrous salt mixtures. Through observation by an XRF movie, it has been found that the growth rate and diffusion behavior of calcium and iron are very different. This results in a macroscopic diversity of the element composition in the finally precipitated chemical garden structures. The present research not only reconfirms the potential of fabricating gradient composites through the self-organized chemical garden approach but also demonstrates the attractive achievements of XRF movies. It has been demonstrated that the XRF movie is an indispensable realtime characterization technique for the study of chemical garden reactions or even other related diffusions.

INTRODUCTION

The chemical garden is a famous chemical phenomenon. The reaction is generally started by seeding a soluble metal salt crystal into sodium silicate solution. When the crystal starts to dissolve, it is immediately enveloped by a semipermeable membrane, which precipitates at the interface of the internal metal salt solution and the external silicate solution. The continuous dissolution of the metal salt increases the osmotic pressure of internal solutions, driving external water molecules to enter the envelope continuously through the membrane. As the internal water pressure increases, the membrane envelope expands, and finally it ruptures at its weakest point, ejecting a fluid of metal salt solution into the external sodium silicate solution. Again the fluid is immediately trapped by a new envelope which precipitates at the interface of two solutions. This envelope precipitation—rupture process is ceaselessly repeated, resulting in a continuous growth of membrane tubules in the solution. Because the metal salt solution is less dense than the sodium silicate solution, the flow direction of the ejected fluids is generally forced upward by the influence of buoyancy. Therefore, the direction of tubular growth is upward as well.

The chemical garden phenomenon was first discovered by Glauber in 1646. At that time, it inspired a broad interest in discussing the original form of life because its growth regime and plantlike tubular shape resemble those of some organisms. In the subsequent three centuries, its self-organized inorganic semipermeable membrane was frequently associated with biological membranes. However, as more and more knowledge was accumulated on biology and biochemistry, this analogy between chemical garden and organic life was finally in decline in the mid-20th century. After that, except for its impressive fascinating appearance, the scientific significance of the chemical garden did not cause much interest until 1980. Since then, a great deal of modern research on the chemical garden has been conducted and many types of chemical garden reactions have been systematically studied. The terminology of the chemical garden has been extended to represent a wide range of chemical reactions, in which a semipermeable membrane precipitates at the interface of two different aqueous solutions and a steep transmembrane chemical gradient automatically forms. In this modern research, the reactants are quite variable. The general formation mechanism of the chemical garden has been clarified. Different growth regimes have been reported, and an oscillation growth model has been established. The precipitated tubular structures have been comprehensively characterized in many aspects, including morphology,11,12 hierarchical nanostructure,13 composition gradient,14–16 crystallography,17 porosity,18,19 magnetism,18,19 catalysis,18,19 etc. Some experiments were conducted in microgravity to discuss fluid convection that is free of buoyancy,20,21 and some experiments were conducted in a magnetic field to influence the ions in the fluid and to induce three-dimensional (3D) morphological chirality.22,23 This gradual deepened understanding of the chemical garden has certainly lead to fruitful achievements in different fields. It has been found that the chemical garden phenomenon also occurs in submarine vents24 and in the process of cement hydration25
and metal corrosion. It has been reported that the chemical garden reaction could be applied to the field of nanowires, fuel cells, cytocompatible biomaterials, and biomineralizations. In view of all of the progress that has been made in the past 40 years, a suggestion was made in 2015 to introduce the new terminology “chemobronics” for representing the entire field of modern research on the chemical garden. Moreover, much future research on synthesizing new materials and fabricating new composites via the chemical garden route can be expected.

Modern research on the chemical garden provides much observational detail and scientific insight compared with the early-stage naturalistic surveys centuries ago. This is mainly due to the advent of many powerful characterization techniques, such as scanning electron microscopy, transmission electron microscopy, energy dispersive spectroscopy (EDS), X-ray diffraction, thermogravimetric analysis, and Raman spectroscopy. However, until now, most of these characterization techniques can only analyze the final precipitated products of the chemical garden as the specimen, which must first be isolated from the solution. As a result, it would be extremely troublesome and probably sometimes unreliable to reveal the stagewise development of precipitated tubules. Although Mach–Zehnder interferometry was once used to observe the formation of chemical gardens, the most general method is still to observe the change in appearance by the human eye or optical microscopy. This method can describe obvious morphological change during tubular growth. Nevertheless, it may not be effective to study gradual chemical diffusion and precipitation during the subsequent aging process. More importantly, this method cannot reveal the nature of element species. To synthesize new materials via the chemical garden route, there is no alternative but to introduce two or more species of metal ions in one chemical garden reaction. Therefore, it is necessary to record the whole process of spatiotemporal diffusion and precipitation of different elements in the same reaction. As a consequence, a new realtime characterization technique is needed.

Full-field X-ray fluorescence (XRF) imaging is a powerful technique for studying the spatial distribution of elements in materials. In 2003, its time-resolved version, sometimes called the XRF movie, was utilized to visualize the chemical diffusion dominated by an ion-exchange resin. The subsequent development of X-ray detectors endowed this technique with spectroscopic resolvability for distinguishing different elements. Most recently, the instrumentation in this technique has been further simplified, making the technique much more cost-effective and serviceable. It has been proved that even with a laboratory X-ray tube one can smoothly take a realtime XRF movie, which displays the process of chemical redistribution in an aqueous reaction system. Therefore, the technique is quite suitable for realtime observation of diffusing elements in the chemical garden.

In this research, a fine mixture of calcium salt and ferrous salt was used as a seed for the chemical garden. Its tubular growth and subsequent aging process were recorded by an XRF movie (Figure 1). By virtue of the movie, it has been established that the calcium distribution differed greatly from the iron distribution in the final precipitated tubular structures. Moreover, calcium and iron showed quite different diffusion behaviors in the aging process over many hours. The reason for such difference was explained.

Figure 1. Schematic illustration of the Hele-Shaw cell and the XRF instruments. The dimension of the cell is 30 mm (H) × 15 mm (V) × 0.5 mm (thickness).

RESULTS AND DISCUSSION

Figure 2 shows the photo of the final chemical garden structure after the reaction. The scale bar is 1 mm. The arrow indicates the upward direction of the vertically placed Hele-Shaw cell. The red-dashed rectangle indicates the observation area of the XRF movie, which is approximately 7 mm (H) × 4 mm (V). Region A indicates a typical tubular structure of white color, and region B indicates a typical structure of green color.

Figure 2. Optical microscopy photo of the final chemical garden structure after 15 h of reaction. The scale bar is 1 mm. The red-dashed rectangle indicates the observation area of the XRF movie, which is approximately 7 mm (H) × 4 mm (V). Region A indicates a typical tubular structure of white color, and region B indicates a typical structure of green color.
parts merely from the appearance. This is the reason why the XRF movie technique has been employed for this observation.

A similar experiment is conducted under the observation of optical microscopy. The rapid tubular growth is recorded by a video (Supporting Information). The same phenomenon is reproduced, proving that the color diversity is not induced by X-rays. As shown in the video, the tubular growth is pioneered by white structures, whereas the green color appears subsequently from the lower to the upper parts.

The XRF movie provides much information in different forms. Figure 3 shows the full-field XRF spectra, which accumulate all detected XRF signals in 15 h. The spectroscopic property of an XRF movie enables it to distinguish different elements. As shown in Figure 3, the spectra peaks of calcium (Ca Kα, Ca Kβ) and iron (Fe Kα, Fe Kβ) can be clearly identified. The spectra peaks of calcium are much weaker than those of iron because XRF photons of calcium have lower energy than those of iron, and consequently they are more intensively absorbed in the solution, in air, and in the detector window. For the same reason, other elements in the reaction system, including hydrogen, oxygen, sulfur, sodium, and chlorine, are not shown in the spectra because their even lower energy XRF photons are totally absorbed. Nevertheless, because the seeded metal cations are generally of the most interest, XRF observation can still provide much useful information even if does not show light elements.

The XRF signals of calcium and iron are extracted to compose time-resolved XRF images of calcium and iron, respectively. Because the observation of the XRF movie lasts for 15 h, it is acceptable to set its frame rate as 1 frame/h to study the gradual chemical diffusion during the long-term aging process. In this case, for each element, in total, 15 movie frames are generated and every movie frame represents the element's

**Figure 3.** Full-field XRF spectra of the chemical garden. The XRF signals are accumulated in the whole 15 h reaction. Spectra peaks of Ca and Fe can be identified.

**Figure 4.** Sequential movie frames of Ca and Fe. The movie indicates the gradual diffusion of calcium and iron during the long-term aging process. The frame rate of the movie is 1 frame/h. Regions A and B have different element compositions. Region C is at the boundary of the big swell, and region D is inside the swell.
spatial distribution in this 1 h. Figure 4 displays some key movie frames, in which the scale bar is 1 mm.

The correlation between optical appearance and element composition is clarified by comparing Figure 2 with the 15th movie frame in Figure 4. It is quite clear that the green structures include both calcium and iron, whereas the white structures include only calcium. Thus, it is presumably inferred that iron is the actual color agent in the green structures. The most typical evidence is marked by A and B in both Figures 2 and 4. At the position of A, the XRF image of calcium does not exactly match the outline of the white plumes in the photo. This is because XRF observation is more sensitive to superficial structures. The gossamer white calcium membranes located in the deeper parts of the Hele-Shaw cell cannot be clearly imaged because calcium XRF photons are intensively absorbed in the solution. It should be realized that the one-to-one mapping of calcium to white and iron to green is a very fortunate case in the field of the chemical garden. In many other cases, the correlation between the appearance color and element composition is confusing. For example, the precipitated membrane of iron appears green when its cations are dissolved in solution, but turns blue when it is precipitated in the form of ferric-dominated. The correlation may become more complicated when two or more metal cations are mixed or coprecipitated. For this reason, it is necessary to utilize XRF imaging to reveal the reliable spatial distribution of different elements in a chemical garden reaction.

After understanding the correlation between the appearance color and element composition, the optical microscopy video (Supporting Information) of the chemical garden reaction is reviewed. As shown in the video, the growth of tubules is quite fast, whereas iron climbs up these tubules in the later stage. This is presumably because the growth of calcium tubules is much faster than that of iron. In 2011, it was reported that calcium chloride has the lowest induction time and the highest linear growth rate among four metal-ion salts of calcium chloride, manganese chloride, cobalt chloride, and nickel sulfate. This tendency is believed to be related to the solubility product constant of these salts in hydroxides. For calcium hydroxide, the solubility product constant is $5 \times 10^{-6}$, which is much larger than that of the other three metal elements.\(^8\) Our experiment is consistent with this conjecture because the solubility product constant of ferrous hydroxide is $8 \times 10^{-16}$, which is significantly smaller than that of calcium hydroxide. This experiment proves that the difference in growth rate remains even when the two reactant metal salts are evenly mixed in advance. The difference in growth rate results in a macroscopic inhomogeneous distribution of calcium and iron, which could be subsequently fixed when the tubular growth stops for some reason. As a result, it looks like a portion of calcium is purified from the mixture of two elements.

The sequential movie frames in Figure 4 show the gradual diffusion of calcium and iron in the long-term aging process after the tubules have been formed. It is quite clear that iron is gradually diffused from the internal solutions to the precipitated boundary walls of the big swell. This phenomenon is not a surprise because hydroxyl ions are continuously driven into the swell through the semipermeable membrane by its transmembrane concentration gradient. As a result, more and more ferrous ions in the internal solution are trapped and precipitated at the interior surface of the membrane. This process leads to a composition gradient of the membrane, which mainly contains metal hydroxides in its interior surface. In general, the composition gradient is characterized by EDS, and it has been widely reported in many other works.\(^15\)–\(^17\)–\(^18\)

In contrast to iron, the spatial distribution of calcium remains quite stable in the aging process over many hours. This contrast could be explained by the solubility product constant as well. As the constant of calcium hydroxide is 10 orders of magnitude larger than that of ferrous hydroxide, the calcium ions are far less sensitive to the entered hydroxyl ions than the ferrous ions. Therefore, the diffusion and precipitation behavior of calcium is obviously different from iron and its redistribution is nearly unnoticeable. The present research reports for the first time such a difference in a mixture-seed chemical garden reaction, but some related clues can be found at least in one paper.
published in 2011. In that paper, the authors stated that the wafer seed of manganese chloride and the wafer seed of cobalt chloride became empty or hollow at the end of their respective chemical garden reaction, whereas this phenomenon is not mentioned in the calcium chloride reaction. The nature of the hollow iron shell would be almost the same with manganese and cobalt because their solubility product constants are in the same level. In the present research, the gradual formation of manganese and cobalt because their solubility product constants are in the same level. In the present research, the gradual formation of hollow iron shell is directly recorded in the XRF movie. It proves that the formation mechanism is dominated by the metal ion’s chemical property rather than fluid convection because the big swelling shell is still fully filled with calcium. This also would explain the reason why calcium structures grow faster than iron structures even if these two elements share the same tubules. During the tubular growth, when ferrous ions are ejected or pumped upward, they are more likely to be trapped and exhausted by the diffusing hydroxyl ions. As a result, the tubular growth is always guided by calcium structures.

To study how one can synthesize new composite materials via the chemical garden route, in many cases people need to quantitatively know the composition or concentration change at different parts in the reaction. The XRF movie can provide such quantitative information. It can generate plenty of time-resolved localized XRF spectra, which reflect the element composition within a microregion in a specific time interval. For example, in Figure 4, two regions are defined. Region C is at the boundary of the big swell, and region D is inside the swell. Many time-resolved XRF spectra of C and D have been collected. Some of them are displayed in Figure S1 in Supporting Information. The localized XRF spectra taken from different hours are clearly different, indicating the respective composition change at C and D. It is possible to calculate the exact element concentration by carefully analyzing the time-resolved localized XRF spectra, but generally this requires much effort in modeling the sample matrix and fitting the spectra. This time, the intensity of XRF peaks is just used to represent the amount of the corresponding element. This semiquantitative approximation is also broadly adopted in many other XRF imaging studies. Figure 5 shows the time-dependent change of calcium intensity and iron intensity at C and D, respectively. As shown in the figure, the intensity of iron increases at C, which is negatively correlated to its intensity decreasing at D. In contrast, the calcium intensity remains quite stable for all 15 h at either C or D. This semiquantitative analysis in Figure 5 agrees with our impression on the sequential movie frames in Figure 4.

The XRF movie also records the rapid tubular growth at the early stage. To see this, the frame rate of the movie is adjusted to 1 frame/3 min. This 3 min-time-resolution movie is generated from the same database of all detected XRF signals. Some key movie frames of iron are displayed in Figure S2 in Supporting Information, showing the growth process of the specific tubules containing iron. In this experiment, because the detected calcium XRF intensity is not so strong, it is difficult to collect sufficient statistics every 3 min to generate a clear frame of the 3 min-time-resolution movie. However, this technical barrier is easily removed by optimizing the X-ray movie instrument in future, mainly by increasing the incident X-ray intensity. Thereafter, the growth rate of calcium tubules and iron tubules can be directly compared by XRF intensity recorded in the movie. This will be more reliable than looking at the appearance color of tubules in an optical microscopy video. In the XRF movie observation, if some necessary data processing parameters have been set in advance, the XRF movie frames can be sequentially generated parallel to the chemical garden reaction. Thus, the XRF movie observation is a realtime observation.

In this research, the chemical garden reaction is confined in a quasi-two-dimensional (quasi-2D) Hele-Shaw cell rather than in a 3D test tube. This is convenient for X-ray observation because generally X-rays cannot penetrate into or escape from deep parts of solutions. This reduction in dimensionality is also adopted in some other works for ease of observation and discussion. Though most chemical garden reactions are 3D, the observation of quasi-2D reactions can still help to construct an approximated model to understand the universal reaction mechanism. It should be realized that the Hele-Shaw cell in this research is vertically placed. It does not eliminate the buoyancy force and consequently the formed tubular structure is the same as with general chemical garden structures. In some other works, the Hele-Shaw cell is horizontally placed and the vertical growth of chemical garden structures is restricted; therefore, some special spiral patterns are finally formed. It should be noted that the chemical garden reactions discussed in this research are different from those horizontal reactions.

CONCLUSIONS

Instead of seeding only one species of metal salt in a chemical garden reaction, the present research used a mixture of two metal salts, which were calcium chloride and ferrous sulfate heptahydrate. It was found that the upward growth of calcium structures was obviously faster than iron structures even though these two elements shared the same tubules in the same reaction. In addition, during the subsequent hours-long aging process, iron diffused to the boundary of a big swell formed around the initial seed position, forming an empty iron shell at the end of the reaction. In contrast, calcium was homogeneously dispersed inside the shell, with no obvious change in distribution over time. The difference in the growth rate and diffusion behavior could be explained by the different solubility product constants of calcium and iron in their hydroxides. As a result, a macroscopic diversity of color and element composition occurred in the final self-organized chemical garden structures, implying a possibility of purifying elements or synthesizing gradient composites via the chemical garden route in future.

The discovery in this research relied on the use of the XRF movie technique. It can reveal the nature of element species and monitor their spatiotemporal change during the reaction. Moreover, the X-ray movie technique can provide plenty of time-resolved XRF spectra for microregion analysis, which semiquantitatively reflects changes in composition and concentration at different parts. In short, the X-ray movie technique provides much information on chemical composition, which cannot be analyzed by an optical microscopy video. Therefore, the technique is immensely helpful in understanding the stagewise formation process of chemical garden structures. Nowadays, to seek material applications for the chemical garden, more and more chemicals are being introduced into the reaction. The use of XRF movies will be an indispensable realtime characterization technique for the observation of diffusing elements in such reactions.
The chemical garden experiment is performed in a Hele-Shaw cell, which is prepared by covering the upper surface of a shallow polystyrene container with a polyester thin film. The depth of the container is 0.5 mm. The thickness of the thin film is 50 μm. The operation of attaching the thin film has to be done very carefully to ensure the film is perfectly flat and parallel to the bottom surface of the container. In the experiment, the seed of the chemical garden is placed in the container prior to attaching the thin film. After attaching, the cell is placed vertically. The chemical garden reaction is triggered by injecting the sodium silicate solution into the cell from the cell’s upper edge. The dimension of the Hele-Shaw cell is 30 mm (H) × 15 mm (V).

In this research, the seed of the chemical garden is a mixture of calcium chloride and ferrous sulfate heptahydrate. The mass ratio of these two salts is 1:1. They are mixed and ground into fine powders in a mortar, and then the powders are pressed into a 0.5 mm thick wafer. The chemical garden seed is a square of approximately 1.5 mm × 1.5 mm, which is cut from the wafer. The color of the seed is pale yellow. The aqueous sodium silicate solution used in this research is diluted from a commercial concentrated solution (55 wt % Na2SiO3). The mass ratio of the commercial solution to the distilled water is 1:2.

The growth of the chemical garden and the subsequent aging process is observed by a real-time XRF movie. The technical details of the XRF movie have been described in another work.37 The Hele-Shaw cell is fixed on the sample holder. Because one surface of the Hele-Shaw cell is made of thin polystyrene, another surface of the cell, which is prepared by covering the upper surface of a thin film, fluoresces X-rays can escape from it. The observation area of the XRF movie is approximately 7 mm × 15 mm (V), which is mainly limited by the size of the incident X-ray beam. The spatial resolution is better than 100 μm.

The schematic illustration of the Hele-Shaw cell under XRF movie observation is shown in Figure 1.
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