Magnetic-Field-Induced Painting-Out of Precipitation Bands of Mn–Fe-Based Prussian Blue Analogues in Water–Glass Gels

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ABSTRACT: The effect of magnetic fields on the precipitation patterns of Mn–Fe-based Prussian blue analogues in water–glass gels was studied using X-ray fluorescence and X-ray absorption near-edge structure spectroscopies. Three sets of two glass tubes, A, B, and C, were prepared using 1.20 M Mn\(^{2+}\)/0.24 M [Fe(CN)\(_6\)]\(^{3-}\), 0.60 M Mn\(^{2+}\)/0.12 M [Fe(CN)\(_6\)]\(^{3-}\), and 0.30 M Mn\(^{2+}\)/0.06 M [Fe(CN)\(_6\)]\(^{3-}\) solutions, respectively. From each of these sets, one tube was subjected to a magnetic field of 0.5 T, whereas the other was not. The magnetic field barely affected the Liesegang bands in the tube from Set A, but there were noticeable differences in the tubes from sets B and C, where (1) the amounts of electrolytes were small, (2) the dominant Mn species was [Mn(H\(_2\)O)\(_6\)]\(^{2+}\), and (3) there was stochasticity of the band formation. In these regions, the magnetic field painted out the spaces between the precipitation bands, even enhancing the formation of additional bands.

INTRODUCTION

Precipitation reactions coupled with diffusion can spontaneously create complex product structures with interesting features.\(^1,2\) Among such structures, some of the most well-known structures are the Liesegang bands,\(^3,4\) that is, the periodic precipitate bands of the slightly soluble inorganic compounds that are mostly present in gel media and named after R. E. Liesegang, who discovered them in the late 19th century.\(^3\) In recent decades, Liesegang bands have again become the subject of intense research interest partially because they can be applied to the rational design of systems that form functional devices in micro- and nanoscale through self-organization processes.\(^5\)

Practical applications of Liesegang bands in materials science/engineering require a deeper understanding of how precipitation bands are influenced by extrinsic factors that can be controlled from outside the gels. Considerable effort has already been expended on investigating the effects of extrinsic factors such as temperature gradient,\(^6\) visible-light,\(^7\) microwave radiation,\(^8\) and gravitational\(^9\) and electric fields\(^10,11\) on band formation. Different extrinsic factors influence Liesegang bands in different ways. For example, the gravitational force occasionally reduces the space between Liesegang bands,\(^9\) and the time-dependent electric current can partially control both band spacing and band width.\(^11\)

Magnetic fields can also influence the self-organization patterns that are formed by various reaction–diffusion processes,\(^2,12–14\) even if the existing magnetic interactions are relatively weak. For example, Boga et al. found that the magnetic fields cause a change of several orders of magnitude in the velocity of the propagating reaction-front in cobalt-catalyzed auto-oxidation of benzaldehyde in glacial acetic acid.\(^1,2\) Nevertheless, over the decades, there have been very few studies on the effect of a magnetic field on Liesegang bands. In 2014, Zhao et al.\(^13\) found that a static magnetic field (0.4 T) could change the geometric morphologies of the Liesegang bands of silver dendrite observed on the surface of a liquid. Very recently, Ibrahim et al.\(^14\) studied the magnetic-field-induced effect on the fractal structures of silver dendrite and discussed the differences between their results and those of Zhao et al.\(^13\) To the best of our knowledge, the effect of a magnetic field on the Liesegang bands that form in the gel media (i.e., the traditional Liesegang bands) has not been reported yet.

In the present study, the magnetic-field-induced effect on the periodic precipitation bands (including Liesegang bands) of Mn–Fe-based Prussian blue analogues (Mn–Fe PBAs) formed in water–glass gels has been examined. Mn–Fe PBAs form Liesegang bands in a water–glass gel,\(^15\) and their precipitation bands exhibit interesting gel-state dependencies.\(^1,6\) The observed magnetic-field-induced changes were investigated by X-ray fluorescence (XRF) and X-ray absorption near-edge
structure (XANES) spectroscopies, as described in previous studies, to monitor the variations in the Mn and Fe elemental distributions (XRF) and to study the local atomic structures around the Mn atoms in the Mn–Fe PBAs (XANES). The local structure around the Fe atoms in the Mn–Fe PBAs was found to be Fe(CN)$_6^{3-}$.

**RESULTS AND DISCUSSION**

**Visually Observed Effect of a Magnetic Field on Periodic Bands.** Figure 1 shows the images of the developed periodic bands for the three sets A, B, and C of two tubes each, for which the preparation conditions are summarized in Table 1, after one of which was subjected to a static magnetic field of 0.5 T and one was not (0 T). Photographs of sets A, B, and C were captured at 211, 359, and 285 h after the addition of the outer electrolyte sols, respectively.

![Figure 1](image)

**Figure 1.** Captured images of the developed periodic bands in sets (a) A, (b) B, and (c) C without (0 T) and with a magnetic field (0.5 T). The images of sets A, B, and C were captured at 211, 359, and 285 h after the addition of the outer electrolyte sols, respectively.

**Table 1. Preparation Conditions for the Tube Sets A, B, and C**

|                         | for the outer electrolyte gel | for the inner electrolyte gel |
|-------------------------|------------------------------|-----------------------------|
| **Mn**$^{2+}$ (M)       | W.G. (mass %)                | [Fe(CN)$_6^{3-}$] W.G. (mass %) |
| A                       | 1.20                         | 0.24                        | 13.8                        |
| B                       | 0.60                         | 0.12                        | 13.8                        |
| C                       | 0.30                         | 0.06                        | 13.8                        |

“Initial concentrations of Mn$^{2+}$ and initial percentages by mass of water–glass (W.G.) for the outer electrolyte gel, and initial concentrations of [Fe(CN)$_6^{3-}$] and initial percentages by mass of W.G. for the inner electrolyte gel.”

As observed in a previous study, relatively sharp, periodic, brown bands formed in the inner electrolyte gel of the set A tube had not been subjected to the magnetic field (Figure 1a). The precipitation bands were found to be very dependent on slight differences in the initial sol states because the bands formed through diffusion processes coupled with chemical reactions, with the inherent randomness that makes the resultant patterns highly sensitive to the initial conditions. Nevertheless, additional two re-experiments for the set A conditions (at 0 T, not shown here for simplicity) revealed that the numbers of discrete bands in the tubes were approximately equal (9 ± 2), and that the band locations $x_{11}$, $x_{12}$, ..., $x_{18}$ as acquired from the gel junction, always separated according to a constant ratio of $x_{11}/x = 1.064 ± 0.013$. In other words, the periodic bands in the set A tubes formed rather constantly and obeyed the spacing law $(x_{11}/x = \text{const})$, which is the one of the best-known scaling laws governing Liesegang bands. In addition, the value of $x_{11}/x = (1.06)$ is typical of the systems producing Liesegang bands ($1 < x_{11}/x < 1.5$) and is very close to that of Mn–Fe PBA systems in which the Liesegang bands form ($1 < x_{11}/x < 1.05$). These results show that the Mn–Fe PBA Liesegang bands in the set A tubes were more stable than expected.

As shown in Figure 1a, the 0.5 T magnetic field had very little influence on the formation of the Liesegang bands in the set A tubes. The additional two re-experiments performed for the set A conditions (not shown here for simplicity) revealed no difference in the band numbers or ratios of the band locations, regardless of whether the magnetic field was applied, within the inherent uncertainties described above. These results suggest that the magnetic-field-induced effect on the Liesegang bands of Mn–Fe PBAs is insignificant, at least, for the preparation conditions for set A.

In contrast, the precipitation patterns for the set B tubes exhibited significant changes as a result of the applied magnetic field (Figure 1b). Here, the 0.5 T magnetic field painted out the spaces between the bands and enhanced the formation of additional bands at the bottom, colorless area. These observations imply that the magnetic field activated the formation of Mn–Fe PBAs precipitates at their low-concentration regions (or “blank” regions).

Note that for set B (where the initial concentrations of the inner and outer electrolytes are half of those for set A; see Table 1), the periodic bands were minimal, and their bandwidths were relatively broad. Similar observations have already been reported for the precipitation bands of low-concentration regions in a Pb(NO$_3$)$_2$–KI system. Furthermore, a subsequent study of the Pb(NO$_3$)$_2$–KI system revealed that the probability of band formation and reproducibility of the band location become increasingly stochastic as the amount of electrolyte in the gels decreases. Thus, because the stochasticity in the set B tubes is expected to be higher than that in the set A tubes, the additional two re-experiments were again conducted for the set B conditions. The results are shown in Figure 2 (where set B-1 corresponds to set B in Figure 1b).

![Figure 2](image)

**Figure 2.** Captured images of the developed periodic bands in set B without (0 T) and with a magnetic field (0.5 T). The set B results in Figure 1b are reproduced as (a) set B-1 for comparison. Sets (b) B-2 and (c) B-3 were prepared under the same initial concentrations of both the electrolytes for checking the reproducibility, and images B-2 and B-3 were captured at 209 and 213 h after the addition of the outer electrolyte sols, respectively.
As shown in Figure 2, the three set B patterns for the tubes that had not been subjected to the magnetic field (0 T) were overall similar, but somewhat different from one another, particularly in terms of the band thickness, which probably reflected the increasing stochasticity. Nevertheless, the 0.5 T magnetic field always painted out the spaces between the bands and even occasionally enhanced the formation of additional bands, despite the stochastic properties observed in the 0 T results. Thus, Figure 2 strongly suggests that the magnetic-field-induced, painting-out effect is not spurious but certainly exists beyond inherent stochastic uncertainties.

Figure 3 shows the spatiotemporal evolution of the set B-2 patterns. The elapsed time after the addition of the outer electrolyte sols is indicated at the bottom of each image. Initially, a short brown band was formed near the gel junction and propagated downward through the tubes. After 18 h, when the continuous band had propagated to ∼8 mm below the junction to form a turbid zone, a relatively thin band (indicated by yellow arrows in Figure 3) was observed at the reaction-front (∼14 mm below). Until this time, no marked magnetic effect was observed in the set B-2 patterns. After 42 h, both the reaction-front and the continuous band were further extended downward, and other considerably thin, discrete bands were produced between the two bands. After 66 h, the reaction-front band reached the bottom of the tubes. Unlike the case of the radical reaction system, no significant magnetic-field effect on the propagation of the reaction-front was observed. Meanwhile, thin periodic bands were newly formed between the reaction-front and the turbid zone around this elapsed time. Up to ∼160 h, while the positions of the periodic bands were almost maintained, the color of these bands continued to darken and the band spaces were gradually painted out, suggesting the growth of Mn–Fe PBA particles over wide regions. From ∼70 h, the 0.5 T magnetic force noticeably enhanced these darkening and painting-out phenomena (see images taken at 66, 90, and 162 h). At ∼200 h, the patterns were well-developed, showing almost no change over time, as seen in the image taken at 209 h.

Modern theories have explained the formation of Liesegang bands as an interplay among several elementary events, including diffusion, reaction, supersaturation, nucleation, formation of homogeneous colloidal sols, and ripening. As described above, the time-dependence of the set B-2 patterns strongly suggests that the magnetic-field-induced, painting-out effect is closely related to particle growth and ripening, which occur gradually and become significant at later stages in band formation.

A similar painting-out effect was also observed for the set C patterns (Figure 1c). However, the effect observed for set C was somewhat more obscure than that observed for set B. Furthermore, the lower electrolyte concentrations of set C (for which the initial concentrations of the inner and outer electrolytes are half of those of set B; see Table 1) caused the band thickness to markedly decrease along with a further increase in the bandwidths, suggesting an increase in the stochasticity. Thus, as the small amounts of both the Mn and Fe species disturbed the accurate X-ray spectroscopic measurements and seemed to increase stochasticity, it was difficult to elucidate the effect of magnetic field. Consequently, we have only focused on the results from set B in the following sections.

Mn and Fe Kα Intensity Distributions with/without Magnetic Field. The Mn and Fe Kα intensity distributions of the fully developed bands in the tubes of set B (B-1 in Figure 2a; at ∼360 h after the addition of the outer electrolyte sols), which were either subjected or not subjected to a magnetic field (0.5 T), are shown in Figure 4. The horizontal axis in Figure 4 indicates the distance from the gel junction (X). Its value is positive at the bottom of the tubes. The vertical axis is the relative XRF intensity, where the Fe Kα intensity distributions of the fully developed bands in the tubes of set B (B-1 in Figure 2a; at ∼360 h after the addition of the outer electrolyte sols) were set to 1, according to the procedure used in a previous study. These XRF distributions have been compared with the positions of the brown bands by displaying the corresponding images at the top of this figure.

![Figure 3. Spatiotemporal evolution of set B-2 patterns. Elapsed time after the addition of the outer electrolyte sols is indicated at the bottom of each image. Yellow arrows indicate the positions of the propagating reaction-front.](https://example.com/image1)

![Figure 4. Mn and Fe Kα intensity distributions of the fully developed bands in set B tubes subjected/not subjected to the 0.5 T magnetic field. The distributions were obtained at ∼360 h after the addition of the outer electrolyte sols. Captured images are displayed at the top of the figure to facilitate a comparison of the XRF distributions with the positions of the brown region. The vertical dashed line and hatched area serve as guides.](https://example.com/image2)
Figure 4 shows that the effect of the magnetic field on the XRF distribution was minimal. Particularly, in the turbid zone (0 ≤ X < 15 mm), there was no marked difference in either the Mn or Fe Kα intensity distributions beyond the experimental uncertainties. However, for a periodic band zone (X ≥ 15 mm) in which the magnetic-field-induced paint-out effect was visually observed, the 0.5 T magnetic field noticeably increased both the Mn and Fe Kα intensities. This finding suggests that the magnetic field slightly, but noticeably, enhanced the introduction of Mn²⁺-related ions into the periodic band zone to stimulate the formation of Mn–Fe PBA precipitates there. This suggestion is consistent with the visual observations in Figures 1b and 2.

It should also be noted that the XRF intensities of the periodic band zone (magnetic-field-sensitive zone) were significantly weaker than those in the turbid zone (magnetic-field-insensitive zone), as already found for similar systems. This result suggests that the magnetic field influences the area in which the amounts of Mn–Fe PBAs and related electrolytes are relatively small, although such concentration effects were less noticeable to the naked eye.

**Mn K-Edge XANES with/without Magnetic Field.** The Mn K-edge XANES spectra of the fully developed bands in the tubes of set B (B-1 in Figure 2a; ~970 h after the addition of the outer electrolyte sols) subjected/not subjected to the 0.5 T magnetic field are shown in Figure 5. The spectra were obtained in the fluorescence mode because the tubes were too thick (4.0 mm diameter) to allow the use of the transmission mode. As was noted in previous studies, the measured fluorescence (XRF) intensities were weak enough to avoid the self-absorption effects. The Mn K-edge XANES spectra were recorded at several sampling positions, indicated by bars in the images in the right-hand panels of Figure 5. These positions are labeled, for example, “1.5 mm” (1.5 mm below the junction: X = 1.5 mm).

With the exception of X = 19.5 mm (in the periodic band zone), the Mn XANES spectra (entirely within the turbid zone) were almost the same and mostly independent of both the measuring positions and the application of the magnetic field. This result suggests that the local structures and symmetries of Mn–Fe PBAs in the turbid zone were highly uniform and stable when subjected to the magnetic field (at least, up to 0.5 T). A possible local structure of the Mn–Fe PBAs is discussed later.

**Figure 5.** Mn K-edge XANES spectra of the fully developed bands in the set B tubes subjected/not subjected to the 0.5 T magnetic field. XANES spectra were obtained at ~970 h after the addition of the outer electrolyte sols. The positions at which the XANES spectra were recorded are shown in the right-hand panel.

**Figure 6a** compares the 19.5 mm XANES spectrum with the Mn K-edge XANES spectrum with the Mn(NO₃)₂·6H₂O, obtained by Hayashi and Abe. As is evident from this figure, the 19.5 mm spectrum is almost identical to the XANES spectrum for Mn(NO₃)₂·6H₂O. This finding indicates that the local structure around the Mn atoms in the periodic band zone, where the 19.5 mm spectrum was observed, was almost the same as that of the hydrated Mn²⁺ ions, [Mn(H₂O)₆]²⁺, where the Mn²⁺ ions are surrounded by six O atoms with an octahedral geometry. This result strongly suggests that, in the periodic band zone, although the brown bands are certainly visible by the naked eye, the amount of Mn–Fe PBAs is very small and the colorless [Mn(H₂O)₆]²⁺ ions are dominant. This finding is consistent with the XRF results that point to the magnetic field enhancing the introduction of Mn²⁺-related ions in the periodic band zone. The apparent lack of Mn–Fe PBA contributions is possibly because of the small amount of [Fe(CN)₆]³⁻ ions (and, therefore, Mn–Fe PBAs); the initial concentration of [Fe(CN)₆]³⁻ is one-fifth of that of Mn²⁺ (see Table 1). The local structures of the few Mn–Fe PBAs in the periodic band zone have not yet been established. The determination of these structures will be an interesting future task.
The turbid-zone XANES spectra obtained in the present study, of which the 1.5 mm spectrum (0.5 T) is shown in Figure 6b as an example, are very similar to the turbid-zone spectra that were previously measured for similar systems. The XANES spectrum is characterized by a white line (∼1.6 at 6552 eV), a second peak at 6560 eV, and a subsequent shallow valley (∼0.85 at 6575 eV). As was performed previously, the turbid-zone XANES spectrum in Figure 6b was analyzed by trial-and-error linear combinations of the two theoretical profiles of Mn(NCFe)2O4K2 and MnO6S4. Both profiles were determined in advance using the FEFF code for model clusters. The Mn(NCFe)2O4K2 profile was calculated using a model for Mn−Fe PBAs, in which the Mn atom is surrounded by two Fe(CN)6 groups and four O atoms (conceivably as H2O molecules), with two K+ ions inserted into the crystal lattice. The MnO6S4 profile was obtained from a model of aqueous Mn2+ ions, in which four H2O molecules were replaced by four OS moieties (conceivably as SO42− ions, the anion of the outer electrolyte).

Liquid chromatography (LC) in Figure 6b, which consists of Mn(NCFe)2O4K2 and MnO6S4 in the ratio 0.55:0.45 (11:9), produced the result with the best fit to the 1.5 mm spectrum. The LC profile reproduced the overall spectral features and white-line intensity, and the values of 0.55 and 0.45 were the same as those obtained in a previous study. These findings suggest that the local structure around Mn in the turbid zone is basically the same as that addressed in a previous study and is related to the mixture of Mn(NCFe)2O4K2-type Mn−Fe PBAs and hydrated Mn2+ ions that are partially coordinated by SO42− ions, where the ratio of Mn−Fe PBAs to Mn2+ ions is 11:9 (approximately 1:1).

Cause of Magnetic-Field-Induced, Painting-Out Effect. Magnetic fields have already been used as one of the external force fields for selectively separating colloidal particles from liquids (see Figure 7). Magnetophoresis has also been applied to evaluate the magnetic susceptibility of several types of particles, including magnetic particles, ion-labeled biological particles, and polystyrene particles in paramagnetic solvents. In these analytical magnetophoresis studies, the magnetic-field-induced effect has been assumed to be as follows. When the magnetic forces act perpendicular to the flow axis to drive magnetically susceptible particles toward the interpolar gap(s) (this is applicable in our case; see Figure 8), those particles with a high magnetic susceptibility, such as those including a predominance of [Mn(H2O)6]2+ ions, are attracted by the magnetic forces and are easily deposited on the zone in the interpolar gap. In contrast, those particles with a low magnetic susceptibility, such as those including a predominance of [Fe(CN)6]3− ions, are less attracted by the magnetic forces. Thus, if the magnetic susceptibility of the particles is different, magnetophoretic separation is possible, as schematically shown in Figure 7.

The above view of magnetophoresis suggests that a possible cause of the magnetic effect currently observed could be subtle but significant magnetic holding of Mn2+−related particles (including Mn(NCFe)2O4K2-type Mn−Fe PBAs) against diffusive flow to the bottom of tubes. Such a holding would be significant to the relatively large (colloidal size) paramagnetic particles. Hence, the magnetic holding effect is expected to become apparent at later stages of band formation, where many Mn−Fe PBA particles ripen.

By assuming the (subtle) magnetic holding effect, the observed painting-out effect can be interpreted as follows.
throughout the inner gel, therefore painting out the spaces between the periodic bands and occasionally leading to the formation of additional bands.

In our interpretation, the key factor to produce the painting-out effect is the stochasticity accompanied with lower electrolyte concentrations, and 0.5 T magnetic field is a cofactor. Therefore, painting-out does not necessarily require the use of a magnetic field. For example, the painting-out effect occurs when some impurities are introduced into the inner gels to increase the heterogeneous nucleation. In fact, for a CuCl2-K2CrO4 system, Lagzi observed that the addition of a small amount of gelatin (impurity) into agarose gel (supporting gel) produced similar effects, that is, the spaces between the CuCrO4 Liesegang bands narrowed, and the length of the turbid zone increased.30

In the study of magnetic effects, the magnetic field intensity and direction dependencies of systems are generally interesting subjects. In fact, such dependencies were investigated for pattern formation in silver dendrite systems.13,14 Unfortunately, because the painting-out effect observed here was basically minimal and considerably stochastic, it is difficult to accurately examine these dependencies using the present setup. Details of the dependencies need to be investigated further using a high-power, superconducting electromagnet.

■ CONCLUSIONS

The magnetic-field-induced effect on the Mn–Fe PBA precipitation bands in water–glass gels can be summarized as follows. This effect is basically minimal. In fact, the turbid zone of set B tubes, in which relatively large amounts of Mn–Fe PBAs [for which the dominant local structure is possibly Mn(NCFe)2O4K2] occur uniformly, was insensitive to the magnetic field. Furthermore, the typical Liesegang bands of the Mn–Fe PBAs of set A tubes, which were formed from concentrated, initial solutions, were also barely influenced by the magnetic field. Nevertheless, the magnetic-field-induced effect was certainly noticeable in those regions in which (1) the amounts of both the inner and outer electrolytes were small, (2) the dominant Mn species was [Mn(H2O)6]2+, and (3) stochasticity was observed in the precipitation pattern formation. For such regions in the gels, the magnetic field painted out the spaces between the precipitation bands for ~70 h after the addition of the outer electrolyte sol, even enhancing the formation of additional bands. A possible cause of this effect is the subtle but significant magnetic holding of the Mn2+-related particles including Mn(NCFe)3O4K2-type Mn–Fe PBAs and the resultant increase in the coagulation of Mn–Fe PBAs.

Thus, we demonstrated that a static 0.5 T magnetic field can be an independent parameter that can change the precipitation patterns in gels, even in the classical setups employed for Liesegang band studies. Our results not only provide an insight into the control and engineering of precipitate structures of functional Mn–Fe PBAs in future self-organization processes.

■ MATERIALS AND METHODS

Materials. Analytical reagent-grade K3[Fe(CN)6]3− and MnSO4·H2O were obtained from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and used as it is without further purification. Acetic acid (1.00 M) and sodium silicate solution [water–glass (or liquid–glass), 52–57% assay, 2.06–2.31 SiO2/Na2O mole ratio] were also acquired from Wako Pure Chemical Industries Ltd. All aqueous solutions were prepared using deionized water.

Magnets. A magnetic field was generated by assembling a pair of neodymium–iron–boron (Nd–Fe–B) magnets (EM-112150P, Echo Electronics Co., Ltd., Japan), which conducted magnetic flux into the interpolar gap. The diameter and thickness of each magnet was 50 and 16 mm, respectively. The magnetic field intensity was 0.5 T for a gap width of 11 mm.

Tube Preparation. Quartz glass tubes containing the inner and outer electrolytes were prepared as follows. For the inner electrolyte ([Fe(CN)6]3−), 1.6 g of water–glass was dissolved in deionized water (10 mL) to prepare 13.8 mass % of sol. Then, appropriate amounts of K3[Fe(CN)6]3− were added to deionized water (5 mL) to prepare 0.06, 0.12, and 0.24 M [Fe(CN)6]3− solutions. The sol and [Fe(CN)6]3− solutions were mixed, after which acetic acid was added (16 mL, 0.53 M). The resulting water–glass sols were stirred continuously for 20 s and then transferred to quartz glass tubes with a length of 80 mm, inner diameter of 4.0 mm, and thickness of 0.010 mm (Mark-tube, Hilgenberg GmbH, Germany) using a Pasteur pipette. The sol solidified to a gel within 10 min. Its height in the tubes was ~30 mm.

For the outer electrolyte (Mn2+), 1.2 or 1.4 g of water–glass was dissolved in deionized water (10 mL) to prepare a 10.7 or 12.3 mass % sol. Then, appropriate amounts of MnSO4·H2O were added to deionized water (5 mL) to prepare 0.30, 0.60, or 1.20 M Mn2+ solutions. The sol and Mn2+ solutions were mixed, after which acetic acid was added (16 mL, 0.53 M). The resulting water–glass sols were stirred continuously for 20 s and then poured over the inner electrolyte ([Fe(CN)6]3−) gel using a Pasteur pipette. The outer electrolyte (Mn2+) sol solidified to a gel within 10 min. Its height in the tube was ~20 mm. After solidification of the outer electrolyte gel, approximately 1 mL of deionized water was poured on top of the gels to prevent them from drying and cracking. The tubes were then closed with silicone rubber stoppers.

Three sets of the two tubes, A, B, and C, for which the preparation conditions are summarized in Table 1, were used in the current experiments. The two tubes in each set were prepared using the same inner and outer electrolyte sols as those used with and without the magnetic field. In these preparations, the ratio of the outer electrolyte concentration to the inner electrolyte concentration was set to 5. This is the ratio under which the Liesegang bands had formed in a previous study.15 It should be noted that dense water–glass gels tend to produce genuine Mn–Fe PBA Liesegang bands,16 but the coupling of concentrated electrolyte solutions and dense water–glass often leads to rapid (<60 s) and nonuniform gelation. Therefore, the 13.8 mass % of the water–glass sol was not employed for the outer electrolyte ([Mn2+ ≥ 0.30 M], whereas the 10.7 mass % water–glass was applied for the 1.20 M Mn2+ solution in set A.

For each set, one tube was placed in a 0.5 T magnetic field perpendicular to the diffusive flow axis of the outer electrolyte for ≥14 days and then mounted on a fabricated holder [acrylic resin, 80 × 35 × 10 mm (h × w × d)] together with the other “control” tube (that had not been subjected to the magnetic field) for monitoring and XRF/XANES measurements, as shown schematically in Figure 8. The height and width of the holders were graduated in millimeter to enable easy measurements of the band positions in the tubes.
Monitoring of Precipitation Patterns. After the addition of the outer electrolyte sol to the inner electrolyte gel, Mn$^{2+}$ ions diffused into the inner electrolyte gel and reacted with [Fe(CN)$_6$]$^{3-}$ to yield Mn–Fe PBAs. Consequently, brown bands were formed in the inner electrolyte gels, as shown in Figures 1–3. The patterns of the bands at room temperature (20 °C) were recorded for 40 days using a digital camera to take intermittent in situ XRF measurements for each tube set. The Mn K-edge XANES spectra of the developed bands (i.e., those exhibiting few further changes over time) in the tubes were also obtained. The patterns in sets A–C were well-developed after 210 h (9 days).

XRF Measurements. The laboratory XRF measurements were performed, as described in previous studies. A schematic representation of the setup is shown in Figure 8. As the excitation source, Cu Kα X-rays from an 18 kW X-ray generator (RU-300, Rigaku, Japan), operating at 40 kV and 106 mA, were used. These were focused within 0.5 mm in the horizontal direction by a SiO$_2$ (1011) Johannson-type crystal monochromator. The divergence of the X-rays in the vertical direction was limited by a homemade collimator with a 0.5 mm slit. Two sample tubes of each set (subjected/not subjected to the magnetic field) in a holder were placed on a computer-controlled X–Z stage (XA05A-L2, Kohzu Precision, Japan). Of the two tubes, one was selected for the XRF measurements by moving the holder in the X direction and then in the Z directions in 1 mm steps. The XRF signals at each Z position were detected using a silicon PIN detector (XR-100CR, Amptek Inc., USA), for which the detection angle relative to the incident beam was set to 135°. The XRF signals were collected for 90 s at each Z point by a multichannel analyzer (MCA8000A, Amptek Inc., USA). The collection of a complete XRF distribution over 50 mm of the tube took ∼4500 s. After subtracting the background from the Mn and Fe Kα peaks, the integrated intensities of these peaks were used to obtain the Mn and Fe Kα distributions in the tubes. Furthermore, the overlap of Mn Kα and Fe Kα lines in the region containing both elements was corrected using a previously reported method. After the completion of these analyses, the other tube was selected for the XRF measurements by moving the holder in the X direction, after which the procedure was repeated. For each XRF measurement, the intensity of the incident X-rays was monitored by an ion chamber, with the variation within 2%.

XANES Measurements. XANES measurements for the Mn–Fe PbA gels were performed as described in previous studies. The XANES spectra at the Mn K-edge were collected at the BL-9C bending-magnet beamline at KEK-PF, High Energy Accelerator Research Organization, Tsukuba, Japan. The sample tubes, secured in their holder, were placed on a computer-controlled Z stage (ALV-102-HP, Chuo Precision Industrial, Japan). XANES spectra were collected at room temperature at 6500–6750 eV.

XANES measurements were conducted in fluorescence mode by placing a Lytle-type detector perpendicular to the incident beam. After approximating the spectra observed at 6450–6520 eV (the region before the Mn pre-edge) to be straight lines and subtracting this background component, the obtained XANES spectra were normalized by assuming that the average absorption coefficients for Mn would be the same at energies of 6700–6750 eV. Normalized XANES data were used to examine the local structures around the Mn atoms in the gels.

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