

## Growth of Mineral with Chemical Inhomogeneity under Surfactant Monolayer at Oil/Water Interface

Syuji Abe and Akihisa Shioi\*

Department of Chemistry and Chemical Engineering  
Yamagata University, Jonan 4-3-16, 992-8510 Japan  
Fax: 81-238-26-3414, e-mail: shioi@yz.yamagata-u.ac.jp

Solid solution with controlled shape and regulated chemical inhomogeneity was formed in a single chemical process. It takes advantages of biomimetic mineralization under surfactants monolayer and reaction-diffusion mechanism. Barium and strontium were supplied to surfactants adsorbed at oil/water interface through organic phase containing anionic surfactant. Cations thus supplied reacted with anion which was present under the oil/water interface. Solid solution grown under the interface exhibited well-regulated shape and chemical inhomogeneity. Conditions at which such minerals were formed and characteristics of formed solid solutions were discussed. We proposed a simple technique for obtaining minerals with controlled shape and chemical inhomogeneity.

Key words: oscillatory zoning, biomineralization, surfactant, solid solution, chemical inhomogeneity

### 1. INTRODUCTION

Many kinds of minerals are formed and utilized in creatures and in the earth crust. They often involve chemical inhomogeneity with various length scales and/or exhibit well-organized shapes. In biological systems, a mechanism called biomineralization works to develop well-organized inorganic matters, and a biomimetic approach mimicking the mechanism is well investigated [1]. While, well regulated oscillations of chemical composition called oscillatory zoning appears in some minerals quite independently of creatures or biological systems [2]. Although many attempts for theoretical understanding are now in progress, nonlinear reaction-diffusion mechanisms seem to operate for the pattern formation [3].

Putnis and coworkers [2] succeeded in formation of solid solution with oscillatory change in chemical composition. They used combination of slow rate of ion diffusion in gels with chemical reaction. Regulated oscillatory zoning develops along radial direction of globular particles. If direction of ion diffusion is restricted along one dimensional axis, distribution of chemical composition may appear along the particular axis. The control of direction of ion diffusion can be achieved by an idea based on biomineralization.

In this work, we propose a simple chemical system for formation of minerals with well-organized shape and regulated chemical inhomogeneity. The proposed process is accomplished only by a system which takes advantages of biomineralization and reaction-diffusion mechanisms. Several experiments were performed, and we obtained solid-solutions with organized shape and chemical inhomogeneity.

### 2. EXPERIMENTS

Figure 1 shows our experimental setup. Organic phase contains anionic surfactant, sodium bis(2-ethylhexyl) sulfosuccinate (AOT). Two kinds of aqueous phases were prepared. One contains  $\text{BaCl}_2$  and  $\text{SrCl}_2$ , and another includes  $\text{Na}_2\text{SO}_4$ . After both aqueous phases were filled separately, organic phase was gently poured onto them. AOT extract cations from an aqueous phase and transport them to the interface on another aqueous phase.  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  come to the interface through organic phase and react with  $\text{SO}_4^{2-}$ . Thus,  $(\text{Ba,Sr})\text{SO}_4$  solid solutions grow under AOT monolayer or in the vicinity of the interface. Solutions near the interface containing the white layer were sucked by a pipette, and formed solid was separated by a membrane filter with pore size  $0.1 \mu\text{m}$ . Solid material thus separated was washed by a large amount of ethanol and water to remove AOT and excess electrolytes. After that, obtained solid was dried in the air. Scanning electron microscope and electron probe X-ray microanalyzer were used for characterization of obtained material.

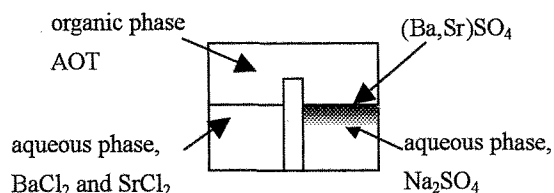


Figure 1 Schematic representation of experimental setup. Area of interfaces are  $38\text{cm}^2$  for  $\text{Na}_2\text{SO}_4$ -containing phase and  $19\text{cm}^2$  for  $\text{BaCl}_2$ ,  $\text{SrCl}_2$ -containing phase. Volumes of aqueous phases are  $20\text{cm}^3$  for  $\text{Na}_2\text{SO}_4$ -containing phase and  $10\text{cm}^3$  for  $\text{BaCl}_2$ ,  $\text{SrCl}_2$ -containing phase. Volume of organic phase is  $50\text{cm}^3$ .

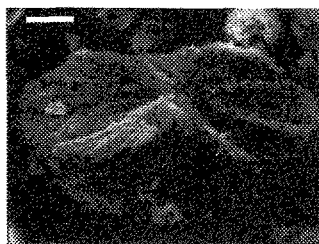
AOT was purchased from Tokyo Kasei and used as supplied. All of other chemicals were of reagent grade and provided from Kanto chemicals. N-heptane was used as organic solvent. Deionized water was used (ORGANO PRO-150). All of experiments were carried out at 25°C.

### 3. RESULTS

#### Oscillatory zoning

Putnis and coworkers [2] found the oscillatory zoning in  $(\text{Ba,Sr})\text{SO}_4$  solid solutions in silica gel. Two kinds of aqueous phases are set at both sides of the gel. One phase contains  $\text{BaCl}_2$  and  $\text{SrCl}_2$ , and another includes  $\text{Na}_2\text{SO}_4$ . Molecular diffusion into silica gel results in formation of  $(\text{Ba,Sr})\text{SO}_4$  solid solutions near central portion of the gel. Then, oscillatory change of Ba/Sr molar ratio is seen, and the length scale of the oscillatory change is in the order of micron. Oscillatory zoning is possibly delicate phenomenon since the essential dynamics are considered to be governed by nonlinear mechanics. Thus, trace amount of impurities may affect the zoning. We performed essentially the same experiment to check our chemicals. Gelatin was used instead of silica gel. An example of  $(\text{Ba,Sr})\text{SO}_4$  solid solution (particles) are shown in Figure 2 where distribution of Sr concentration is also shown. A particle with oscillatory zoning is clearly seen.

(a)



(b)



Figure 2 (a) SEM image of  $(\text{Ba,Sr})\text{SO}_4$  solid solution formed in gelatin. Initial concentration of  $\text{BaCl}_2$  and  $\text{SrCl}_2$  are 0.1 M in each. Concentration of  $\text{Na}_2\text{SO}_4$  is 0.3 M. Weight of gelatin in the gel is 0.12 g/cm<sup>3</sup>. Length of gelatin is 15 cm. Particles are formed about a week after the beginning of experiment. (b) Dot map of Sr distribution. Dotted portion is Sr-rich, and white one corresponds to Ba-rich (Sr-poor) region. Scale bar represents 10  $\mu\text{m}$ .

#### Mineral growth under AOT monolayer

For present purpose, oil-soluble ionic surfactant must be used since it strongly interacts with ions in aqueous phase. AOT is a typical oil soluble ionic surfactant, and structure of molecular assemblies and phase diagram are well investigated [5]. However, AOT monolayer at oil/water interface is not typical for mineral growth experiments. Thus, we checked whether or not AOT monolayer can control mineral growth by formation of calcium phosphate. It is well known that calcium phosphate exhibits crystal growth controlled by surfactant monolayer [1,4]. We prepared metastable supersaturated solution of calcium phosphate by mixing of  $\text{CaCl}_2$  and  $\text{KH}_2\text{PO}_4$ . Pouring AOT-containing n-heptane onto surface of the metastable solution, we obtained white thin layer of calcium phosphate. Figure 3 shows an example of formed mineral. Structures like pile of thin sheet can be seen. This type of structure was not formed in bulk solutions, and we can conclude that AOT monolayer controls crystal growth.

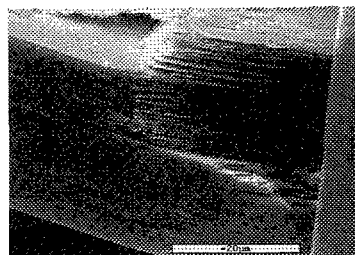


Figure 3 SEM image of calcium phosphate formed under AOT monolayer. Concentration of AOT in organic phase is 10 mM. Initial concentrations of  $\text{CaCl}_2$  and  $\text{KH}_2\text{PO}_4$  are 26 mM and 20 mM, respectively. Initial and final pH are 5.7 and 5.5, respectively. Scale bar represents 20  $\mu\text{m}$ .

#### Formation of solid solution under AOT monolayer

After pouring organic phase onto aqueous phases, nothing happens during a day. About a day after the beginning, white thin layer appeared at the interface on  $\text{Na}_2\text{SO}_4$ -containing phase, while nothing was seen on  $\text{BaCl}_2$ ,  $\text{SrCl}_2$ -containing phase. AOT is an anionic surfactant and preferentially extracts cations, i.e.,  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  move from the left to the right in Figure 1 and  $\text{Na}^+$  is transferred oppositely.  $\text{NaCl}$  formed at the left can be dissolved in the aqueous phase.  $(\text{Ba,Sr})\text{SO}_4$  appears as white thin layer at the right side.

Figures 4 and 5 show time-course of SEM-images of formed minerals. Concentrations of AOT are 0.2 M and 0.002 M, respectively. Concentrations of  $\text{BaCl}_2$ ,  $\text{SrCl}_2$  and  $\text{Na}_2\text{SO}_4$  are 0.1 M, 0.3 M and 0.1 M, respectively. Rate of mineral growth at the dilute condition ( $[\text{AOT}] = 0.002 \text{ M}$ ) was faster than that at the concentrated one ( $[\text{AOT}] = 0.2 \text{ M}$ ): After about 24 hrs from the beginning, fine particles are already formed at

the dilute condition, and the sizes are less than 1  $\mu\text{m}$ . On the contrary, for the concentrated case, amount of formed mineral is too little to observe it by SEM. At 48-50 hrs, we can see significant difference in the shapes between both cases. For the dilute one, fine particles are still observed. Although the whole shape looks like sheet or plate, they are composed of a large number of small particles. For the concentrated case, while, we can see sheet-like structure, the surface of which being flat and smooth. Sheet-like solid for the concentrated condition grows along the thickness. Then, structure along the thickness is like a bundle of pillars after 72 hrs. Concentration distribution of Ba and Sr are shown in Figure 4 as dot map. The distribution was homogeneous in most of cases at 50 hrs. However, inhomogeneity in Sr distribution appears after about 72 hrs. A slope of Sr-concentration is observed along the thickness. While, concentration of Ba looks almost independently of positions. (It should be noted that strontium is present even in Sr-poor region of Figure 4b. It just shows the presence of Sr-concentration gradient.) A sheet-like structure is also observed at the dilute case after sufficiently long time, but SEM image of the surface exhibits that it is composed of small particles. Inhomogeneous distribution of Sr concentration seems to be observed. However, it looks irregular, and the reproducibility was not satisfactorily. Concentration of Ba was homogeneously distributed. No time-dependency of chemical inhomogeneity was observed for time-resolved experiments for both AOT concentrations. Thus, it is unclear which surface is formed earlier, Sr-rich or Sr-poor surface.

Figure 6 shows results for  $[\text{BaCl}_2] = 0.1 \text{ M}$  and  $[\text{SrCl}_2] = 1.1 \text{ M}$ . 72 hrs has passed from the beginning of experiment. Both of species distribute inhomogeneously. Ba is concentrated on a planer surface, and Sr-concentration is larger in the side (part of bundle of pillars). Further, the SEM-image shows that the structure is multilayered, and we observed that the number of layers increased with increase in Sr-concentration. Therefore, we can consider that Ba and Sr are, respectively, contribute to form planer and pillar-like structures.

#### Results under equimolar conditions

The solid solutions with well-regulated shape and chemical inhomogeneity was successfully generated under uneven concentrations of  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$ . While, equimolar condition of  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  gives patterns of oscillatory zoning in the gel-using experiments. Figure 7 shows SEM images of equimolar experiments with AOT monolayer. Shapes of solid solutions are dependent on AOT concentrations. Formed mineral is composed of small particles in the dilute condition. While, it takes sheet-like structure in the concentrated case. This feature

is quite similar to results shown in Figures 4 and 5. Although irregular distributions of Sr concentration was obtained, the reproducibility was not satisfactorily.

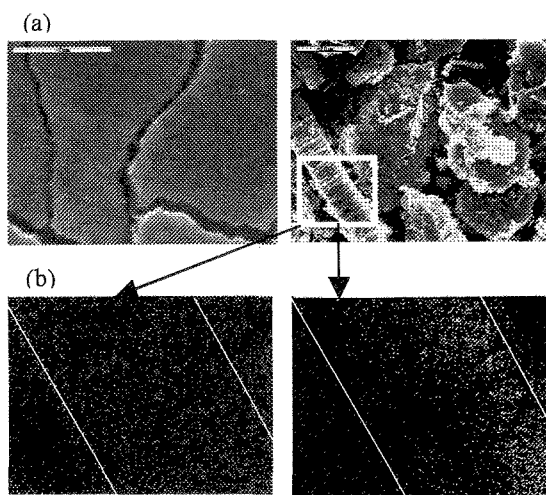


Figure 4 solid solution for  $[\text{AOT}] = 0.2 \text{ M}$ .

(a) SEM-image of  $(\text{Ba,Sr})\text{SO}_4$  solid solution. Time after the beginning of experiment is 48 hrs (left) and 72 hrs (right). Scale bars are 5  $\mu\text{m}$  (left) and 20  $\mu\text{m}$  (right). (b) Dot map of Ba (left) and Sr (right) for corresponding portion shown in Figure.

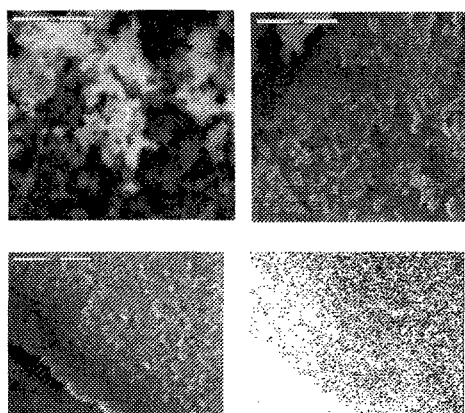


Figure 5 solid solution for  $[\text{AOT}] = 0.002 \text{ M}$ .

SEM-image of  $(\text{Ba,Sr})\text{SO}_4$  solid solution. Time after the beginning of experiment are 20 hrs (top left), 50 hrs (top right) and 96 hrs (bottom left). Scale bars are 5  $\mu\text{m}$  (top left), 10  $\mu\text{m}$  (top right) and 10  $\mu\text{m}$  (bottom left). Bottom right: Dot map of Sr corresponding to SEM-image of bottom left.

#### 4. DISCUSSIONS

Since diffusion coefficients of  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  in gel are not different so much, local concentrations of both ions near the central portion of the gel are almost equal to each other. Thus, particles with oscillatory zoning shown in Figure 2 can be formed when the local concentrations of both ions are similar to each other.

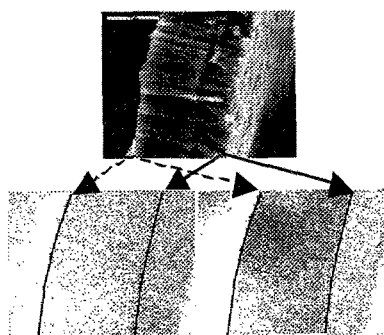


Figure 6 SEM-image (top) and dot map for  $[\text{BaCl}_2] = 0.1\text{M}$  and  $[\text{SrCl}_2] = 1.1\text{M}$ .  $[\text{Na}_2\text{SO}_4] = 0.1\text{M}$ , and  $[\text{AOT}] = 0.2\text{M}$ . Scale bar is  $5\ \mu\text{m}$ . bottom left: Ba-distribution. bottom right: Sr-distribution. Sample is of 72 hrs from the beginning of experiment.

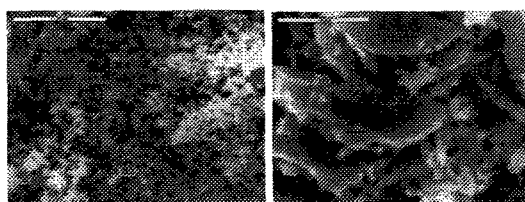


Figure 7 SEM-image for equimolar experiments. Left:  $[\text{AOT}] = 0.002\text{M}$ ,  $[\text{BaCl}_2] = [\text{SrCl}_2] = 0.3\text{M}$  and  $[\text{Na}_2\text{SO}_4] = 0.1\text{M}$ . Scale bar is  $10\ \mu\text{m}$ . Right:  $[\text{AOT}] = 0.2\text{M}$ ,  $[\text{BaCl}_2] = [\text{SrCl}_2] = 0.3\text{M}$  and  $[\text{Na}_2\text{SO}_4] = 0.1\text{M}$ . Scale bar is  $5\ \mu\text{m}$

AOT molecules form reverse micelles in n-heptane over the critical aggregates concentrations (cac). It is about  $5 \times 10^{-4}\ \text{M}$  [6] although it slightly depends on ion species and concentrations in coexisting aqueous phase. In our concentrated condition,  $[\text{AOT}] = 0.2\text{M}$ , almost all of cations are transported by reverse micelles. Harada et al. [6] reported distribution coefficient  $D$  of cations between AOT-containing organic phase and electrolytes solution. They found that  $D/[\text{AOT}]$  of  $\text{Ba}^{2+}$  is several through ten times larger than that of  $\text{Sr}^{2+}$ . Thus, mole flux of  $\text{Ba}^{2+}$  coming to the interface where the reaction proceeds is several through ten times as large as that of  $\text{Sr}^{2+}$  if concentrations in aqueous phase are equal to each other. To compensate the difference, it is required to keep initial concentration of  $\text{SrCl}_2$  several through ten times larger than that of  $\text{BaCl}_2$ . Conditions of  $[\text{BaCl}_2] = 0.1\ \text{M}$  and  $[\text{SrCl}_2] = 0.3\ \text{M}$  or  $1.1\ \text{M}$  satisfy it.

When local concentrations of both ions are almost equal to each other, regulated distribution of chemical compositions appears. Results of Figures 2, 4 and 6 suggest that regulated chemical inhomogeneity appears only when structure of formed mineral is like bundle of pillars. The bundles develop radially in the gel (Figure 2) and uni-dimensionally under the monolayer

(Figures 4 and 6).

In our dilute condition,  $[\text{AOT}] = 0.002\ \text{M}$ , sheet-like structure with bundle of pillars is not seen. Surfactants monolayer adsorbed at interface is not fully saturated or compressed near cac. Then, growth of minerals under surfactant monolayer may induce structural perturbation to the monolayer. Thus, mechanism of the mineral growth may be quite different from that of concentrated case where minerals grow under saturated or compressed monolayer of AOT. In the dilute experiments, particles are preferentially formed instead of sheet independently of  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  concentrations. Then, gradient in Sr concentration does not appear in a single particle. Instead, a large number of particles with various concentration of Sr should be generated. Thus, chemical inhomogeneity in the dilute case is irregular, which reflects treatments of samples for SEM experiment. Thus, reproducibility of the pattern is not satisfactorily.

## 5. CONCLUSION

$(\text{Ba,Sr})\text{SO}_4$  solid solution was formed under surfactant monolayer adsorbed at oil/water interface. Organic phase containing anionic surfactant, sodium bis(2-ethylhexyl) sulfosuccinate (AOT), connected two kinds of aqueous solutions. One included  $\text{BaCl}_2$  and  $\text{SrCl}_2$ , and another contained  $\text{Na}_2\text{SO}_4$ . AOT transported  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  ions to oil/water interface on  $\text{Na}_2\text{SO}_4$ -containing aqueous phase. The solid solution grew and white thin layer was formed. Observation by scanning electron microscopy and electron probe X-ray microanalyzer revealed that the solid solution had well-regulated disk-like shape and gradient in Sr-concentration along the thickness. These characteristics were observed when concentration of AOT was large enough. For dilute condition of AOT, globular particles were formed, and chemical inhomogeneity was not well-regulated. We proposed a simple chemical system which was able to form minerals with regulated shape and chemical inhomogeneity.

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