## Analog experiment on vesiculation by crystallization with H<sub>2</sub>O-KCI-CO<sub>2</sub>

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Volatile components such as  $H_2O$  and  $CO_2$  are dissolved in the magma chamber under the volcano. These volatile components cause the bubble formation in the magma leading to the volcano eruptions.

One type of bubble formation in the magma chamber is induced by cooling and crystallization (so called "second boiling"). Crystals formation due to cooling by the host rock reduces the melt volume, and the volatile components that cannot be dissolved in the crystals concentrate in the melt.

Yoshigai (2011) investigated this process by an analog system using carbonated water. The carbonated water was used as the analog material of the melt, and the  $CO_2$  as the volatile component in the melt. When the solution was cooled below freezing point, the crystallization of ice, the bubble formation ,and the pressure increase were observed. However, since the ice has larger molar volume than the solution, it was unclear whether the pressure increase was due to the generation of bubbles or the formation of the ice.

Therefore, the purpose of this study was to reproduce the cooling crystallization and the bubble formation by analog experiments without pressure increase due to the ice formation. In order to do that, we use the system H<sub>2</sub>O-KCI-CO<sub>2</sub>, taking the advantage of the crystallization of KCI.

From the  $H_2O$ -KCl phase equilibrium diagram, assuming the room temperature of 20 °C, the 25 wt% KCl solution is thought to be just saturated at 20 °C. When the solution of that concentration is cooled, it can be expected that KCl crystals gradually crystallize and bubble formation occurs.

The acrylic cylindrical container(the diameter: 5 cm, the height: 5 cm) was used in the experiment. Only the lower bottom (aluminum plate) of the container was cooled by using a Peltier device throughout the experiment. During the experiment, the temperature was measured by thermo-couples(both K type) at the top and bottom in the container and the pressure inside the container was measured by the pressure-transduce(made by KISTLER). The video image was taken by GoPro (HERO 7 BLACK).

The experimental results above the eutectic point of  $H_2O$ -KCl binary system show that the crystallization of KCl was observed, but no  $CO_2$  bubble was generated. This can be interpreted that the concentration rate of  $CO_2$  by the KCl crystallization is smaller than the solubility increasing rate by cooling, from the calculation.

In the experiments below the eutectic point -10  $^{\circ}$ C the total volume of H<sub>2</sub>O and KCl crystals is expected to increase until the totally crystallized and to change depending on the amount of heat loss compensating the release of latent heat. We also examine the effect of surrounding temperature by controlling the variable temperature of used incubator where the container of solutions and sensors are set.

In the experiments performed at 10  $^{\circ}$ C and 16  $^{\circ}$ C of surrounding temperature, KCl was crystallized first, and below the eutectic point, ice and KCl crystals formed, and bubbles formed only near the inner side wall of the cylindrical container. However, in the experiment kept at 3  $^{\circ}$ C, no bubbles formed even after

the solution nearly totally crystallized.

Bubbles were generated only around the crystals. It is suggested that, the crystals were thick and the gap between the crystal and the container was large. When the experiment performed above the eutectic point, no bubble was observed. The reason is considered that in the initial concentration performed in this experiment, the amount of crystals generated during cooling is insufficient. The calculation for silicate systems shows that the concentration of  $H_2O$  by crystallization dominates or is similar to the solubility increase of  $H_2O$  by cooling. So, in the silicate system, the crystallization can induce the volatile concentration and lead to the bubble formation.

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