

## FORMATION OF BRIGHT MATERIALS ON CERES BY EXPLOSIVE CRYOVOLCANIC ERUPTION OF DEEP SUBSURFACE BRINES.

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**Introduction:** The Dawn spacecraft has found bright materials, mainly composed of Na carbonate ( $\text{Na}_2\text{CO}_3$ ) with small amounts of  $\text{NH}_4$ -bearing salts, on Ceres [1]. Gravity and geomorphic data around Occator Crater suggest the occurrence of upwelling of deep oceanic water by the impact and subsequent eruption of the brines from a shallow subsurface reservoir [2]. However, the presence of  $\text{Na}_2\text{CO}_3$  in bright materials generally requires highly alkaline brines ( $\text{pH} > 11$ ) [3], which may contradict with water chemistry of proposed deep oceanic water interacting with the rocky core of Ceres (e.g.,  $9 < \text{pH} < 10.5$ ) [4, 5].

Here, we suggest that rapid decompression and consequent degassing of volatile-containing brines would have caused alkalinization, enabling to form  $\text{Na}_2\text{CO}_3$  salts from moderately-alkaline ( $\text{pH}$  down to 10.0) deep oceanic water in Ceres based on laboratory experiments. In order to form  $\text{NH}_4$ -bearing salts in addition to  $\text{Na}_2\text{CO}_3$ , we suggest that concentration of deep oceanic water in a shallow reservoir due to freezing would be necessary. Our results support the geophysical view that bright materials originate from deep oceanic water if they were brought by explosive cryovolcanisms with efficient degassing.

**Methods:** We performed laboratory experiments on rapid and slow decompression of alkaline brines with  $\text{pH}$  9–10.5. Decompression was done in a vacuum chamber, in which a fluid sample was set with a  $\text{CO}_2$  atmosphere. The vacuum chamber was then evacuated with a rotary pump via variable values to control the evacuation rate. In rapid and slow decompression, the average decompression rates were  $10^4 \text{ Pa s}^{-1}$  and  $1\text{--}100 \text{ Pa s}^{-1}$ , respectively, former of which corresponds to a decompression rate for upwelling velocity of brines with 30 m/s for Ceres [6]. As for starting solutions, we prepared two types of brines: One is  $\text{Na-HCO}_3\text{-CO}_3$ -type and the other is  $\text{Na-NH}_4\text{-HCO}_3\text{-CO}_3$ -type brines. The  $\Sigma\text{NH}_3$  ( $=[\text{NH}_3(\text{aq})] + [\text{NH}_4^+]$ ) and  $\Sigma\text{CO}_2$  ( $=[\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ ) of brines were adjusted from 0.001 to 3 mol.  $\text{L}^{-1}$ . After decompression, we collected salt precipitates and analyzed the mineral composition with an X-ray Diffraction (XRD) spectrometer.

**Results:** In rapid decompression, we observed bubble formation from brines induced by degassing of dissolved  $\text{CO}_2$ , leading to disruption and fragmentation

of brines. In contrast, no bubble formation and disruption were observed in slow decompression.

Our results of XRD analysis show that both in rapid and slow decompression,  $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$  salts form from brines with initial  $\text{pH}$  of 10.5, and  $\text{NaHCO}_3$  salts tend to form when  $\text{pH}$  is initially low ( $< 9.5$ ). However, comparing the results of rapid and slow decompression for  $\text{pH}$  range of 10.0–10.3,  $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$  salts formed in rapid decompression; whereas, more  $\text{NaHCO}_3$  was generated in slow decompression (Fig. 1). The measured difference in salt composition would be caused by efficient degassing of  $\text{CO}_2$  upon rapid decompression.  $\text{CO}_2$  degassing resulted in alkalization of brines, leading to precipitation of more  $\text{Na}_2\text{CO}_3$ .

Figure 2 summarizes our experimental results of the mineral composition of salts precipitates as functions of initial  $\text{pH}$  and  $\text{NH}_4^+/(\text{HCO}_3^- + \text{CO}_3^{2-})$  ratio of brines. Based on the results, we can constrain initial water chemistry of brines, from which  $\text{Na}_2\text{CO}_3$ -rich salts can form upon rapid decompression (orange area in Fig. 2). Comparing with the results of slow decompression, the area for  $\text{Na}_2\text{CO}_3$ -rich salt precipitation expands toward lower  $\text{pH}$  down to  $\text{pH} \sim 10$ .

We also find that  $\text{Na}_2\text{CO}_3$ -rich salts cannot precipitate for brines with initially high  $\text{pH}$  ( $\sim 10.5$ ) when  $\text{NH}_4^+/(\text{HCO}_3^- + \text{CO}_3^{2-})$  ratio is high ( $> 0.15$ ) (Fig. 2). This happened because efficient degassing of  $\text{NH}_3$  would be acidified brines, leading to  $\text{NaHCO}_3$  precipitation rather than  $\text{Na}_2\text{CO}_3$ -rich salts. In our experiments,  $\text{NH}_4\text{HCO}_3$  were also found in XRD pattern in rapid decompression when  $\text{NH}_4^+/(\text{HCO}_3^- + \text{CO}_3^{2-})$  ratio of initial brines is  $\sim 0.15$  (red circles in Fig. 2). Our results show that there is particular water chemistry of initial brines, which allow precipitation of both  $\text{Na}_2\text{CO}_3$ -rich salts and  $\text{NH}_4$ -bearing salts in rapid decompression.

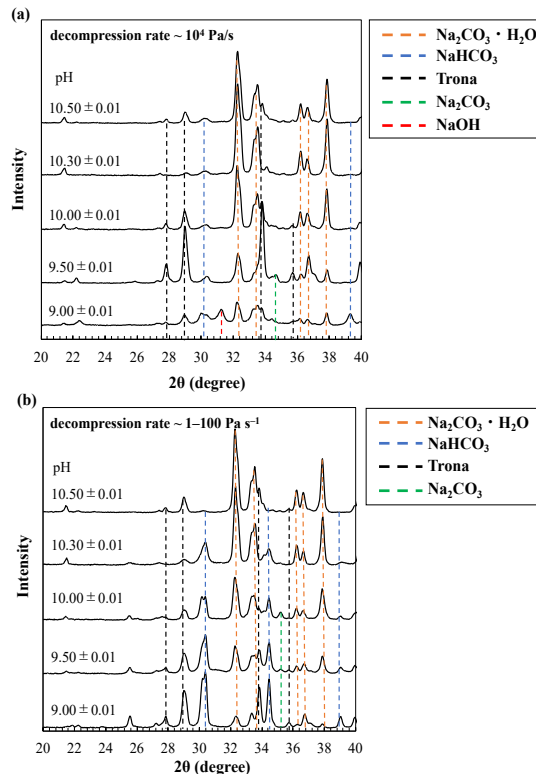
**Discussion:** To discuss whether required brine chemistry to form  $\text{Na}_2\text{CO}_3$ -rich salts (and  $\text{NH}_4$ -bearing salts) can be achieved in a shallow brine reservoir of Ceres, we performed thermodynamic equilibrium calculations in two ways. First, we calculated possible compositions of deep oceanic water of Ceres based on thermodynamic equilibrium calculations using rock compositions of CV chondrites and cometary water with  $\text{CO}_2$  10 mol.% and  $\text{NH}_3$  0.5 mol.% [7]. Then, we calculated evolution of brine compositions in a freezing shallow reservoir using a combined model of salt partitioning between ice and brines and low-

temperature aqueous chemistry using the FREZCHEM code [8]. As for the starting solutions for evolution of freezing brines, we used the results of fluid compositions of the thermodynamic equilibrium calculations using chondritic rocks and cometary water for different water-to-rock (W/R) ratios.

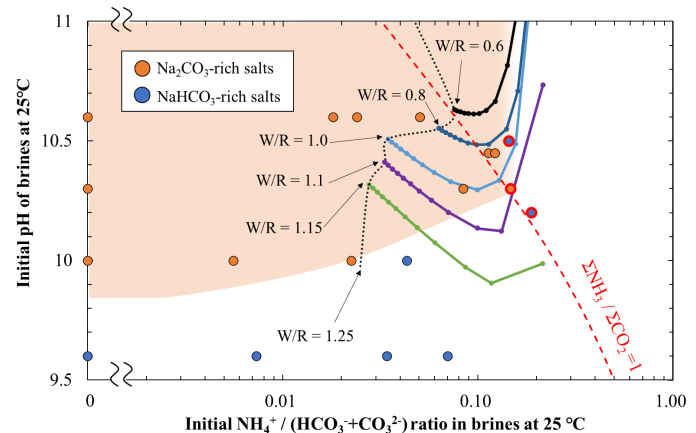
Figure 2 shows our results of pH and  $\text{NH}_4^+/(\text{HCO}_3^- + \text{CO}_3^{2-})$  of deep oceanic water suggested from thermodynamic equilibrium calculations using chondritic rocks and cometary water (black dotted line) and evolution of the brines upon freezing in a shallow reservoir (solid lines) for different W/R ratios. Comparing the calculation results with our experimental results (Fig. 2),  $\text{Na}_2\text{CO}_3$ -rich salts can form from deep oceanic water for W/R ratios of less than  $\sim 1.25$  when rapid decompression occurs, despite of the initial pH of the brines  $< 11$ . This suggests that  $\text{Na}_2\text{CO}_3$  in bright materials over Ceres could originate from explosive eruption of deep oceanic water. In bright materials of Occator Crater,  $\text{NH}_4$ -bearing salts were found together with  $\text{Na}_2\text{CO}_3$ -rich salts [1]. To explain this observation, we suggest that brine compositions beneath Occator

Crater might fall in the orange area with initial  $\text{NH}_4^+/(\text{HCO}_3^- + \text{CO}_3^{2-}) \sim 0.15$  in Fig. 2. To achieve this water chemistry, freezing of deep oceanic water with initial  $\text{W/R} < 1.1$  and consequent  $\text{NH}_3$  concentrations in a shallow reservoir would be necessary, which is consistent with the observation that bright materials were erupted  $\sim 15$  Myrs after the Occator impact cratering [2]. Our results suggest that bright materials could originate from deep oceanic water and subsequent freezing in shallow reservoirs with its explosive cryovolcanic eruption. Given the young formation age of bright materials, liquid brines would exist within Ceres on today.

**References:** [1] De Sanctis, M. C. et al. (2016) *Nature*, 536, 54–57. [2] Raymond, C. A. et al. (2020) *Nature Astronomy*, 4, 741–747. [3] Zolotov, M. (2017) *Icarus*, 296, 289–304. [4] Castillo-Rogez et al. (2018) *MAPS* 53, 1820; [5] De Sanctis, M. C. et al. (2020) *Space Science Reviews*, 216(60), 1–33. [6] Ruesch, O. et al. (2019) *Icarus*, 320, 39–48. [7] Kurokawa, H. et al. (2021) *AGU Advances*, 2, e2021AV000568. [8] Yoda, M. et al. (2021) *JGR Planets*, 126, e2021JE006972.



**Figure 1. XRD patterns of salts collected by decompression experiments of Na-HCO<sub>3</sub>-CO<sub>3</sub>-type brines.** (a) Results of rapid decompression, and (b) slow decompression. Orange, blue, black, green and red broken lines indicate the peaks of  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{NaHCO}_3$ , trona,  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$ , respectively.



**Figure 2. Comparison of our experimental results with the model calculations.** Orange and blue circles indicate the experimental data points, where  $\text{Na}_2\text{CO}_3$ -rich salts ( $\text{NaHCO}_3 < 10$  wt.%) and  $\text{NaHCO}_3$ -rich salts ( $\text{NaHCO}_3 > 10$  wt.%) were generated, respectively, in our experiments.  $\text{Na}_2\text{CO}_3$ -rich salts ( $\text{NaHCO}_3 < 10$  wt.%) can be formed within the orange area. Red frame of circles represents formation of  $\text{NH}_4$ -bearing salt ( $\text{NH}_4\text{HCO}_3$ ). Red broken curve represents  $\Sigma\text{NH}_3 / \Sigma\text{CO}_2 = 1$ . Black dotted line represents our results of thermodynamic equilibrium calculations using chondritic rocks and cometary water for different W/R ratios [7]. Solid lines show our results of thermodynamic equilibrium calculations of evolution tracks of freezing brines. The initial solutions are same as the fluid compositions of thermodynamic equilibrium calculations using chondritic rocks and cometary water. Colors of the solid line represent W/R ratios of 0.6 (black), 0.8 (dark blue), 1.0 (blue), 1.1 (purple), and 1.15 (green).