

**CHEMICAL PROCESSES OCCURRING IN BRINES FREEZING UNDER CERES SURFACE: THE CASE OF JULING AND KUPALO CRATERS.** M. Pedone<sup>1</sup>, E. Ammannito<sup>1</sup>, C. Plainaki<sup>1</sup>, M. C. De Sanctis<sup>2</sup>, A. Raponi<sup>2</sup>, S. De Angelis<sup>2</sup>, M. Ciarniello<sup>2</sup>, M. Ferrari<sup>2</sup>, A. Frigeri<sup>2</sup> and F. G. Carrozzo<sup>2</sup>, <sup>1</sup>ASI, Agenzia Spaziale Italiana, via del Politecnico s.n.c., 00133, Rome, Italy, (corresponding author e-mail address: maria.pedone@est.asi.it), <sup>2</sup>IAPS, Istituto di Astrofisica e Planetologia Spaziali, INAF, Via del Fosso del Cavaliere, 100, 00133, Rome.

**Introduction:** In the dwarf planet Ceres, a residual ocean at shallow depth may still exist today in the form of localized reservoirs [1]. We constrained the physiochemical properties of initial aqueous fluids, characterizing potential reservoirs, located under two craters: Kupalo (39.6°S, 173°E) and Juling (36°S, 168.3°E), located in the eastern part of Toharu Quadrangle Ac-H-12 [2, 3]. These two craters are selected because they are close each other but are mineralogical distinct, showing the presence of different carbonates (Kupalo) and water ice (Juling).

**This work:** We investigate if the distinct mineralogy at surface could be the result of the upwelling of different subsurface aqueous solutions, characterized by different initial conditions (in terms of pressure, temperature, and chemical composition).

At first, our simulations were performed using the FREZCHEM code [4] assuming that the Ceres reservoir is characterized by a mixture of chloride and sodium carbonate and has the same physical properties as the ones summarized in [5]. We used the code to infer the initial speciation of aqueous solutions that possibly were under Kupalo and Juling craters. In the model, for each crater, we selected fractional crystallization pathway by changing temperature value from the initial  $T_i=273$  K to the final  $T_f=245$  K in which the starting solutions have frozen to precipitate the solid phases characterizing the surface. The given temperatures are relevant since the first value is the melting point of pure ice and the latter is the eutectic temperature of relevant salt-ice mixtures [6]. Moreover, we carried out the freezing simulations by selecting three different values of initial total pressure: 1, 1.5 and 30 bar which correspond to a depth value ranging from 300 m to 10 km. Then, we compared the results deriving from the simulations with chemical equilibria calculations to understand the stability for each precipitated mineral, during the cooling process. In fact, the mineral (solid) equilibrium state is related to the activities of solutes (liquid) and the ionic strength of solutions.

**Results and Discussions:** Our preliminary study revealed that lower temperature and elevated salinity cause salt precipitation. The formation of water ice occurred at  $T < 270$  K and its concentration exponentially decreased for lower temperature affecting the ionic strength of remaining solution. Decreasing temperature caused the precipitations of carbonates (thermodynamically favored since  $\Delta G > 0$ ), followed by

the formation of sulphates and, later, of Cl-bearing salts from more saline brines.

In other words, regarding carbonates,  $MgCO_3$ ,  $CaCO_3$  and  $CaMg(CO_3)_2$  could have been the first solids to precipitate (before water ice formation) during the freezing of brines.

The formation of hydrated sodium carbonate (natron  $Na_2CO_3 \cdot 10H_2O$ ) is highly favored in Na-enriched solution (anhydrous sodium carbonate has been detected in Kupalo [2]); instead, natron could form only after water ice precipitation in Na-depleted solutions (water ice was detected in Juling [7]).

Natrite ( $Na_2CO_3$ ) was found in Kupalo's surface layers and not in Juling. We suggest that it could have been directly formed from the hydrated natron and nahcolite ( $Na_2CO_3 \cdot 10H_2O$  and  $NaHCO_3$  respectively) at 1 bar of total pressure. We can emphasize that, alternatively, at higher pressure ( $P > 1$  bar), natrite could only derive from dehydration of natron since nahcolite could not have formed.

Freezing drives chemical and physical changes in the solutions, and these processes change the velocity/density ratios of aqueous solutions from which precipitated minerals would have arrived at surface erupting with a velocity at least of  $\sim 8 \cdot 10^{-5}$  m/s.

Our models suggested that Na and Cl-enriched (Kupalo-like) solutions could freeze at a lower temperature with respect to Na and Cl-depleted (Juling-like) solutions. As temperatures are inversely correlated with salinity values, it cannot be excluded that Kupalo brines have frozen, reaching temperatures lower than Juling, becoming more saline.

In a high-salinity and high ionic strength condition, under shallower layers, also gases escaping is more favorable so that the gas-driven transport may be more decisive for bringing high-density solids (as sodium carbonate particles) to the surface.

Moreover, some solids' formation is highly pressure-dependent, as for sodium compounds. Beneath Kupalo, at specific pressure conditions, some kinetics-dependent salts could form, suggesting that aqueous solutions plausibly were affected by cooling processes slower than the nearby Juling.

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Data deriving from the mission Dawn are available at repository PDS (Planetary Data System) at url:

<https://sbn.psi.edu/pds/resource/dawn/dwncvirL1.html>  
and also <https://sbib.psi.edu/data/PDS-Ceres/about.html>. FREZCHEM code is free and available at url: <https://www.dri.edu/frezchem>.

**References:** [1] Quick L. C. et al. (2019) *Icarus*, <https://doi.org/10.1016/j.icarus.2018.07.016>.  
[2] De Sanctis M. C. et al. (2019) *Icarus*, 318, 230–240.  
[3] Frigeri A. et al. (2019) *Icarus*, 318, 14–21.  
[4] Marion G. M. et al. (2010) *Computers & Geosciences*, 36, 10–15.  
[5] Zolotov M. Yu. (2017) *Icarus*, 296, 289–304.  
[6] Castillo-Rogez J. C., et al. (2018) *Meteoritics and Planetary Science*, <https://doi.org/10.1111/maps.13181>.  
[7] Raponi A. et al. (2018) *Science Advances*, doi:10.1126/sciadv.aao3757.