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Chemical equilibria in saline aqueous solutions under Juling and Kupalo craters (Ceres dwarf planet): a model for the H_2O-CO_2-NaCl supply ascent system

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Abstract

In Ceres dwarf planet, a portion of a prior ocean at shallow depth [1] may still exist today as localized reservoirs [2]. A Ceres' reservoir was assumed to have had an initial temperature of 273 K, characterized by a mixture of chloride and sodium carbonate brines and, in this work, we used chemical equilibrium calculations for salt-bearing systems to constrain speciation, salinity, pressure and temperature of initial aqueous fluids located under Kupalo (39.6°S, 173°E) and Juling (36° S, 168.3° E) craters, located in the eastern part of *Toharu Quadrangle Ac-H-12* [3, 4, 5]. After a gradual freezing, an excess of pressure in the reservoirs, could have supported an intrusion of briny materials to surface, and, after our simulations, we could suggest that sodium-salts formation is pressure-dependent as well as depending on temperature as mentioned so far. Here, we explore the possibility to characterize the initial aqueous solutions from a physical and chemical point of view investigating about the stability of carbonates forming under different P-T conditions under Kupalo and Juling craters. Finally, our work may offer a clue in understanding the causes and processes that led to Ceres' surface composition, and finding a model for the evolution of the supply and ascent H_2O-CO_2-NaCl systems.

1. Introduction and motivation

The NASA *Dawn* mission [6] provided evidence of subsurface liquid delivery to the surface and precipitation of different minerals after dehydratation/water depletion, confirmed by the presence, on Ceres' surface, of an assemblage of Mg-phyllosilicates, ammoniated species, dark materials, and Mg-Ca carbonates [7]. Moreover, Visible and InfraRed spectrometer's data [8] suggested a different style of aqueous alteration occurred locally [7]. Spectral analysis of Juling and Kupalo evidences the existence of water ice and sodium carbonates [3], nevertheless, some substantial compositional differences have been identified too. In particular, whereas the Ca-Mg carbonates characterize Juling and Ceres' average composition [9], at Kupalo the Na carbonate is present. In this work, we model the initial aqueous solutions to speculate on the stability of carbonates forming under different P-T conditions under the two craters.

2. Brines' characterization

At first, we used FREZCHEM code [10] to infer the initial speciation of aqueous solutions possibly was 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=273.15 K to the final T_f=243.15 K (decrement value of ΔT=5 K) at three different initial total pressure values (1, 1.5 and 3 bars) in which the starting solutions have freezed to precipitate the solid phases characterizing the surface. Kupalo and Juling solutions had initial chemical composition close to that Occator and the *Langelier-Ludwig diagram* [11] suggests that from a compositional point of view, they are both characterized by the predominance of bicarbonate ion species. However, they differ in the alkaline and alkaline-earth contents (Fig. 1). Since the diagram consider the aqueous solutions only by a chemical point of view excluding physical properties, we can explore the possibility to see our given solutions in a broader perspective whose extremes include three main end-members on Earth (Fig. 1). Juling solutions are closer to the Earth cold groundwater field and, similarly to Earth, an interaction between Ceres' brines and CO_2 cannot be excluded. We obtained the amount of precipitated solids (expressed in moles) from the initial solutions during decreasing temperature and, then, we compared the results of the applied code with our chemical equilibria calculations to understand the equilibrium state for each precipitated mineral, during cooling process, related to the the activities of solutes, the ionic strength and density of solutions.

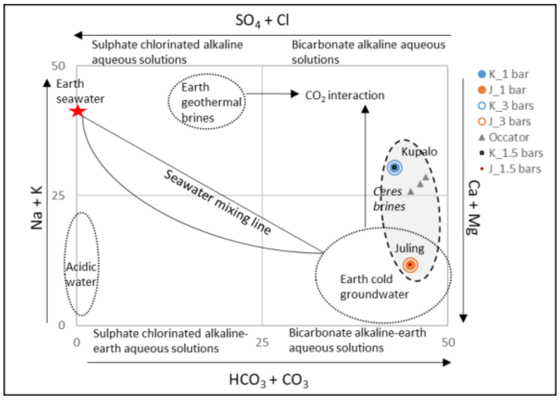

Figure 1: Langelier-Ludwig diagram [11] showing Ceres' brines in comparison with the main Earth aqueous targets.

Our preliminary study revealed that lower temperature and elevated salinity cause salt precipitation. The formation of water ice occurred at T<270.15 ± 2 K (in line with results by [12]) and its concentration exponentially decreased for lower temperature affecting the ionic strength (IS in Fig. 2) of remaining solution. Decreasing temperature caused the precipitations (thermodynamically favorited since ΔG>0, see Fig. 2) of carbonates, at first, followed by the formation of sulphates and, later, of Cl-bearing salts (KCl) from more saline brines. Solids precipitation feeds cooling process occurring in Kupalo and Juling craters, changing density of aqueous solutions and, as consequence, the velocity/density ratio. Aqueous solutions enriched in chloride salts would have arrived at surface at "warm" enough temperatures to erupt with a velocity of at least $6.9*10^{-5}$ m/s (in line with results by [2]) assuming a laminar flow regime, moving upward in a cylindrical conduit of a radius of 1 km. After crystallization, an over-pressure (ΔP/D=56 Pa/m) could facilitate the brines upwelling, in 10 m wide fractures, as proposed by [2]; we calculated an ascent speed (v) of about $8*10^{-5}$ m/s considering gravity acceleration (g) of 0.28 m/s^2, crust density (ρ_c) of 1300 kg/m^3, brines density (ρ_b) of 1140 kg/m^3, and the dynamic viscosity (μ) of 10^7 Pa·s given by [2].

3. Summary and Conclusions

Reservoirs at 45 km beneath Ceres' surface may exist [1] as a remnant of a prior subsurface ocean [2]. We find here that an excess of pressure in the reservoir, after a gradual freezing, could have supported an intrusion of briny materials up to Ceres' surface, resulting in floor-crater fracturing. The reservoir is characterized by a mixture of chloride and sodium carbonate brines and, our simulations suggest that sodium-salts formation are pressure-dependent. Our results support the hypothesis that different "cooling chambers" at different pressure conditions may exist under the Juling and Kupalo craters. Further investigations in this direction will be done in the near future.

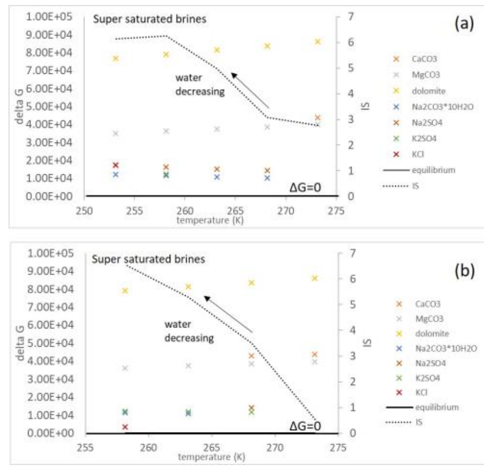

Figure 2: Variations of IS (ionic strength) and ΔG (the Gibbs free energy) calculated at each ΔT decrement in a) Kupalo and b) Juling at 1 bar of total pressure.

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