

**SORPTION AND MOBILIZATION OF ORGANICS IN CERES ANALOGUE MINERAL SYSTEMS.** D. Valadez, E. Flores, E. Martinez, J. M. Weber, J. Castillo-Rogez, M. Melwani Daswani, R.P. Hodyss, L. M. Barge. NASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA, 91109 (valadez@jpl.nasa.gov)

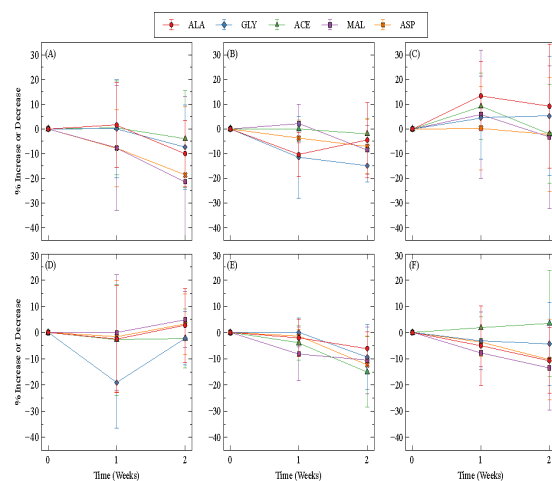
**Introduction:** The detection of organics on ocean worlds such as Ceres may imply formation in the interior and/or alteration on the surface. Ceres is likely to have undergone water-rock reactions in the past and thus primordial organics could have become further altered through reactions with reactive minerals; also, organics could have been altered and/or re-mobilized by successive cryo-eruptions on the surface. In this study, we attempted to create experimental analogues of Ceres surface minerals representing material that could have been formed in the interior and adsorbed organics, then erupted from the interior bringing those organics to the surface; as well as Ceres brine analogs representing successive eruptions that may have re-mobilized organics previously emplaced on the surface. In particular, we explored the organic synthesis and sorption of organics onto Fe-sulfide and Fe-hydroxide minerals in a Ceres context. These studies may guide and inform future mission concepts for Ceres.

**Methods:** We began our study of the sorption capability of organics onto Ceres analog minerals, testing 7 prebiotically relevant organics that are likely to form in abiotic mineral-containing systems [1-3] (glycine, alanine, glycolic acid, acetate, malic acid, ascorbic acid, and lactic acid) with two Ceres-relevant iron minerals (Fe-hydroxide and Fe-sulfide). Experiments took place within a  $N_2$  filled glove box in order to replicate anoxic conditions on Ceres. First, we prepared stock solutions of 25mM concentrations of each organic which were titrated to pH 10. Simultaneously, we synthesized iron minerals Fe-(oxy)hydroxides and Fe-sulfides using varying redox states of Fe. The iron sulfide mineral was precipitated by addition of a 50mM sodium sulfide solution; and the Fe-(oxy) hydroxide mineral was precipitated with a 50mM solution of sodium hydroxide (NaOH); to the solution containing dissolved Fe(II)/Fe(III). Each experiment, contained in a 100ml serum bottle, began by addition of 5ml of an organic stock solution to 20ml of the precipitated mineral suspension. Each experiment was titrated to pH 10 with NaOH and HCl, then was sampled initially, after one week, and after two weeks for  $^1H$  NMR and colorimetry analysis. The concentration of organics in the liquid phase was monitored by  $^1H$  NMR, to determine the fraction of organics that had adsorbed on the minerals.

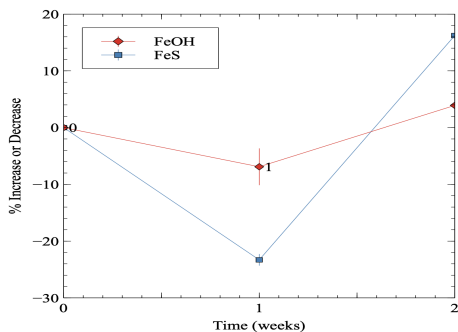
*Ceres Brine Experiments:* Laboratory Ceres Brine analogue was generated using Geochemist's Workbench models of Ceres brine for a pH of 6.5 and

water/rock ratio of 10. The brine was composed of 0.0786 M  $(NH_4)_2CO_3$ , 0.166089 M  $NaHCO_3$ , 0.01913 M  $NH_4Cl$ , 0.00648 M  $MgCl_2 \cdot 6H_2O$ , 0.01712 M  $NiCl_2$ , 0.006884 M  $MgCO_3$ , and 0.002125 M  $KCl$ ; and titrated to pH 6.5. Then, Fe-hydroxide and Fe-sulfide minerals were created using the same methods mentioned above, and an organic was added. For the Ceres brine experiments, only one Fe redox state (1:1 solution of  $Fe^{2+}$  and  $Fe^{3+}$ ) and glycine was explored. The mineral/organic samples were freeze-dried, and the dried mineral/organic sample was then submerged in the Ceres brine for several days, monitoring the organics present in the liquid phase with  $^1H$  NMR.

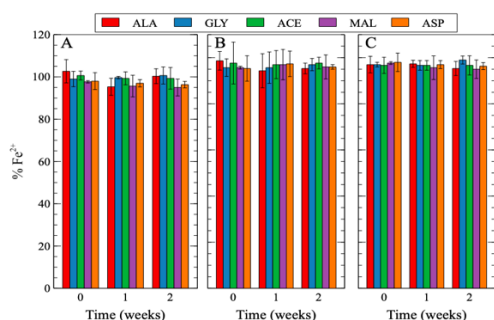
**Results and Discussion:**  $^1H$  nuclear magnetic resonance (NMR) was utilized to determine the concentrations of organics present and iron colorimetry was utilized to track the redox state of the iron minerals during the experiment. **Figure 1** depicts the preliminary results of the NMR analysis for our experiments of varying Fe-sulfide minerals (varying redox states  $Fe^{2+}$ ,  $Fe^{3+}$ , and 1:1 ratio of  $Fe^{2+} : Fe^{3+}$ ) with each organic. **Figure 2** below depicts the  $^1H$  NMR results for the Ceres Brine experiments.



**Figure 1:** The figure above depicts the average percent increase/decrease of organics at  $t=1$  and 2 weeks in comparison to  $t=0$  initial for Fe hydroxide (upper) and Fe-sulfide (lower). (A) Experiments with 100%  $Fe^{2+}$  (B) Experiments with 50%  $Fe^{2+}:Fe^{3+}$  (C) Experiments with 100%  $Fe^{3+}$  (D) Experiments with 100%  $Fe^{2+}$  (E) Experiments with 50%  $Fe^{2+}:Fe^{3+}$  (F) Experiments with 100%  $Fe^{3+}$ .

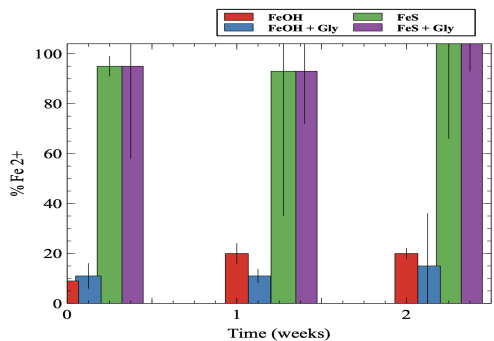


**Figure 2:** Average percent increase/decrease of glycine at  $t=1$  and 2 weeks in comparison of initial  $t=0$  weeks. Positive values represent organics released from the mineral (higher concentration of organic was detected in the supernatant). Negative values represent the percentage of organics bound to the mineral increase at  $t = 1$  and  $t = 2$  weeks compared to initial  $t = 0$ . All minerals started with an iron mineral redox state of 50%  $\text{Fe}^{2+}$  / 50%  $\text{Fe}^{3+}$ .



**Figure 3:** Iron oxidation state of Fe-sulfide minerals represented by the % of  $\text{Fe}^{2+}$  detected in dissolved samples. (A) Experiments starting with 100%  $\text{Fe}^{2+}$  (B) experiments starting with 50%  $\text{Fe}^{2+}$  and 50%  $\text{Fe}^{3+}$  and (C) experiments starting with 100%  $\text{Fe}^{3+}$ .

**Figure 4:** Iron oxidation state of FeOH



and FeS minerals in Ceres Brine experiments (in the absence and presence of glycine) represented by the % of  $\text{Fe}^{2+}$  detected in dissolved samples. Experiments started with 50%  $\text{Fe}^{2+}$  and 50%  $\text{Fe}^{3+}$ .

We observed in these experiments that there were trends of initial increase vs. decrease of organics (**Figs 1 & 2**); observed decreases are indicative of organics being bound to the mineral and increases are indicative of organics being released from the mineral. In Fe-sulfide organic sorption experiments, we observed that Fe in the presence of sulfide gets completely reduced regardless of the starting oxidation state of the mineral (**Fig. 3**); this is due to the reducing ability of sulfide and was not observed in the Fe-hydroxide adsorption experiments. In the experiments where the dried mineral/organic mixture was submerged in the Ceres brine solution, we did not observe much decrease in glycine concentration in the supernatant after 2 weeks (**Fig. 2**). We also observed additional iron redox changes in the minerals that were submerged in the Ceres brine (**Fig. 4**); in the case of the Fe-(oxy)hydroxide experiments with glycine, the mineral oxidized (likely due to the freeze-drying procedure) and then remained mostly stable; and in the case of Fe-sulfide experiments with glycine, immediate reduction of the iron mineral was observed regardless of oxidation state (similar to the adsorption experiments).

**Conclusion:** Minerals such as Fe-sulfides and Fe-hydroxides, relevant to Ceres, are capable of sorption of organics. In all cases tested, The NMR analysis revealed that organics remained in the aqueous phase which means they remained available for reactivity. In general, no significant changes in the sorption capabilities of the mineral were observed over 2 weeks and thus the mineral and organic remained stable. In the case of Fe-sulfide, the Fe in the presence of sulfide completely reduces regardless of the initial redox state of the Fe mineral. When organic-mineral samples were dried and exposed to a Ceres brine, the organics that were dried on the mineral are re-dissolved and detectable in the brine solution. This indicates that – at least for these organics tested – organics emplaced via eruptions of organic-containing minerals on the surface of Ceres could be re-mobilized by successive brine eruptions, and possibly migrate to locations other than where they were originally formed. Future experiments are needed to further investigate these and other minerals and organics, and testing how organic may be further altered in the presence of Ceres surface conditions.

**References:** [1] Barge, L. M. et al (2019) *PNAS*, 116 (11) 4828-4833. [2] Flores, E. et al. (2021) *ACS Earth Space Chem.*, 5, 5, 1048–1057. [3] Stubbs, R. T. et al. (2020) *Nat. Chem.* 12, 1016–102.