

MODELING THE AQUEOUS GEOCHEMISTRY OF CERES AND OTHER DWARF PLANETS. M. Neveu¹, S. J. Desch¹, and J. C. Castillo-Rogez². ¹School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA. ²Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA. (mneveu@asu.edu).

Dwarf Planets in the Spotlight: 2015 will see the first exploration of dwarf planets by spacecraft, with *Dawn* scheduled to enter Ceres’ orbit in April and *New Horizons* to fly through the Pluto system in July. Motivated by these imminent visits, we have previously modeled the possible thermal and geophysical evolution of these worlds. We have found their interiors likely to be differentiated into a rocky core and hydrosphere, possibly harboring subsurface liquid water over geological timescales [1-4]. These findings concur with observations of hydrated minerals on Ceres’ surface [5] and raise the possibility of cryovolcanism on dwarf planets, compatible with detections of water vapor at Ceres [6] and ammonia dihydrate, seemingly recently emplaced, on Pluto’s moon Charon [7].

The long-term presence of liquid water in contact with a rocky core suggests that water-rock interactions may occur. These seem necessary to explain Ceres’ surface minerals, and can produce species such as H₂ or N₂ whose exsolution may drive explosive cryovolcanism [8]. Interactions may be favored by extensive core fracturing: our models have shown that Ceres’ core could be cracked to at least 10% by volume, up to 100%. Thus, aqueous alteration of the core may have taken place at a water:rock ratio near Ceres’ bulk ratio.

Geochemistry Matters: Water-rock reactions can feed back on the thermal evolution of dwarf planets in several ways. Rock hydration may result in a ten-fold change in its thermal conductivity at a given T , and cause a 30% increase in core volume [2,4]. Here, we investigate two other prominent geochemical feedbacks not yet captured in our evolution models:

Fate of antifreezes. The extent and duration through which liquid persists depends strongly on the presence of volatiles (NH₃, CH₃OH) and salts, which depress its melting temperature. Volatile antifreezes, likely accreted by dwarf planets [1,2,8], may be oxidized to N₂ or carbonates, removing all or part of antifreeze capabilities. Conversely, salts may be leached from the core.

Fate of radionuclides. The long-lived heat producing elements K, Th, and U, present in the rocky core, may be leached into the fluid, taking away part of the core’s radiogenic fuel [9-11].

#	Rock	W:R	T(°C)	P(bar)	pH	pe
1	OC	0.42	50	1000	10	FMQ
2	OC	1.46	50	1000	10	FMQ
3	OC	1.46	50	1000	10	FMQ-1
4	CM	0.18	300	500	12	FMQ
5	CM	0.18	50	1000	10	FMQ
6	CM	0.18	50	1000	13	FMQ
7	CM	0.18	175	1000	12	FMQ
8	CM	0.05	175	1000	12	FMQ

Table 1: Parameter sets for the eight equilibrium geochemical simulations performed.

Models: We modeled the aqueous alteration of core rock, constrained by six parameters: starting rock composition (ordinary (“OC”) [12,13] or CM carbonaceous chondrite (“CM”) [13,14]), water:rock ratio (bulk W:R \approx 0.18 by mass for a hydrated core; 0.42 for a dry core on Ceres and Pluto, both of density \sim 2 g cm⁻³), temperature T , pressure P , pH, and redox (given as the departure in electron potential, pe, from the mineral buffer fayalite-magnetite-quartz or FMQ). The initial solution composition (35% C as CO, 2% N as NH₃, 0.5% S as SO₂ by mass) was chosen to approximate cometary ice [8]. We used the geochemical modeling software PHREEQC v3 [15] to determine equilibrium solution compositions and mineral assemblages. Only T and P were fixed in a given simulation. We used the thermodynamic data included in the *llnl.dat* database [15], which we expanded to add molar volumes converted from the CHNOSZ OBIGT database [16] for most minerals and solutes, as well as data for salts [17], NH₄-bearing minerals [18-20], and organics [21]. Simulation conditions, summarized in Table 1, were chosen to favor the formation of brucite Mg(OH)₂ and Mg-bearing carbonates observed at Ceres’ surface [6,22].

Results: In all runs starting with an OC rock composition (#1-#3), as well as run #4, the final pH (11.9 to 13.6) was higher than the initial value due to serpentinization. The pH remained relatively unchanged in all other CM runs.

Forming Ceres’ surface minerals. Despite initial conditions chosen to favor brucite formation, brucite was never formed. Its precipitation seems

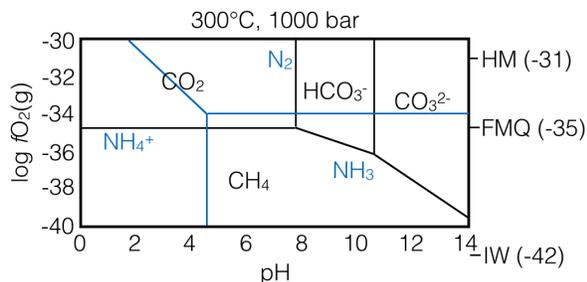


Figure 1: Stability of C and N solutes at 300°C and 1000 bar. At the FMQ buffer, both carbonates and NH₃ are stable. Thus, the persistence of NH₃ antifreeze is not incompatible with the formation of Ceres' carbonates. However, the overlapping range is narrow: at other common mineral buffers such as hematite-magnetite (HM) or iron-wustite (IW), NH₃ and carbonate cannot coexist at equilibrium. Most of our simulations seem to end near the HM buffer.

impeded by the formation of phyllosilicates bearing both Mg and Si (antigorite, saponites, biotite, and chlorites), as well as Mg-carbonates. However, in runs #3 and 5, the final concentration of Mg was $\sim 10^{-2}$ molal, mostly as MgOH⁺, suggesting that brucite might precipitate should solutes be concentrated further by, e.g., freezing. Dolomite CaMg(CO₃)₂ was formed in simulations #5, 6, and 8. In run #7, CaCO₃ was the preferred carbonate. In the reducing run #3, carbon was massively outgassed as C₂H₆, depleting carbonate solutes; this discouraged us from simulating more reducing conditions. In the remaining runs, carbonates remained in solution. In all simulations, minor to massive C₂H₆ outgassing seems to have left the equilibrium solution and rock oxidized (Fig. 1). Among other minerals possibly present on Ceres [5], magnetite formed in runs #1, 3, 4, and 8 (hematite was the dominant Fe oxide in the other runs). We did not obtain any cronstedtite [5].

Fate of antifreezes. N₂ outgassing was always significant, whereas NH₃ persisted only in run #3 at conditions too reducing for carbonates. However, the stability fields of NH₃ and CO₃²⁻ overlap over a small redox range (Fig. 1) and NH₃ persistence cannot be excluded. In our high-pH simulations, no NH₄-bearing species formed. CH₃OH being metastable with respect to CH₄ or carbonates, its equilibrium abundance in solution was always negligible. MgCl₂ and H₂SO₄ hydrates were produced in our runs; although likely unstable at the *T* of our simulations, these salts could prevent

freezing down to 240 K and 213 K, respectively.

Fate of radionuclides. Since our models tracked elements with a chondritic abundance above 500 ppm; K was the only radiogenic element included. In all runs, less than 0.02% K ended up in solution (either as KSO₄⁻ or K⁺); the remainder being precipitated as biotite (KAl(Fe,Mg)₃Si₃O₁₀(OH)₂).

Conclusions: We have explored the role of water-rock reactions in shaping the composition and internal evolution of dwarf planets, at conditions facilitating the formation of the minerals observed on Ceres' surface. These reactions may make volatile antifreeze persistence unlikely, although their loss might be partially offset by salt formation in a freezing ocean. Radionuclide leaching was negligible under the conditions simulated. All simulations yielded significant C₂H₂ and N₂ outgassing, which could drive explosive cryovolcanism. Runs covering a broader range of conditions, as well as simulations of freezing of the output solutions (e.g., using FREZCHEM [17]) will assess the validity of these findings.

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References: [1] Desch S. J. et al. (2009) *Icarus* 202, 694. [2] Castillo-Rogez J. C. and McCord T. B. (2010) *Icarus* 205, 443. [3] Rubin M. E. et al. (2014) *Icarus* 236, 122. [4] Neveu M. et al. (2015) *JGR*, in press. [5] Milliken R. E. and Rivkin A. S. (2009) *Nature Geosc.* 2, 258. [6] Koppers M. et al. (2014) *Nature* 505, 525. [7] Cook J. C. et al. (2007) *ApJ* 663, 1406. [8] Neveu M. et al. (2015) *Icarus* 246, 48. [9] Kirk R. L. and Stevenson D. J. (1987) *Icarus* 69, 91. [10] Engel S. et al. (1994) *JGR* 99, 3745. [11] Castillo-Rogez J. C. and Lunine J. I. *GRL* 37, L20205. [12] McSween H. Y. et al. (1991) *Icarus* 90, 107. [13] Wasson J. T. and Kallemeyn G. W. (1988) *Phil. Trans. R. Soc. Lon. A* 325, 535. [14] Howard K. T. et al. (2011) *GCA* 75, 2735. [15] Parkhurst D. L. and Appelo C. A. J. (2013) *USGS Techniques and Methods* 6, A43, 497 pp. [16] Reference list compiled by Dick (2013): <http://www.chnosz.net/download/refs.html>. [17] Marion G. (2014) FREZCHEM 16.1 release notes (<http://www.dri.edu/frezchem>) and refs therein. [18] Watkins (1981) MS Thesis, MIT. [19] Clegg S. L. et al. (1998) *J. Phys. Chem. A* 102, 2137 and 2155. [20] Christov C. (2002) *Calphad* 26, 85 and 341. [21] Richard L. and Helgeson H. C. (1998) *GCA* 62, 3591. [22] Zolotov M. Yu. (2014) *Icarus* 228, 13.