

REACTION CONDITIONS FOR FORMATION OF ALTERATION MINERALS ON CERES INFERRED FROM HYDROTHERMAL EXPERIMENTS. M. Mori¹, Y. Sekine², T. Shibuya³, T. Kuwatani⁴, K. Suzuki^{3,5,6}, Y. Masaki⁶, S. Tachibana⁷, ¹Dept. of Earth & Planetary Sci., Univ. Tokyo, Bunkyo, Tokyo, 133-0033, Japan, mo-ri@astrobio.k.u-tokyo.ac.jp, ²Dept. of Complexity Sci. & Engr., Univ. Tokyo, ³Precam. Ecosys. Lab., Japan Agency for Marine-Earth Sci. & Tech., ⁴Grad. Sch. of Envir. Studies, Tohoku Univ., ⁵Inst. for Res. on Earth Evol., Japan Agency for Marine-Earth Sci. & Tech., ⁶Submarine Resource Res. Project, Japan Agency for Marine-Earth Sci. & Tech., ⁷Dept. of Natural History Sci., Hokkaido Univ..

Introduction: The icy dwarf planet Ceres is the largest object in the asteroid main belt and is frequently referred as one of the remaining protoplanets in the solar system [1]. From collisional accretion of this class of objects, the planets are considered to have been formed in the protoplanetary disk [2]. Given the similarity of its reflectance spectra with those of C-type asteroids [3], Ceres might have formed along with the main-belt asteroids. Alternatively, considering its low bulk density ($\sim 2.1 \text{ g/cm}^3$) [1], it would have formed in the outer solar system with Kuiper belt objects and subsequently would have moved to the main belt, associated with giant planet migration [4]. Thus, knowledge on the formation and building materials of Ceres provides unique insights into planetary formation processes in the early solar system.

The observations with Hubble Space Telescope suggest that Ceres' interior is differentiated into a water-ice mantle and a rocky core [5,6]. Theoretical models of thermal evolution suggest that Ceres underwent large-scale ice melting and had possessed a liquid interior ocean over geological timescales. This implies that primitive minerals in the solar system, such as olivine, would have been hydrothermally altered in the interior of Ceres in the early stages of its evolution [6,7].

Ceres' reflectance spectra support the idea of occurrence of active aqueous alterations in the past. Recent ground-based observations suggest the presence of brucite, Mg-rich carbonate, Fe-rich phyllosilicate (cronstedtite), and magnetite on the surface of Ceres, which may have been produced from olivine-rich primitive minerals [8]. Constraining the reaction conditions (e.g., primitive materials, aqueous compositions, and temperature) for formation of these alteration minerals is essential to understand the origin of Ceres. A previous study examined the reaction conditions with chemical equilibrium calculations [9]. However, understanding of kinetics would be important for the aqueous alterations at low- to moderate high temperatures (e.g., $\sim 100\text{--}300^\circ\text{C}$), which have been poorly understood due to a lack of laboratory experiments.

In this study, we have carried out laboratory experiments of hydrothermal reactions, to constrain the reaction conditions of temperature and composition of building materials of Ceres. In particular, we aim at investigating the effects of temperature, the amount of

CO_2 , and the composition of primitive minerals to account for the observed alteration minerals. Based on these results, we discuss the location of the formation of Ceres in the protoplanetary disk.

Methods: The experiments were conducted with using a steel-alloy autoclave [10] at various temperatures of $120\text{--}400^\circ\text{C}$ and a constant pressure of 400 bar, which corresponds to a pressure at the boundary between a liquid interior ocean and a rocky core of Ceres. Aqueous solution of 0.02% or 0.6% of NaHCO_3 and 1% of NH_3 was used in the experiments. We used two types of starting minerals: First is powdered San Carlos olivine ($\text{Mg}/(\text{Mg}/\text{Fe}) = 0.9$) and the other is a mixture of orthopyroxene (enstatite) and San Carlos olivine (orthopyroxene : olivine = 7 : 3). The water to rock mass ratio was fixed at ~ 4 . A flexible gold tube was used for a reaction cell to avoid catalytic reactions on the wall of reaction cell [10]. The flexible reaction cell allows on-line sampling of the fluid at a constant temperature and pressure during the experiments [10].

We investigated the mineralogical and chemical compositions of the altered solid samples and time variations in dissolved gases and elements in the fluid samples. Solid samples were collected from the reaction cell at the termination of the experiments. Mineralogical and chemical analyses were performed with X-ray diffraction, Electron Microprobe Analysis, and Scanning Electron Microscopy. The chemical analyses of dissolved gases and elements in the fluid samples were conducted with gas chromatography and inductive coupled plasma-atomic emission spectroscopy, respectively.

Temperature dependency on Fe/Mg ratio in serpentine: Our experimental results show that temperature dependency of oxidation of Fe(II) to magnetite strongly affects the mineralogical and chemical compositions of the alteration minerals. Magnetite formation proceeds efficiently at higher temperatures, such as 300°C , which diminishes partitioning of Fe(II) into serpentine and results in low Fe/Mg ratios of serpentine formed at 300°C . At 200°C , we found serpentine with higher Fe/Mg ratios and less magnetite in the collected solid samples, suggesting that oxidation of Fe(II) proceeds less efficiently at 200°C . The results of H_2 production efficiency are consistent with the view of temperature dependency of Fe(II) oxidation.; that is, H_2

production is more efficient at 300°C than 200°C. Our results also suggest that Fe(II) oxidation reaches a level of chemical equilibrium over geological time on Ceres at $\geq 200^\circ\text{C}$.

Brucite Formation: Brucite is abundant in the solid samples formed at 300°C in the experiment using olivine. Microscopic observations show that brucite, together with serpentine and magnetite, was found between olivine crystals or in contact with an olivine crystal in the samples (Fig. 1). This suggests that these minerals precipitate in the fluids, implying that they could have been supplied to Ceres' ocean if hydrothermal circulation had occurred between the core and ocean [6].

On the other hand, brucite is very rare in the solid samples formed in the olivine experiment at 200°C, which is consistent with the prediction by the chemical equilibrium calculations [9]. No brucite was also found in the experiments using orthopyroxene and olivine at 120–300°C. This is because high SiO₂ concentrations in the fluids achieved in the orthopyroxene-olivine experiments prevent the brucite formation

Effect of CO₂: The results of gas analyses indicate that respective formations of CH₄ and N₂ from CO₂ and NH₃ are kinetically inhibited. On the other hand, carbonate formation from dissolved CO₂ proceeds efficiently (Fig. 2). Our results suggest that the carbonate formation rate is sufficiently high to reach a chemical equilibrium over geological timescales in Ceres.

Efficient carbonate formation affects the compositions of the altered minerals. Brucite tends to be less abundant in the solid samples formed at higher CO₂ concentrations in the olivine experiments. This is because high CO₂ concentrations result in a decrease in pH, and because carbonate formation consumes dissolved Mg in fluids. Both effects prevent the formation of brucite. We also found that the Fe/Mg ratio of serpentine becomes high under high CO₂ conditions. This is also because of consumption of Mg due to carbonate formation.

Discussion: Our results suggest that there is no single condition of starting minerals, aqueous composition, and temperature, under which the alteration mineral assemblages found on Ceres would be produced.

As carbonate formation proceeds efficiently, and as high CO₂ conditions prevent the formation of brucite, we conclude that, at least, low CO₂ concentrations in fluids are required to form brucite on Ceres. To implement such a low CO₂ concentration, Ceres should have been formed near the snowline of the protoplanetary disk, where temperatures were not very low (e.g., ~100–160 K), so that a large amount of CO₂ was not incorporated into building materials of Ceres as ice. This implies that the presence of brucite on Ceres does not support the idea of migration of the icy body from

the outer solar system to the main belt.

We also suggest that the formation of brucite requires high temperatures (e.g., ~300°C); whereas that of Fe(II)-containing phyllosilicates needs relatively low temperatures (e.g., $\leq 200^\circ\text{C}$). This implies the presence of a mineralogical and chemical heterogeneity on the surface of Ceres, which reflects a wide variety in experienced temperatures caused by internal or external heating processes. We propose that the Dawn spacecraft may be able to observe such heterogeneity associated with geological features, such as impact craters or ridge-like fractures, on the surface of Ceres.

References: [1] McCord, T.B. et al. (2011) *Space Sci. Rev.* 163, 63–76. [2] Weidenschilling, S.J. & Cuzzi, J. (2006) *Meteorites and the Early Solar Systems II*, 473–485. [3] Hiroi, T. et al. (1995) *Antarct. Meteorit.* 20, 72–75. [4] Walsh, K.J. et al. (2011) *Nature* 475, 206–209. [5] Thomas, P.C. et al. (2005) *Nature* 437, 224–226. [6] Castillo-Rogez, J.C. & McCord, T.B. (2010) *Icarus* 205, 443–459. [7] Rivkin, A.S. et al. (2011) *Space Sci. Rev.* 101, 1–22. [8] Milliken, R.E. and Rivkin, A.S. (2009) *Nat. Geosci.* 2, 258–261. [9] Zolotov, M. Y. (2014) *Icarus*, 228, 13–26. [10] Shibuya, T. et al. (2013) *Chemical Geology* 359, 1–9.

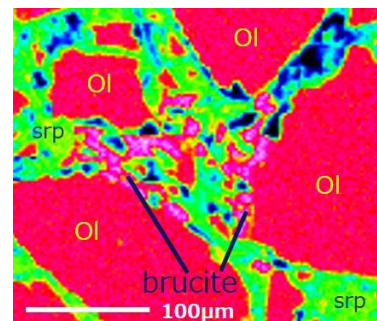


Fig.1: Mg concentration map of a solid sample formed at 300°C and CO₂ concentration of ~0.02% in the olivine experiment. This figure suggests that brucite (pink) and serpentine (green) formed using dissolved Mg from olivine crystals (red).

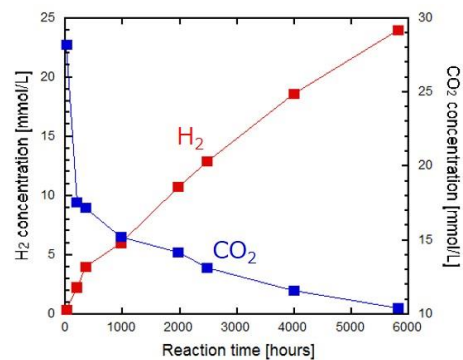


Fig.2: Time variations in dissolved H₂ and CO₂ in the olivine experiment at 300°C and CO₂ of ~0.02%.