EXPERIMENTAL EVIDENCE FOR HIGH-TEMPERATURE WATER–ROCK INTERACTIONS IN A CHONDRITIC CORE OF ENCELADUS. Y. Sekine[1], T. Shibuya[2], F. Postberg[3,4], H.-W. Hsu[5], K. Suzuki[2,6,7], Y. Masaki[7], T. Kuwatani[8], and S. Tachibana[9], [1]Dept. Complexity Sci. & Engr., Univ. Tokyo (5-1-5 Kashiwanoha, Kashiwa 277-8561 Japan, sekine@k.u-tokyo.ac.jp), [2]Precam. Ecosystem Lab., JAMSTEC, [3]Inst. für Geowissenschaften, Univ. Heidelberg, [4]Inst. für Raumfahrtsysteme, Univ. Stuttgart, [5]LASP, Univ. Colorado, [6]Inst. for Research on Earth Evol., JAMSTEC, [7]Submarine Resource Research Project, JAMSTEC, [8]Graduate School of Environmental Studies, Tohoku Univ., [9]Dept. Natural History Sci. Hokkaido Univ.

Introduction: A plume of vapor and water ice particles rich in sodium salts erupting from the south polar region of Enceladus suggests the presence of a liquid water reservoir in the interior [1–3]. Thus, Enceladus' plumes provide unique opportunities for understanding the physical and chemical conditions of its interior ocean.

The recent discovery of silica nanoparticles derived from the plumes by the Cassini spacecraft [4, 5] indicates the presence of silica in Enceladus' ocean [5]. In terrestrial geothermal fields, the formation of silica nanoparticles occurs when hydrothermal fluids with high concentrations of dissolved silica are cooled [6, 7]. Accordingly, the discovery of silica nanoparticles implies in turn the presence of a thermal gradient in the interior of the moon [5]. However, silica formation is controlled not only by temperature, but also by rock composition and fluid pH [6, 7]. Thus, the interpretation of the observations critically depends on our understanding of the nature of water–rock interactions in Enceladus, which are poorly constrained. Many laboratory experiments have been performed under the conditions of terrestrial hydrothermal vent fields, but there are few experiments focusing on Enceladus, where interactions between fluids containing primordial volatiles and minerals from the solar system may have occurred [8, 9].

Here we conduct laboratory experiments and chemical equilibrium calculations simulating hydrothermal reactions in Enceladus. Based on these results, we constrain the temperature and rock compositions for the water–rock interactions that can sustain the formation of silica nanoparticles.

Methods: We performed hydrothermal experiments using a flexible gold tube reaction cell, which is pressurized at 400 bar and heated at 120–300°C with a steel alloy autoclave [10]. As starting materials, we used an aqueous solution of NH_3 and $NaHCO_3$. These components were chosen because NH_3 and CO_2 are abundant in the gas component of Enceladus' plumes [3]. As Cassini has found sodium salts to be abundant in the plume's ice grains [1], Na^+ should also be abundant in Enceladus' ocean [1, 8] with an alkaline pH (pH 8.5–9). To investigate the effect of rock composition on the water–rock interactions, we used two types of starting minerals: (a) powdered San Carlos olivine (olivine experiment); (b) a mixture of powdered orthopyroxene (opx) (synthetic orthoenstatite: 70 wt.%) and San Carlos olivine (30 wt.%) (opx experiment). The opx experiment (Mg/Si = ~1.2) simulates alteration of a relatively Si-rich, undifferentiated rocky core, such as a parent body of carbonaceous chondrites, whereas the olivine experiment (Mg/Si = ~1.8) simulates alteration of ultramafic rocks formed by large-scale silicate melting, similar to Earth's upper mantle. The initial water/rock ratio was fixed at ~4 in the experiments. The experiments were performed for 3–10 months.

Results: We observed considerable variability in the dissolved total silica concentrations ($\sum SiO_2 = SiO_{2(aq)} + HSiO_3^- + NaHSiO_{3(aq)}$) in the experiments (Fig. 1A). To understand the factors that determine the observed trends, mineralogical analyses of the hydrothermally altered solid samples were performed. The major alteration products of the olivine experiments were serpentine, along with brucite, magnetite, and carbonate. In contrast, the alteration products of the opx experiments were dominated by serpentine and saponite, along with talc, magnetite, and carbonate, which are typical of carbonaceous chondrites.

In geothermal fields on Earth, the $\sum SiO_2$ value of fluids is thought to be strongly influenced by reactions of these alteration minerals [11]. Figure 1B shows the calculated equilibrium concentrations of $\sum SiO_2$ for the reaction between serpentine and talc (serpentine–talc buffer) and between serpentine and brucite (serpentine–brucite buffer). This figure indicates that the calculated $\sum SiO_2$ for the two buffer systems are in good agreement with the measured $\sum SiO_2$ in the opx and olivine experiments, respectively. These results strongly suggest that $\sum SiO_2$ of fluids in Enceladus' interior is also controlled by the buffer systems of the alteration minerals in geological timescales.

Discussion: We discuss the temperature and rock compositions of water–rock interactions in Enceladus that can sustain the formation of silica nanoparticles. We consider a simple scenario where high-temperature fluids in chemical equilibrium with the deep rocky core enter a low-temperature ocean. In Enceladus, penetration of fluids would have occurred to a depth of

>100 km below the ocean–rock interface [12]. In this scenario, colloidal silica nanoparticles would form upon cooling in the ocean when the ΣSiO_2 value of hydrothermal fluids exceeds the solubility of amorphous silica in the ocean. Our study assumes that silica nanoparticles are generated in an ocean at 0°C.

Figure 1B shows that ΣSiO_2 for the serpentine–talc buffer exceeds the solubility of silica at 0°C when the fluid temperature becomes sufficiently high. In contrast, ΣSiO_2 for the serpentine–brucite buffer is much lower than the solubility of silica for fluid temperatures of ≤350°C. These results suggest that to sustain high $\sum SiO_2$ sufficient to form silica nanoparticles, hydrous silicates in Enceladus would have been dominated by serpentine and saponite/talc, which are similar phases to those found in carbonaceous chondrites.

Figure 2 shows the required minimum temperatures of hydrothermal reactions for the serpentine–talc buffer as a function of fluid pH, in order to produce silica nanoparticles in Enceladus. To form silica nanoparticles, the fluid temperature in Enceladus needs to exceed ~100°C. Therefore, our results suggest that hydrothermal activity at ≥100°C is required to account for the formation of silica nanoparticles in Enceladus.

The timing of the occurrence of hydrothermal activity in Enceladus' history cannot be definitively determined. However, the existence of nanoparticles over geological timescales in the ocean is implausible [5]. Accordingly, the formation of silica nanoparticles is most likely sustained by geologically recent or ongoing hydrothermal activity. Thermal evolution models suggest that Enceladus' core would have reached high temperatures due to both short- and long-lived radiogenic heating over geological timescales [13], if it formed within 5 Myrs of formation of the solar system. Alternatively, hydrothermal activity may have been triggered by a recent incidental heating event. This might have happened if large parts of the core had been cold and contained pristine minerals, and if a recent heating event [14] increased the interior temperature, triggering a positive feedback between ice melting, serpentinization, and large tidal dissipation.

References: [1] Postberg, F. *et al*. (2009) *Nature* **459**, 1098–1101. [2] Postberg, F., *et al*. (2011) *Nature* **474**, 620–622. [3] Waite, Jr., J. H. *et al*. (2009). *Nature* **460**, 487–490. [4] Hsu, H. –W. *et al.* (2011) *J. Geophys. Res. -Space Phys.* **116**, A09215, doi:10.1029/2011A016488. [5] Hsu, H. -W. *et al*. (2014). (submitted). [6] Iler, R. K. (1979) *The chemistry of silica* (John Wiley & Sons) pp. 866. [7] Shibuya, T., *et al.* (2010). *Precam. Res.* **182**, 230–238. [8]. Zolotov, M. Y.(2007). *Geophys. Res. Lett.* **34**, L23203, doi:10.1029/2007GL031234. [9] Glein, C. R., *et al.* (2008) *Icarus* **197**, 157–163. [10] Shibuya, T. *et al.* (2013) *Chemical Geology* **359**, 1–9. [11] Frost, B. R. & Beard, J. S. (2007) *J. Petrology* **48**, 1351–1368. [12] Vance, S. *et al*. (2007) *Astrobiology* **7**, 987–1005. [13] Castillo-Rogez, J. C., *et al.* (2007) *Proc. 38th Lunar & Planet. Sci.* **38**, 2265. [14] O'Neill, C. O., & Nimmo, F. (2010) *Nature Geosci.* **3**, 88–91. [17] Wisdom, J. (2004) *Astron. J.* **128**, 484–491.

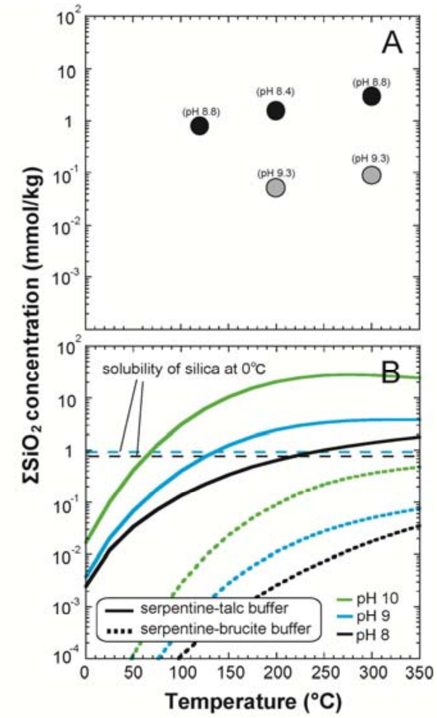

Figure 1. A. Experimental results of the measured $\sum SiO_2$ values of the olivine experiments (gray) and opx experiments (black) at various temperatures. The numbers annotated to the data points are in situ pH in the experiments. **B**. Calculation results of the $\sum SiO_2$ values determined by chemical equilibria of the reactions between the alteration minerals.

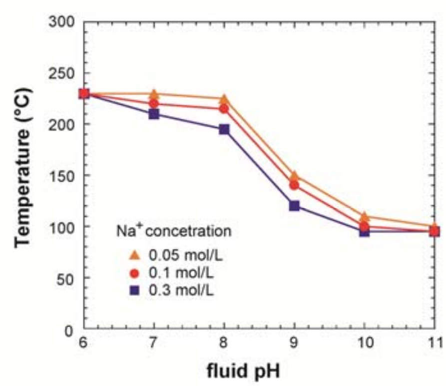

Figure 2. Required minimum temperatures of hydrothermal fluids in Enceladus for the formation of silica nanoparticles at variable Na^+ concentarations and pH. The results are calculated for the serpentine-talc buffer.