

CAN NANO-PHASE SILICA ORIGINATE FROM CHONDRITIC FLUIDS? THE APPLICATION TO ENCELADUS' SiO_2 PARTICLES. M. Yu. Zolotov¹ and F. Postberg^{2,3}, ¹School of Earth and Space Exploration, Arizona State University, Tempe AZ 85287-1404, USA, E-mail: zolotov@asu.edu. ² Institut für Geowissenschaften, Universität Heidelberg, 69120 Heidelberg, Germany. ³IRS, Universität Stuttgart, 70569 Stuttgart, Germany, E-mail: postberg@irs.uni-stuttgart.de.

Introduction: The presence of Na salts in the plume emissions of Enceladus indicates water-rock interaction in the history of the icy moon [1,2]. Silica (SiO_2) nano-size particles detected in the saturnian system could be from Enceladus [3,4], further supporting aqueous processes [5]. Interaction of silicate rocks with water leads to the formation of Si-bearing ions and neutral aqueous (aq) species in solution (mainly SiO_2 , HSiO_3^- and NaHSiO_3) and condensed SiO_2 phases may form upon cooling, evaporation or freezing of the fluids. On Earth, amorphous opaline silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$ or $\text{SiO}_2(\text{am})$) commonly deposits at hot springs (e.g., at the Yellowstone National Park) and at the seafloor hydrothermal vents. Similar processes have been proposed to explain the origin of opaline silica in Gusev crater on Mars [6]. However, silica phases may not easily deposit from solutions that are strongly undersaturated with respect to SiO_2 . Fluids formed during serpentinization of olivine-rich rocks are SiO_2 -undersaturated [7]. Secondary silica phases have not been reported in carbonaceous chondrites [8] and corresponding parent body fluids could have been undersaturated as well.

Our initial models for early Enceladus demonstrated a possibility for deposition of amorphous silica through cooling of ocean-forming fluids [13]. The recent experimental work [14,15] makes a case about formation of silica nano-size particles during cooling of hot ($T > 100^\circ\text{C}$) fluids on today's Enceladus. Here, we have evaluated concentration and speciation of Si-bearing solutes in typical chondritic fluids. We explored conditions of saturation of solutions with respect to silica phases in order to constrain the origin of silica particles on Enceladus.

Modeling Approach: Chemical equilibria have been calculated in a water-rock system at temperature ($T = 0$ to 300°C), pressure ($P = P[\text{H}_2\text{O liquid-gas saturation}]$ to 100 bars), and water/rock mass ratio ($W/R = 0.3$ to 2) which are applicable to Enceladus and other bodies consisting of solids of near-solar composition. The rock was presented by the H_2O -free composition of Orgueil CI carbonaceous chondrite, which is a proxy for rocks in the outer solar system. Redox conditions ($f\text{H}_2$) were varied from H_2 -rich environments in a closed system at 100 bars to oxidized conditions that correspond to complete removal of H_2 gas at the pressure of H_2O liquid-gas saturation. Some

oxidizing cases were modeled by simulated setting $f\text{H}_2$ in agreement with the CO_2/CH_4 ratio in the plume [cf., 13], even if CH_4 does not equilibrate with CO_2 in natural fluids. The oxidized cases provided a better match to the composition of Enceladus' plume and E-ring particles [1,2], though the origin of H_2 in plume gases remains unclear. Calculations were performed with GEOCHEQ codes [16] which we used elsewhere [13,17]. Conditions for saturation of $\text{SiO}_2(\text{am})$ in cooled fluids were explored by calculation of chemical equilibria in initial rock-free solutions at 0°C . Additional mineral deposition through fluid evaporation or freezing was modeled with the FREZCHEM code [18].

Concentration and Speciation of Si-bearing Solutes in Chondritic Fluids: The concentration and speciation of Si solutes are mostly controlled by solubilities of secondary Fe-Mg serpentine, Na-K-Ca-Mg saponite, and Fe-Mg chlorite in altered chondritic rock. The concentration of $\text{SiO}_2(\text{aq})$ gradually increases with T and is not very sensitive to the P and redox state of the system. Commonly, $\text{SiO}_2(\text{aq})$ is the dominant Si-bearing solute in high- T systems (Fig. 1). Serpentine-saponite secondary mineralogies, which are typical for CI/CM chondrites [8], correspond to slightly lower concentrations of $\text{SiO}_2(\text{aq})$ than in chlorite-bearing mineral assemblages shown on Fig. 1.

Some models that involved a major oxidation of organic C [c.f., 13] led to talc-carbonate serpentine-free assemblages equilibrated with $\text{SiO}_2(\text{aq})$ -enriched fluids. Elevated concentrations of $\text{SiO}_2(\text{aq})$ in the contact with talc-bearing rocks are consistent with experiments [14,15]. However, talc-rich assemblages are inconsistent with observations in chondrites [8] and corresponding $\text{SiO}_2(\text{aq})$ -rich fluids could have not occurred on asteroids and icy moons.

Aqueous species HSiO_3^- and NaHSiO_3 dominate in high- pH and low- T fluids (Fig. 1), consistent with equilibria $\text{HSiO}_3^- + \text{H}^+ = \text{SiO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$ and $\text{NaHSiO}_3(\text{aq}) + \text{H}^+ = \text{Na}^+ + \text{SiO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$. $\text{NaHSiO}_3(\text{aq})$ is more abundant in Na-rich solutions. $\text{NaHSiO}_3(\text{aq})$ and HSiO_3^- could be very abundant (up to 10^{-2} mole $(\text{kg H}_2\text{O})^{-1}$) in hypothetical super-alkaline NaOH-type fluids coexisting with Na-less serpentine±chlorite mineralogy without Na-bearing saponite [17]. The concentration of $\text{SO}_2(\text{aq})$ is not elevated and solutions are far from saturation with respect to silica.

NaOH-type fluids may not characterize parent bodies of CI/CM carbonaceous chondrites [8] and could be inconsistent with the Na-Cl-carbonate composition of Enceladus' plume particles [1].

With the exception of unusual NaOH-type and talc-related cases, bulk concentration of Si species in CI-chondritic fluids at 0–300 °C is about 10^{-4} mole $(\text{kg H}_2\text{O})^{-1}$ and may not exceed 10^{-3} mole $(\text{kg H}_2\text{O})^{-1}$.

Saturation of Low-*T* Fluids with Respect to Amorphous Silica: A solution becomes supersaturated with respect to $\text{SiO}_2(\text{am})$ if the activity (*a*) of dissolved silica exceeds $a\text{SiO}_2(\text{aq})$ set by equilibrium $\text{SiO}_2(\text{am}) = \text{SiO}_2(\text{aq})$; $K_{eq} = a\text{SiO}_2(\text{aq})/a\text{SiO}_2(\text{am}) \approx a\text{SiO}_2(\text{aq}) \approx -3.11$ (at 0 °C and 1–100 bars). In the considered hydrothermal solutions, calculated $a\text{SiO}_2(\text{aq})$ was much less than at solution saturation with respect to quartz or $\text{SiO}_2(\text{am})$. Cooled rock-free fluids remain undersaturated with respect to amorphous silica (Fig. 2). Furthermore, the increase in *pH* upon cooling decreases concentration and activity of $\text{SiO}_2(\text{aq})$ at the expense of other Si-bearing solutes. One exception is the observed precipitation of $\text{SiO}_2(\text{am})$ upon cooling of hydrothermal ($T > \sim 220$ °C) fluids equilibrated with a talc-rich rock without serpentine discussed in the previous section.

Modeled freezing of cooled fluids led to precipitation of amorphous SiO_2 . However, a freezing scenario for Enceladus needs to be reconciled with the coagulation of nano-size silica particles at even moderate ionic strengths [15,19].

Conclusions: Aqueous alteration of carbonaceous chondritic materials forms fluids which are strongly undersaturated with respect to silica phases, consistent with observations in chondrites. Cooling of typical chondritic fluids to ~ 0 °C may not cause precipitation of silica as suggested in [14,15]. If hydrothermal activity is the source of the observed nano-particles further efforts are needed to understand the process.

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Fig. 1. Concentrations of solutes, the pH, and total concentration of Si-bearing species which represent interaction of CI-type chondrites with water at $W/R = 1$, 100 bars total pressure and 10% of C reacted. The redox state is set to be consistent with the CO_2/CH_4 ratio of ~ 2.5 in the Enceladus' plume [c.f., 13]. The fluid coexists with secondary mineralogy dominated by serpentine, saponite, chlorite, and magnetite.

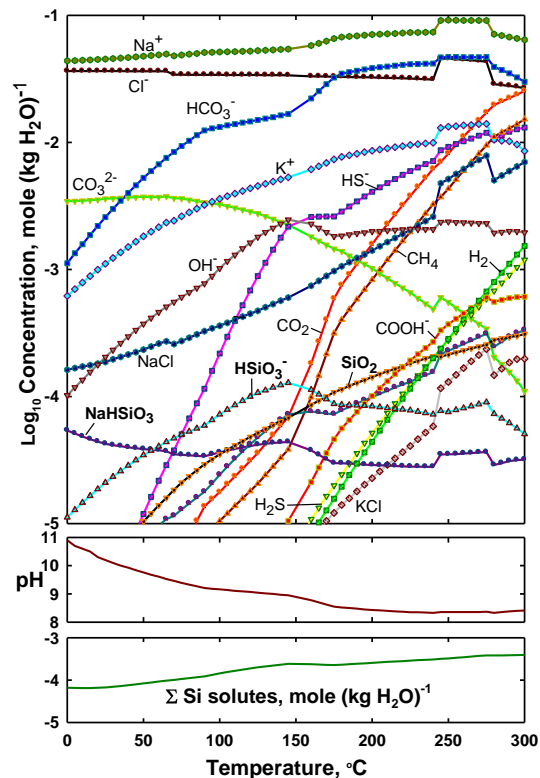


Fig. 2. Activities of Si-bearing species in aqueous fluids cooled to 0 °C. The plot corresponds to the P - $f\text{H}_2$ conditions used to calculate high- T fluids (Fig. 1). The dashed line shows conditions of solution saturation with respect to $\text{SiO}_2(\text{am})$. The solution is not saturated and additional cooling and/or solution concentration is needed to precipitate $\text{SiO}_2(\text{am})$.

