

FORMATION OF MARTIAN SILICA-RICH DEPOSITS THROUGH ROCK ALTERATION: A THEORETICAL ASSESSMENT. A. C. McAdam¹, M. Yu. Zolotov¹, M. V. Mironenko², and T. G. Sharp¹, ¹School of Earth & Space Exploration, Arizona State University, Tempe, AZ 85287-1404, amcadam@asu.edu, ²Vernadsky Institute of Geochemistry & Analytical Chemistry, Russian Academy of Sciences, 19 Kosygin Str., Moscow 119991, Russia.

Introduction: The secondary mineralogy of martian surface materials is consistent with aqueous alteration of mafic and ultramafic rocks [e.g., 1-3]. Alteration of mafic silicates results in the release of SiO₂ into aqueous solution, followed by the precipitation of silica [4] and/or silica-rich minerals. The presence of these phases is consistent with data obtained at the Mars Pathfinder [4] and Opportunity rover [5] landing sites and with thermal infrared spectra of large surface regions [e.g., 6]. Recently, silica-rich outcrops and soil (up to 95 wt% SiO₂) have been found in Gusev crater [7, 8]. These samples generally also have high Ti concentrations (up to 1.2 wt% TiO₂ [8]). Thermal infrared spectra of these materials are consistent with opaline silica [9]. Here we use theoretical models to investigate conditions under which abundant silica can form by alteration of olivine basalt.

Approach: We are exploring the effects of pH, solution/rock mass ratio (W/R) and temperature (*T*) on secondary mineralogy, solution chemistry, and timing of alteration. Equilibrium mineral assemblages are calculated with the GEOCHEQ code [10]. The bulk chemical composition of Adirondack-type olivine basalt from Gusev crater [11] is used to represent the protolith. For 0°C models, aqueous solutions of H₂SO₄-HCl with pH<5 are used, because of preferential deposition of silica at low-pH [12]. High *T* work is exploring a broader range of pHs. Some models are constant-pH open systems while others are closed, allowing pH to increase with weathering. Temperatures ≤200°C are used because of the inability of metastable amorphous silica to form in higher *T* solution-rock systems [13].

To explore the timescale of silica precipitation we are using a coupled kinetic-thermodynamic model developed for acid weathering [14]. This model considers mineral dissolution rates and solubility-controlled precipitation. We are exploring the timing of acid weathering of 0.1 mm mineral grains with the normative mineralogy of the basalt [11] exposed to different amounts of H₂SO₄-HCl solutions with initial pHs<5.

Results at 0°C: Amorphous silica forms over a wide range of solution pH at W/Rs<~10⁴ (Fig. 1). This high W/R boundary implies that acid ground water, spring waters and surface streams would be saturated with silica. Evaporation, freezing, or other consumption (e.g., rock hydration) of these solutions would result in silica deposition. Less silica precipitates at

higher pH, corresponding to the increase in silica solubility [12] and decrease in solubility of secondary silicates. At pH<~1-1.5, silica is the only precipitate. Deposits with 60-100 wt.% silica form at pHs<~3 (Fig. 1).

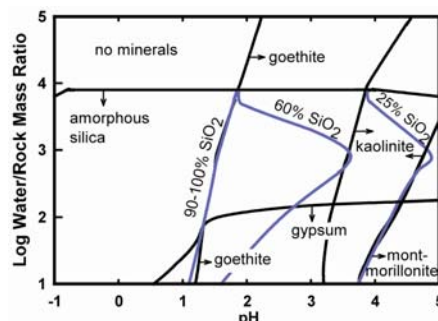


Figure 1. Precipitation conditions of secondary minerals formed through acid alteration of olivine basalt at 0°C. Blue curves delineate conditions where silica comprises a given wt.% of the mineral assemblage.

In systems with initial solution pH<~2, abundant silica precipitates at W/R~10²-10³ and is the only modeled precipitate (Fig. 2). However, little or no silica precipitates from the highest W/R systems, reflecting dissolution of silica in large volumes of solution. When solution reacts with a comparable mass of rock, only minor silica precipitates in equilibrium with neutralized solution. In this case, the mineral assemblage consists of mostly clays, goethite, carbonates, and gypsum. If initial solution pH is >~2-3, silica is less abundant and there are no conditions where it forms alone.

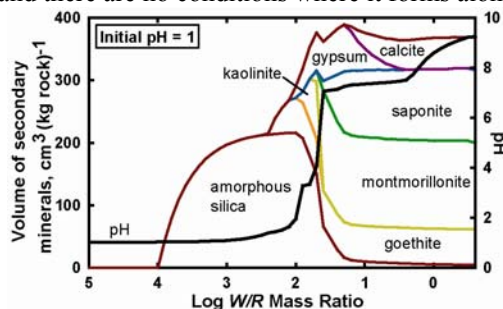


Figure 2. Equilibrium mineralogy from alteration of 1 kg of olivine basalt at 0°C by a solution with initial pH 1. The bold black curve shows changes in pH with W/R.

Kinetic modeling of rock alteration also demonstrates that silica-rich deposits form at pHs<2-3 and W/Rs~10²-10³ (Fig. 3). Most primary silicates dissolve, and silica is the only or most abundant precipitate. Lower W/R ratios lead to rapid solution neutralization, most primary minerals remain unaltered, other

secondary minerals precipitate (e.g. Fig. 2), and abundant silica does not form. In turn, W/R s above $\sim 10^3$ lead to SiO_2 accumulation in the aqueous phase. For initial solution pH s $> 2-3$, silica is not dominant at any W/R and most primary minerals remain unaltered at 10^2-10^3 yrs.

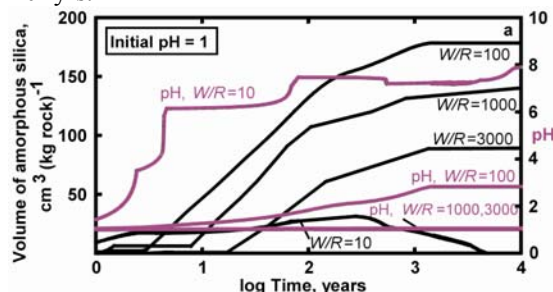


Figure 3. Volume of silica formed through weathering of mineral grains that represent the olivine basalt. The purple curves show changes in pH. For this initial solution $\text{pH}=1$ system, silica dominates the mineral assemblage at $W/R \sim 10^2-10^3$.

Results at higher temperatures: The amount of silica formed decreases with increasing T , though the pattern of decrease depends on pH and W/R (Figs. 4 and 5).

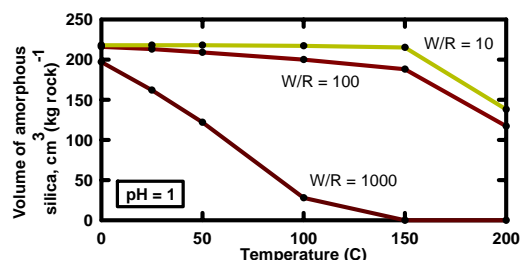


Figure 4. Volume of silica formed through weathering of olivine basalt at several temperatures and W/R values.

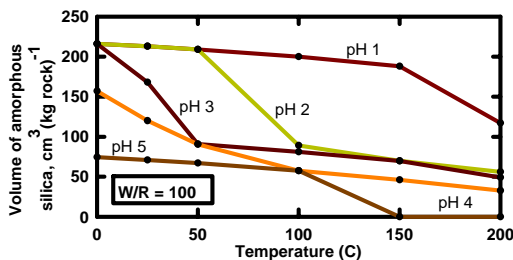


Figure 5. Volume of silica formed through weathering of olivine basalt at several temperatures and pH conditions.

In general, the W/R conditions where the most silica precipitates ($\sim 10-10^2$) are lower than those at 0°C . This reflects the increase in silica solubility at higher T [12]. The effect of pH on silica precipitation is similar to that observed at 0°C ; at a given W/R , lower pH s will result in more silica (Fig. 5). This reflects the decrease in silica solubility with decreasing pH .

At T s $< \sim 50^\circ\text{C}$, silica is the only precipitate under very low pH ($< \sim 1$) and high W/R ($> 10^2-10^3$) conditions. In all our models, we typically observe precipi-

tation of rutile (TiO_2) together with silica. At lower W/R ratios, and higher solution pH s, the mineral assemblage varies with T but consists mainly of clay minerals, iron oxides/oxyhydroxides (goethite, hematite), sulfates (gypsum, anhydrite), and in some cases carbonates and albite.

If cooling of high- T solutions is modeled, for example from 200°C to 0°C , secondary mineral assemblages dominated by silica can form even at relatively high pH s (near neutral, for example). In neutral pH solutions at high T , amorphous silica is relatively soluble and other minerals precipitate instead (e.g. clays). If the remaining solution is then cooled, silica becomes more insoluble and precipitates. Our models show that if this cooled solution was removed from the minerals precipitated at the higher T , such as by flow of the solution as it was cooling, this can result in a new secondary assemblage dominated by silica.

Summary and Implications: Silica-rich deposits, like those observed at the Home Plate in Gusev crater [7, 8], could form at solution $\text{pH} < \sim 1-3$, W/R ratios of $\sim 10^2-10^3$ and T s of $< \sim 50^\circ\text{C}$. Low- T ($\sim 0^\circ\text{C}$) formation of silica-rich deposits may be more likely because this can occur at slightly higher pH values and because of more vigorous boiling of high- T fluids at low atmospheric pressure. High W/R conditions may imply spring discharge and subsequent outflow. Without flow of solutions, which is required to transport elements, silica would be a small component of surface deposits formed through evaporation or cooling/freezing. Other secondary phases (e.g. salts, clays) would precipitate from neutralized solutions farther from acid springs. Calculated association of TiO_2 with silica is consistent with observations in Gusev crater [7,8]. These inferences are consistent with the suggestion that the Home Plate depression was filled by spring water at the time of silica deposition [9].

References: [1] Clark B.C. et al. (2005) *EPSL*, 240, 73. [2] Bibring J.P. et al. (2005) *Science*, 307, 1576. [3] Ming D.W. et al. (2006) *JGR*, 111, E02S12. [4] McLennan S.M. (2003) *Geology*, 31(4), 315. [5] Glotch T.D., et al. (2006) *JGR*, 111, E12S03. [6] Kraft M.D., et al. (2007) *7th Int. Conf. on Mars*, abst. 3396. [7] Squyres S.W., and Athena Science Team (2007) *Eos Trans. AGU*, 88(52), Fall Meet. Suppl., Abst. P21C-01. [8] Yen A., et al. (2007) *Eos Trans. AGU*, 88(52), Fall Meet. Suppl., Abst. P23A-1095. [9] Ruff S.W. et al. (2007) *Eos Trans. AGU*, 88(52), Fall Meet. Suppl., Abst. P23A-1097. [10] Mironenko M.V. et al. (2000) *Herald DGGGMS RAS*, 5(15), 96. [11] McSween H.Y. et al. (2006) *JGR*, 111, E02S10. [12] Dove P.M. (1995) In *Chem. Weath. Rates Silicate Min.*, MSA, Washington, D.C.. [13] Dove P.M. and Rimstidt J.D. (1994) In *Silica: Phys. Behavior, Geochem., and Mat. Apps.*, MSA, Washington, D.C. [14] Zolotov M.Yu. and Mironenko M.V. (2007) *JGR*, 112, E07006.