EFFECT OF TEMPERATURE ON SILICA FORMATION DURING ACID-BASALT ALTERATION: CHEMICAL EQUILIBRIUM CONSTRAINTS. A. C. McAdam¹, M. Yu. Zolotov², M. V. Mironenko³, and T. G. Sharp². ¹Atmospheric Experiments Laboratory, Code 699, Goddard Space Flight Center, Greenbelt, MD 20771, Amy.McAdam-1@nasa.gov. ²School of Earth & Space Exploration, Arizona State University, Tempe, AZ 85287-1404, Amy.McAdam-1@nasa.gov. ³Vernadsky Institute of Geochemistry & Analytical Chemistry, Russian Academy of Sciences, 19 Kosygin Str., Moscow 119991, Russia.

Introduction: The presence of silica and/or silica-rich minerals on Mars is consistent with in-situ data [e.g., 1, 2] and with orbital thermal infrared [e.g., 3, 4] and near infrared [e.g., 5] spectral observations of surface regions. Recently, the Spirit rover investigated silica-rich outcrops and soil (up to ~98 wt % SiO₂) at the Columbia Hills in Gusev crater [6]. These samples commonly have significant Ti abundances (up to 1.5 wt %) [6] and are probably opaline silica [7]. Although the silica is likely a result of aqueous processes [6-8], the conditions of rock alteration and silica deposition remain to be constrained. In [8], we show that the silica-rich deposits could form through low-temperature (T) alteration of martian rocks. The deposits have also been interpreted to have formed under hydrothermal conditions [e.g., 6, 7]. Here, we used thermochemical equilibrium calculations to investigate the conditions under which silica-dominated deposits may have formed at higher T. Potential additional constraints afforded by the presence of significant Ti in the deposits was also studied.

Approach: We used the GEOCHEQ code [9] to explore the effects of solution pH, solution/rock ratio (expressed as water/rock ratio, W/R) and T on equilibrium secondary mineralogy and solution chemistry of systems during water-rock interactions. A series of H₂SO₄-HCl solutions with pH<~7 were chosen because of chemical and mineralogical signs of low-pH alteration of martian rocks [e.g., 10, 11] and preferential deposition of silica from low-pH solutions [12, 13]. Temperatures between 0 and 200°C were used; an upper limit of 200°C was chosen because of the inability of metastable amorphous silica to form in higher T solution-rock systems [13]. A simplified chemical composition of the Adirondack-type olivine basalt from Gusev crater was used as the input composition [14]. Systems were calculated open with respect to current martian atmospheric O₂ and CO₂. Some models were open with respect to solution pH; this modeled continuous input of acid. Other modeled systems were closed, allowing pH to change from an initial system pH with rock alteration.

Effect of pH: Equilibrium calculations open with respect to acid solution show that silica-dominated assemblages can form at T<~25°C, high W/Rs (~10⁻²-10⁻¹), and pHs<~2-3 (Fig. 1). Ti-oxide phases, represented by rutile and titanite in the model, form under all conditions in which amorphous silica forms. Significant amounts of silica can form over a greater range of W/R ratios and at higher temperatures (T<~150°C) at pH<~2-3. In these equilibrium assemblages, the other minerals consist mainly of iron oxides/oxhydroxides (hematite or goethite), Al-phyllosilicates and Ti-oxide minerals (rutile or titanite) (Fig. 1 and 2).

Equilibrium calculations in systems closed with respect to the acid solution show similar trends to those discussed above. For example, systems with initial pH=1 and W/R=10³ produced the mineral assemblages shown in Fig. 3 as functions of T. In this case, a silica-only assemblage occurs at T<~30°C. At higher T, assemblages consisting of silica and iron oxides/oxhydroxides form up to T~100°C.

For a given W/R and T, the volume of silica in a secondary assemblage will increase with a decrease of the solution pH. At pH>~3, some silica may form in some systems, but secondary assemblages also consist of phyllosilicates, iron oxides, zeolites, and/or carbonates.

Silica deposition from cooling fluids: If equilibrium cooling of high-T solutions is modeled, for example from 200°C to 0°C, secondary mineral assemblages dominated by silica can form over a wide range of pH at 0°C. When systems equilibrate at high T, only some silica (more at lower initial pH) and many other minerals (e.g., phyllosilicates) form. The solution remaining at high T will have been neutralized in the process of water-rock interaction, in some cases to relatively high pH (as high as ~10). If the remaining solution is then cooled, silica that was still in solution precipitates. Our models show that if this cooled solution is 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. These silica-dominated assemblages would have greater volumes of silica if cooled from higher T (Fig. 4), if the system is higher W/R (not shown), or lower pH (Fig. 4). These silica-dominated deposits do not generally have Ti-oxide phases present, as Ti minerals tend to precipitate at higher T.

Summary and Implications: Without fluid cooling, silica-dominated assemblages only formed at low T, low pH, and high W/R ratios. Ti-bearing phases occur with the silica, consistent with observations in
Gusev crater [6]. High \( W/R \) conditions may imply fluid flow (e.g., spring discharge). Without flow of solutions, which is required to transport and remove elements, silica would be a small component of surface deposits formed through cooling or evaporation/freezing in place.

In the case of cooling of hydrothermal fluids, silica-dominated assemblages can form over a much larger range of pH values, initial temperatures, and \( W/R \) values. However, these assemblages generally do not have significant Ti-bearing phases.

Overall, these results suggest that the Gusev deposits, and other silica deposits on Mars, could form from high or low \( T \), but low pH (\(<\sim 2-3\) ), flowing solutions, for example in spring settings. However, for the Gusev materials, if Ti-materials are not part of a lag deposit and instead result from dissolution and precipitation, the low-\( T \) setting may be more likely to produce those silica deposits that are also TiO\(_2\) rich.

**References:**


![Figure 1](image1.png)  
**Figure 1.** Equilibrium mineral assemblage with temperature, from a fixed pH 1, \( W/R=100 \) run.

![Figure 2](image2.png)  
**Figure 2.** Equilibrium mineral assemblage with temperature, from a fixed pH 3, \( W/R=100 \) run.

![Figure 3](image3.png)  
**Figure 3.** Equilibrium mineral assemblages with temperature in an initial pH = 1 and \( W/R = 1000 \) system.

![Figure 4](image4.png)  
**Figure 4.** Volume of silica formed after solution flow and cooling from several temperatures (200°C, 100°C and 50°C) to 0°C, in \( W/R = 1000 \) systems of several initial pHs. The pH 5 and 7 lines overlap.