EFFECT OF TEMPERATURE ON SILICA FORMATION DURING ACID-BASALT ALTERATION: CHEMICAL EQUILIBRIUM CONSTRAINTS. A. C. McAdam[1], M. Yu. Zolotov[2], M. V. Mironenko[3], and T. G. Sharp[2], [1]Atmospheric Experiments Laboratory, Code 699, Goddard Space Flight Center, Greenbelt, MD 20771, Amy.McAdam-1@nasa.gov, [2]School of Earth & Space Exploration, Arizona State University, Tempe, AZ 85287-1404, Amy.McAdam-1@nasa.gov, [3]Vernadsky 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 % SiO_2) 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 H_2SO_4-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 200ºC were used; an upper limit of 200ºC 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 O_2 and CO_2. 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<~25ºC, high W/Rs (~10^2-10^4), 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/oxyhydroxides (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 $W/R=10^3$ 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/oxyhydroxides 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 200ºC to 0ºC, secondary mineral assemblages dominated by silica can form over a wide range of pH at 0ºC. 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 (<~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.

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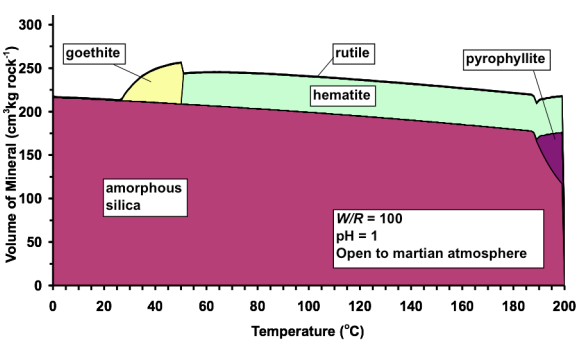

Figure 1. Equilibrium mineral assemblage with temperature, from a fixed pH 1, *W/R*=100 run.

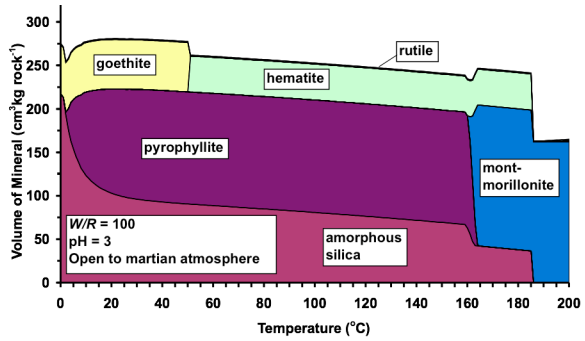

Figure 2. Equilibrium mineral assemblage with temperature, from a fixed pH 3, *W/R*=100 run.

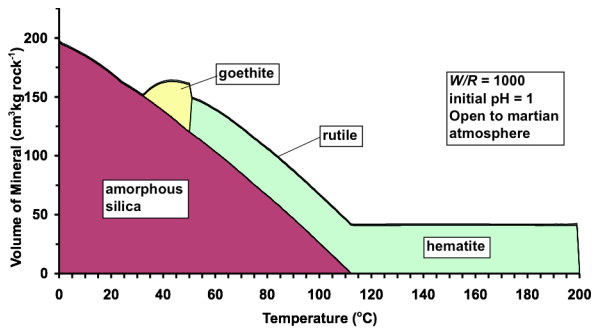

Figure 3. Equlibrium mineral assemblages with temperature in an initial pH = 1 and *W/R* = 1000 system.

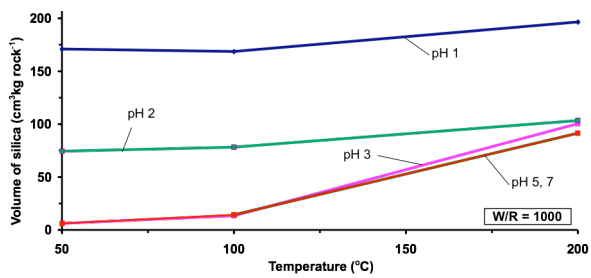

Figure 4. Volume of silica formed after solution flow and cooling from several temperatures (200°C, 100 °C and 50°C) to 0°C, in *W/R* = 1000 systems of several initial pHs. The pH 5 and 7 lines overlap.