Laboratory simulations of acid-sulfate weathering under volcanic hydrothermal conditions: Implications for early Mars

Emma C. Marcucci1,2,3 and Brian M. Hynek1,2

1Department of Geological Sciences, University of Colorado Boulder, Boulder, Colorado, USA, 2Laboratory for Atmospheric and Space Physics, University of Colorado Boulder, Boulder, Colorado, USA, 3Now at Geophysical Institute, University of Alaska Fairbanks, Fairbanks, Alaska, USA

Abstract We have completed laboratory experiments and thermochemical equilibrium models to investigate secondary mineral formation under conditions akin to volcanic, hydrothermal acid-sulfate weathering systems. Our research used the basaltic mineralogy at Cerro Negro Volcano, Nicaragua, characterized by plagioclase, pyroxene, olivine, and volcanic glass. These individual minerals and whole-rock field samples were reacted in the laboratory with 1 molal sulfuric acid at varying temperatures (65, 150, and 200°C), fluidrock weight ratios (1:1, 4:1, and 10:1), and durations (1–60 days). Thermochemical equilibrium models were developed using Geochemist’s Workbench. To understand the reaction products and fluids, we employed scanning electron microscopy/energy dispersive spectroscopy, X-ray diffraction, and inductively coupled plasma-atomic emission spectroscopy. The results of our experiments and models yielded major alteration minerals that include anhydrite, natroalunite, minor iron oxide, and amorphous Al-Si gel. We found that variations in experimental parameters did not drastically change the suite of minerals produced; instead, abundance, size, and crystallographic shape changed. Our results also suggest that it is essential to separate alteration minerals that include anhydrite, natroalunite, minor iron oxide, and amorphous Al-Si gel. We found that variations in experimental parameters did not drastically change the suite of minerals produced; instead, abundance, size, and crystallographic shape changed. Our results also suggest that it is essential to separate alteration phases formed during experiments from those formed during fluid evaporation to fully understand the reaction processes. Our laboratory reacted and model predicted products are consistent with the mineralogy observed at places on Mars. However, our results indicate that determination of the formation conditions requires microscopic imagery and regional context, as well as a thorough understanding of contributions from both experiment precipitation and fluid evaporation minerals.

1. Introduction

The first indications that sulfate salts existed on Mars came from the Viking missions. High concentrations of sulfur in soil samples suggested sulfate-cemented fines formed pebbles and duricrusts [e.g., Toulmin et al., 1977]. Soils studied by the Pathfinder rover had some sulfate, but they were depleted with respect to Viking levels [Bell et al., 2000], which has been attributed to instrument resolution, masking differences, or a different kind of soil. More recently, Phoenix used water chemistry experiments to detect soluble ionic species consistent with Mg or Ca sulfate [Kounaves et al., 2010]. Extensive observations of the Martian surface by the Mars Exploration Rovers (MERs) and the Observatoire pour la Minéralogie, l’Eau, les Glaces et l’Activité (OMEGA) and Compact Reconnaissance Imaging Spectrometer (CRISM) instruments on board orbiters identified numerous sulfate mineral deposits widespread on the planet [e.g., Gendrin et al., 2005; Squyres et al., 2006, 2007; Murchie et al., 2009]. Concordant and ongoing remote sensing results from the OMEGA and CRISM instruments have revealed sulfate deposits in discrete locales that are globally distributed. Data from visible and near-infrared spectroscopy have matched bands of specific spectra to kieserite (MgSO₄ · H₂O) and gypsum (CaSO₄ · 2H₂O), as well as other polyhydrated sulfates [Gendrin et al., 2005; Bishop et al., 2009; Ehlmann et al., 2009; Murchie et al., 2009; Wray et al., 2009a, 2009b]. Often the spectra for the latter cannot be uniquely assigned to specific minerals (thus the general polyhydrated identification) but may include epsomite (MgSO₄ · 5H₂O), hexahydrate (MgSO₄ · 6H₂O), starkeyite (MgSO₄ · 4H₂O), melanterite (FeSO₄ · 7H₂O), ferricopiapite (Fe₂/₃Fe³⁺₄(SO₄)₃(OH)₂ · 20H₂O), copiapite (Fe²⁺Fe³⁺₄(SO₄)₃(OH)₂ · 20H₂O), or halotrichite (FeAl₂(SO₄)₄ · 22H₂O) [Gendrin et al., 2005; Bishop et al., 2009].

Supporting Information:

Table S1
Table S2
Table S3
Table S4
Table S5
Table S6

Correspondence to:
E. C. Marcucci, emma.marcucci@colorado.edu

Citation:
Marcucci, E. C., and B. M. Hynek (2014), Laboratory simulations of acid-sulfate weathering under volcanic hydrothermal conditions: Implications for early Mars, J. Geophys. Res. Planets, 119, 679–703, doi:10.1002/2013JE004439.

Received 23 MAY 2013
Accepted 27 FEB 2014
Accepted article online 4 MAR 2014
Published online 28 MAR 2014
The interior layered deposits of Valles Marineris and associated chaos regions contain the most aerially extensive sulfate deposits identified to date by OMEGA and CRISM [e.g., Choynacki and Hynek, 2008; Murchie et al., 2009]. Areas with deposits of hydrated silica and a hydroxylated ferric sulfate, hydronium jarosite suggest an acidic, hydrothermal origin [Milliken et al., 2008; Bishop et al., 2009].

The Columbia Hills regions of Gusev crater contain a silica-rich material and Fe phases, magnetite (Fe₃O₄), and nanophase oxides [Squyres et al., 2007]. Initial textural and morphological clues, like fine layering and a bomb sag, and chemical clues, such as high-volatile content, at Gusev crater support a pyroclastic origin for the deposits known as Home Plate [Arvidson et al., 2006; Squyres et al., 2007; Schmidt et al., 2009; Ruff et al., 2011]. The Home Plate deposits and Paso Robles soils in Gusev crater consist of silica-rich deposits and ferric sulfates that are thought to represent volcanic material hydrothermally altered by acidic gas emissions and/or hot springs [e.g., Lane et al., 2008; Squyres et al., 2008; Yen et al., 2008; Schmidt et al., 2009; Ruff et al., 2011].

Sulfates can form in a wide variety of environments. Suggested mechanisms for the formation of the Martian deposits include evaporation of briny water [Squyres et al., 2004, 2006; McLennan et al., 2005], distribution of meteorite impact ejecta [Knauth et al., 2005], formation in dirty ice [Niles and Michalski, 2009], condensation of volcanic acid fog [Banin et al., 1997; Tosca et al., 2004], and exposure to hydrothermal systems [McCollom and Hynek, 2005; Squyres et al., 2007; Choynacki and Hynek, 2008; Ruff et al., 2011]. Although each of these formation mechanisms can plausibly produce sulfate deposits, they should have distinct geomorphic and regional expressions and it is likely that various formation mechanisms occurred on the surface throughout Martian history. The ability to distinguish among the formation mechanisms is critical for understanding local geologic history and evolution. This differentiation requires an understanding of the geochemical reaction pathways, how mineral products may vary within each due to environmental conditions, as well as how the sulfates fit the geologic and geomorphic context. Additionally, each mechanism has different implications for the role of liquid water, hence past habitability potential of the planet. This work focuses on characterizing the expression of acid-sulfate alteration in volcanic environments.

Numerous studies have examined basalt weathering in the field, by laboratory experiments, and with thermodynamic/kinetic models. Each of these methods has utilized different pH conditions, temperatures, and solution compositions. Basalt weathering is influenced by solution temperature and pH as well as mineral precipitation. Mars analog work has examined the acid-sulfate weathering of basalt, but the experiments to date have generally focused on lower temperatures or restricted parameter space [Banin et al., 1997; Tosca et al., 2004, 2005; Golden et al., 2005; Hurowitz et al., 2005; Zolotov and Mironenko, 2007; McAdam et al., 2008; Dehouck et al., 2012]; they were not necessarily aimed at high-temperature, volcanic environments. Additionally, of the previous studies, only Hurowitz et al. [2005] took evaporation into consideration as a separate phase. Tosca et al. [2004] and Banin et al. [1997] evaporated fluid without removing the grain products. In these previous studies, a variety of sulfates formed with some additional amorphous silica and iron oxides. However, all studies attributed the formation of the sulfates to evaporation. Experimental work of McCollom et al. [2013] examined acid-sulfate alteration of Cerro Negro basalt cinders and is most similar to the experiments presented in this paper. Alteration of these cinders dominantly produced amorphous silica, anhydrite, Fe-bearing natroalunite, with lesser amounts of iron oxides and sulfates, including hexahydrate in experiments with low fluid:rock ratios. Modeling done in conjunction with these experiments produced similar alteration minerals [McCollom et al., 2013].

Similarly, there is limited thermodynamic modeling work related to Mars under acidic conditions. Two studies that have created extensive models were run using 0°C or focused on the evaporation process [Zolotov and Mironenko, 2007; McAdam et al., 2008]. While the models of Zolotov and Mironenko [2007] detailed both alteration and freezing/evaporation minerals, the low temperature used is not relevant to hydrothermal systems. The models showed formation of amorphous silica, Fe-hydroxides, and then phyllosilicates as the main alteration products. Limited gypsum was also formed under very low pH conditions. Additional Mg, Fe, and Ca sulfates formed during the progression of the freezing model. Similar sulfates formed in evaporation models created for the Meridiani Planum system [Tosca et al., 2005]. The 0°C models found that plagioclase weathers more slowly than pyroxene and olivine [Zolotov and Mironenko, 2007; McAdam et al., 2008]. Berger et al. [2009] also used 0°C in their models; however, their very low pH, pure sulfuric acid, and low fluid:rock ratio are more akin to the experiments and models presented in this paper. Under these conditions the alteration mineralogy was composed of amorphous silica and jarosite, which is consistent with alteration
mineralogy at Meridiani Planum. As the system evolved Mg, Ca, and Fe sulfates formed and phyllosilicates became more stable [Berger et al., 2009].

To further elucidate acid-sulfate alteration in a volcanic system, we based our study on Cerro Negro Volcano in Nicaragua, which has been studied as an analog for this process on ancient Mars [Hynek et al., 2011, 2013; Rogers et al., 2011; Marcucci et al., 2013; McCollom et al., 2013]. Cerro Negro (CN) is a young, active volcanic complex in western Nicaragua and its eruptive products are composed of plagioclase, olivine, and pyroxene phenocrysts, glass, and titanian magnetite (Fe2+(Fe3+,Ti)2O4) [e.g., Walker and Carr, 1986]. It first erupted in 1850; the most recent eruptions occurred in 1992, 1995, and 1999. This volcano was chosen as a Mars analog because its lithology closely matches that of Martian bedrock and meteorites, although iron content is lower at CN (Figure 1). This is significant because parent rock lithology controls fluid composition, which in turn controls secondary mineralogy [Tosca et al., 2004]. It is also a young volcano with a well recorded history and ongoing S-rich fumarolic activity allows real-time observations of alteration. Differences can be examined between alteration sites that have been exposed for varying lengths of time based on eruption date (few years to decades). While other Mars analog sites have been used to examine acid-sulfate weathering, CN more accurately represents the composition of analyzed Martian rocks and possible conditions for an early hydrothermal volcanic environment on Mars; it also has extensive ongoing alteration. Here we report results from experiments and models used to characterize the chemical and mineralogical pathways to assess basaltic acid-sulfate alteration at CN and in the broader context, a type of alteration that could form the sulfates formed on Mars early in its history.

Experiments were designed to test a range of parameters, including mineral type, weathering duration, fluid:rock weight ratio, and temperature. The goal was to characterize the acid-sulfate weathering reactions occurring at Cerro Negro and ultimately on early Mars. Our work differs from previous work in three ways: (1) the hottest experiments were conducted at a temperature higher than most previous Mars laboratory work, (2) we separated the phases precipitated during the experiment and those precipitated during the evaporation of fluid, and (3) we use a combination of models and experiments to more fully understand the reaction pathways. Our goal was to use a systematic approach by varying initial parameters to determine if they produce diagnostic mineral suites or features that can be used to characterize acid-sulfate weathering in a relic hydrothermal system on Mars, such as the Paso Robles soils or Home Plate [Squyres et al., 2007; Lane et al., 2008; Yen et al., 2008; Ruff et al., 2011]. Key questions we address include the following: Which secondary minerals do specific primary minerals produce during weathering? Do variations in duration, fluid:rock ratio, or temperature create distinct characteristics in the secondary mineralogy? Do these experiments yield insights into the reaction kinetics?

2. Methods

2.1. Experiments

We reacted pure minerals representative of CN basalt composition as well as whole-rock field samples. The CN pyroxene has a calcium and magnesium rich composition [Walker and Carr, 1986; Ruggensack et al., 1997], so augite was chosen as the representative mineral [Hoch et al., 1996] (Table 1). The CN plagioclase is calcium-rich and bytownite was used in experiments [Morrison et al., 1983]. San Carlos olivine was used to simulate the CN olivine. San Carlos olivine is less Fe-rich than CN olivine; however, it was a readily available composition most similar to CN. All minerals were acquired from Ward's Natural Science and prepared by grinding, sieving, and rinsing for a consistent grain size of 106–212 microns for uniformity between starting materials. Unaltered CN cinders collected during a field campaign from the 1999 cone were also reacted.
The dominant alteration environment at CN is a gas-dominated fumarolic system. In such environments, acidic steam condenses on rock surfaces and alteration takes place at rock/atmosphere boundaries thus representing a nearly closed system. Open system processes such as precipitation on rock surfaces do occur in the environment. However, the closed system aspects exert the greatest control on the secondary mineralogy. For the purposes of this paper, we consider CN as a closed system and used sealed reaction vessels to represent the alteration of the rocks from condensed steam that accumulates on their surfaces. This is a straightforward experimental setup that could be run in bulk in the laboratory. Additionally, we chose to use H$_2$SO$_4$ exclusively to isolate the sulfur reactions and explore the formation of sulfates specifically. The presence of chloride minerals show that other acids (e.g., HCl) were present on Mars; however, we were most interested in the dominance of sulfur in solutions expected for Mars and thus considered chlorides and other acids to be beyond the scope of this study.

The majority of experiments presented in this paper had an experimental temperature of 65°C. Figure 2 displays a summary of experimental design. In Savillex perfluoroalkoxy (PFA) acid digestion vessels, approximately 3 g of mineral grains or CN basalt were mixed by weight with 1 molar (m)
These reactions occurred in a Parr acid digestion bomb, which consists of a polytetrafluoroethylene (PTFE) liner inside a sealed metal pressure vessel. The highest experimental temperature, 200°C, was limited by the specifications of the Parr reaction vessel. A middle temperature of 150°C was chosen as a point between the high and low temperatures. Mass loss for these containers over the duration of the experiments was <0.05%. Given the similarity of alteration products despite the large range of temperature conditions, we decreased the number of high-temperature experiments completed. Three minerals—pyroxene, plagioclase, and olivine—were reacted at a 4:1 fluid:rock ratio with 1 m H₂SO₄ for 1 day at 150 and 200°C; pyroxene and olivine were also reacted at 1:1 and 10:1 fluid:rock ratios (Figure 2 and Table 2). Savillex vessels were sealed using a hand wrench per manufacturer specifications. High oxidation of iron in olivine experiments indicated a headspace of Earth atmosphere and potential penetration of atmospheric O₂ into these containers. These experiments were reacted in the presence of Earth atmosphere to represent conditions at terrestrial analog sites. The containers were sufficiently sealed against loss from vapor escape below 70°C (limiting experimental temperature) with less than 0.1% mass loss in containers. We chose 3 g as the total amount of initial material because it provided sufficient sample for analysis on multiple instruments. We chose the 4:1 fluid:rock weight ratio for comparison to previous experiments that used a similar ratio [McCollom et al., 2013]. We used a 1:1 ratio to represent a much lower fluid:rock ratio, simulating thin surface coatings of acid on rocks, but still providing enough fluid for analysis. For a high fluid:rock ratio, 10:1 was chosen based on the volume capacity of the reaction vessels. These above experiments were conducted for 3 to 60 days, and a single fluid:rock ratio (4:1) experiment set was reacted for 7.5 months (Table 2). Durations were chosen to examine regular intervals within the 60 day period for a reasonable total completion time given the number of experiments to be completed.

Each time step was a discrete setup so that containers remained closed and undisturbed throughout the duration of the experiment (Figure 2). At the termination of each step, a fluid sample was taken and diluted; nitric acid was used to acidify samples above pH of 3 to retain dissolved species. For the first set of experiments, remaining fluid was siphoned off and discarded. Grains were subsequently air-dried at ambient temperatures. Sampling procedures were refined approximately halfway through the experimental study when we recognized the importance of evaporation producing alteration products while the grains dried. New procedures included filtering the fluid sample, retaining the excess fluid for evaporation at room temperature, and rinsing the grain products with ethanol while filtering with a handheld vacuum pump (hereafter referred to as rinse-filtering). This added step separated minerals precipitated during fluid evaporation from the minerals precipitated during the experiments. For clarity, the data presented in this paper only represent the rinsed experiments.

To examine the secondary mineralogy produced at higher temperatures, an abbreviated series of experiments ran at 150 and 200°C with similar mineral preparation as the lower-temperature experiments (Figure 2). These reactions occurred in a Parr acid digestion bomb, which consists of a polytetrafluoroethylene (PTFE) liner inside a sealed metal pressure vessel. The highest experimental temperature, 200°C, was limited by the specifications of the Parr reaction vessel. A middle temperature of 150°C was chosen as a point between the high and low temperatures. Mass loss for these containers over the duration of the experiments was <0.05%. Given the similarity of alteration products despite the large range of temperature conditions, we decreased the number of high-temperature experiments completed. Three minerals—pyroxene, plagioclase, and olivine—were reacted at a 4:1 fluid:rock ratio with 1 m H₂SO₄ for 1 day at 150 and 200°C; pyroxene and olivine were also reacted at 1:1 and 10:1 fluid:rock ratios. To examine the secondary mineralogy produced at higher temperatures, an abbreviated series of experiments ran at 150 and 200°C with similar mineral preparation as the lower-temperature experiments (Figure 2). These reactions occurred in a Parr acid digestion bomb, which consists of a polytetrafluoroethylene (PTFE) liner inside a sealed metal pressure vessel. The highest experimental temperature, 200°C, was limited by the specifications of the Parr reaction vessel. A middle temperature of 150°C was chosen as a point between the high and low temperatures. Mass loss for these containers over the duration of the experiments was <0.05%. Given the similarity of alteration products despite the large range of temperature conditions, we decreased the number of high-temperature experiments completed. Three minerals—pyroxene, plagioclase, and olivine—were reacted at a 4:1 fluid:rock ratio with 1 m H₂SO₄ for 1 day at 150 and 200°C; pyroxene and olivine were also reacted at 1:1 and 10:1 fluid:rock ratios. To examine the secondary mineralogy produced at higher temperatures, an abbreviated series of experiments ran at 150 and 200°C with similar mineral preparation as the lower-temperature experiments (Figure 2). These reactions occurred in a Parr acid digestion bomb, which consists of a polytetrafluoroethylene (PTFE) liner inside a sealed metal pressure vessel. The highest experimental temperature, 200°C, was limited by the specifications of the Parr reaction vessel. A middle temperature of 150°C was chosen as a point between the high and low temperatures. Mass loss for these containers over the duration of the experiments was <0.05%. Given the similarity of alteration products despite the large range of temperature conditions, we decreased the number of high-temperature experiments completed. Three minerals—pyroxene, plagioclase, and olivine—were reacted at a 4:1 fluid:rock ratio with 1 m H₂SO₄ for 1 day at 150 and 200°C; pyroxene and olivine were also reacted at 1:1 and 10:1 fluid:rock ratios. To examine the secondary mineralogy produced at higher temperatures, an abbreviated series of experiments ran at 150 and 200°C with similar mineral preparation as the lower-temperature experiments (Figure 2). These reactions occurred in a Parr acid digestion bomb, which consists of a polytetrafluoroethylene (PTFE) liner inside a sealed metal pressure vessel. The highest experimental temperature, 200°C, was limited by the specifications of the Parr reaction vessel. A middle temperature of 150°C was chosen as a point between the high and low temperatures. Mass loss for these containers over the duration of the experiments was <0.05%. Given the similarity of alteration products despite the large range of temperature conditions, we decreased the number of high-temperature experiments completed. Three minerals—pyroxene, plagioclase, and olivine—were reacted at a 4:1 fluid:rock ratio with 1 m H₂SO₄ for 1 day at 150 and 200°C; pyroxene and olivine were also reacted at 1:1 and 10:1 fluid:rock ratios.

### Table 2. Parameter Variations for Experiments and Models

| Models          | Experiments                                                                 |
|-----------------|-----------------------------------------------------------------------------|
| Fluid           | 1 M H₂SO₄                                                                   |
| Minerals        | Plagioclase, pyroxene, and olivine                                          |
| Fluid:rock ratio| 1:1, 4:1, and 10:1 (weight)                                                |
| Temperature     | 65°C, 150°C, and 200°C                                                     |
| Duration        | For 4:1 experiments: 3, 6, 9, 12, 30, 35, 40 days, and 7.5 months. For 1:1 and 10:1 experiments: 3, 12, 30, and 60 days |
| Added steps     | Filtering fluid sample and rinsing-filtering products with ethanol          |
| Analysis        | pH², XRD, SEM/EDS, ICP-AES, and petrography                                 |

*The pH was measured at experiment termination at room temperature, and GWB was used to determine the actual pH using a one-step or two-step speciation calculation. Fluid was first speciated in REACT at 25°C, while balancing on sulfate. The system was then respicated with the adjusted sulfate value at 65°C, allowing charge balance on pH, giving in situ pH and speciation. Due to available supplies, pH was initially measured using pH paper, which had a lower limit of 0.8, although actual pH was lower in some cases. In cases where pH was measured at this limit, initial balancing on sulfate caused too great a compensation of sulfate in the charge balance, skewing speciation results. In cases where pH was measured as 0.8, fluid was balanced on pH at 65°C in one step. This affected augite experiments in the 4:1 and 10:1 fluid:rock ratio experiments. This issue was rectified with the purchase of a micropH meter, used in 60 day, 1:1 and 10:1 experiments, all CN cinder experiments, and subsequent higher-temperature experiments.*
olivine were also reacted for 15 days at 200°C. Experimental products were processed for analysis by rinse-filtering solid products and evaporating fluid remnants.

### 2.2. Experimental Analysis

Solid products were analyzed for elemental, mineralogical, and crystallographic variations. We prepared grain mounts to assess the mineralogy and magnitude of alteration for 15 samples of primary and altered materials and observed by a petrographic microscope using both plain and crossed-polarizing light. We used a Scintag X-ray diffraction (XRD) instrument to examine the solid reactants and products for detailed mineralogy. Diffraction patterns were collected for the range of 2–65° with a 2°/min counting time, 35 mA current, and —40 kV voltage. A JEOL scanning electron microscope (SEM) showed the microscopic crystal formations and the accompanying energy dispersive spectrometer (EDS) measured the associated elemental composition using an accelerating voltage between 10 and 15 kV. Fluid aliquots were analyzed for major, minor, and trace components using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). We completed fluid analysis, including pH measurements, at 25°C rather than experimental temperature. Because fluid chemistry and speciation is temperature dependent, the results of fluid analysis were not entirely representative of in situ chemistry, which ultimately dictates precipitation. The in situ fluid speciation was calculated using Geochemist’s Workbench (see next section).

### 2.3. Thermodynamic Equilibrium Models

To further understand the alteration pathways within the experiments, we built thermodynamic models to replicate the experiments. We completed our analysis using Geochemist’s Workbench (GWB) [Bethke, 2008], a software program that models chemical reactions by calculating thermodynamic equilibria. Although the program also has the ability to incorporate kinetics into the reaction progress, that option was not used in our models because of a lack of experimental constraints at high temperatures. We used an expanded version of the GWB thermodynamic database, “thermo.dat.” The species activities in the models were calculated using the “B-dot equations” (an extended version of the Debye-Hückel equation), which is valid to concentrations of 3 m [Bethke, 2008]. Our database was modified to include a broader range of sulfate mineral data than the standard libraries, such as complex sulfate natroalunites (NaAl3(SO4)2(OH)6), to better represent our potential experimental products. The thermodynamic information for added minerals was calculated using SUPCRT92 [Johnson et al., 1992] and summarized in McCollom et al. [2013]. We outline a specific model example in section 3.

In brief, a reaction was set up by creating a sulfuric acid solution at a set temperature and incrementally adding solid material to the solution. We held the temperature constant throughout the reaction. Because kinetics were not incorporated into our models, we suppressed more thermodynamically stable, but kinetically inhibited crystalline forms for silica, such as quartz, tridymite, coesite, and cristobalite, using controls in GWB to disallow their growth. The models were used to elucidate reaction pathways of the experiments and ultimately compare to the field and Mars. Therefore, we only suppressed phases that were known to be absent from the Cerro Negro field site. A related paper [McCollom et al., 2013] presents results in which phyllosilicate phases were also suppressed since they were not present in experimental results.

A second use for GWB was to determine the in situ experimental pH and fluid speciation. Elemental fluid composition measured by ICP-AES was first speciated in REACT in a one- or two-step process depending on pH (see footnote of Table 2). The pH inputs in the experiments were measured with pH paper and an Accumet® micropH meter.

### 3. Results

Alteration occurred very rapidly in plagioclase, pyroxene, and olivine experiments with extensive macroscopic and microscopic alteration observed even in the shortest time step (Table 3). Table 3 outlines the experimental minerals detected for each starting material according to type and instrument. It is divided into two main parts and two subdivisions. Table 3 presents the minerals formed during the experiment and the minerals formed during evaporation. These sections are each subdivided so that minerals detected by XRD are shown first and trace minerals identified by SEM shown second. Additionally, the suites of secondary minerals were different for each primary mineral but were consistent for that mineral regardless of duration, fluid:rock ratio, and temperature. Variations in these three parameters, temperature, fluid:rock ratio, and
duration, affected crystal abundance, size, and morphology, which we detail in the following sections and Table S2.

3.1. Experimental Products of 65°C Reactions

3.1.1. Plagioclase (Bytownite)

The macroscopic alteration evident at the end of each plagioclase experiment was a clear gel on top of the largely unaltered grains (Figure 3a). It was hard to remove all traces of this gel in rinsed experiments; as a result, trace amounts of gel remained with the grain products. The gel also likely included entrained fluid. This gel material dominated grain mount petrography, and there were no changes in grain appearance observed with time. However, differences in secondary products were observed on the microscopic scale through XRD and SEM. The main experimental products for all timescales were natroalunite, amorphous silica, and alunogen (Al₂(SO₄)₃ · 17H₂O). Gypsum was also present and likely precipitated during evaporation of experimental fluid.

XRD patterns of rinsed grain products consisted mainly of primary material with some gypsum and alunogen peaks (Table 3 and Figure 4a). Based on the elevated temperature of experiments and geochemical models (section 4.4), the presence of gypsum was unexpected. We attribute the formation of gypsum, instead of the dehydrated Ca sulfate anhydrite, to the evaporation of fluid entrained in the gel. SEM confirmed the presence...
of a Ca sulfate phase in the alteration products and showed two additional alteration phases not identified by XRD (Table 3 and Figure 5). The additional phases were distinct cubic crystals and fans or blocky surface coatings. The EDS data for the cubic crystals determined these were consistent with natroalunite and had an average composition of $\text{Na}_{0.67}(\text{H}_3\text{O})_{0.33}\text{Al}_{2.15}(\text{SO}_4)_{1.34}(\text{OH})_{3.44}(\text{H}_2\text{O})_{2.56}$. Composition was calculated from EDS data using the techniques of Drouet and Navrotsky [2003], which assumes two $\text{SO}_4$ per unit formula and hydronium ($\text{H}_3\text{O}$) to complete the $1^+$ ion balance. SEM images showed that increasing fluid:rock ratio
decreased the relative abundance of natroalunite, and no natroalunite was apparent in the 10:1 ratio experiments, which is related to the ability of higher fluid:rock ratios to hold more dissolved species (Figures 5b and 5c). The amorphous surface fans and blocks had an EDS signature of Al-S-Si, with blockier features having a higher Si content than the fans (Figure 5a), hereafter gel features (surface coatings) are called amorphous silica. The fans were seen in a prior set of whole basalt experiments, which also formed gels [McCollom et al., 2010, 2013]. There were noticeably less Al-S-Si gel features in rinsed samples than in the unrinsed ones.

Evaporation of experimental fluid produced sufficient material for XRD analysis in only one case, and alunogen was the main product identified (Table 3). All evaporation precipitates were examined with SEM/EDS, which showed Ca and Al sulfate. The Al sulfate crystal likely accounts for the alunogen XRD peaks, while the Ca sulfate relates to the gypsum.

3.1.2. Pyroxene (Augite)

The pyroxene experiments yielded the most distinctive and diverse suite of minerals formed during both the experiment and fluid evaporation. Clear, acicular crystals, which were approximately 1 cm in length and dried white were visible at the end of each experiment (Figure 3b). Despite these distinct macroscopic crystals, petrographic images of grain mounts showed very little change from the original pyroxene. XRD patterns showed predominantly augite with additional peaks identified as anhydrite, which correspond to the macroscopic and microscopic crystals (Table 3 and Figures 4b and 6a). SEM/EDS measurements confirm that Ca sulfate was abundant as an alteration product. Grain characteristics observed in SEM images show that all mineral phases change in size and abundance with experiment duration and fluid:rock ratio. As may be expected, abundance increased with duration and lower fluid:rock ratio. Anhydrite alteration crystals were thinner, shorter, and more abundant with those parameters. While crystals in experiments with 10:1 ratios were still fine, they were less abundant. A unique feature of the macroscopic anhydrite crystals occurred in the 60 day, 1:1 ratio experiment where in addition to short rods, white spheres were visible to the naked eye (Figure 3e). SEM images showed that these spheres were a conglomeration of microscopic rods (Figure 6a).
The post experiment rinsing step was most critical for the pyroxene experiments, which had abundant and varying forms of evaporitic Mg sulfate evident in SEM images (Table 3 and Figures 6b–6f). The rinsed secondary products contained no Mg sulfates, while they dominated in the evaporated fluid. The universal Mg sulfate form was a dipyramid crystal (Figure 6e). Kieserite (MgSO$_4$·H$_2$O) and hexahydrite (MgSO$_4$·6H$_2$O) have similar crystal shape, and we hypothesize that one or both of these were the observed minerals. Given formation during evaporation at room temperature, thermodynamic stability suggests kieserite is the mostly likely mineral. The evaporitic Mg sulfates appeared in multiple crystal forms in SEM images of each fluid:rock ratio. The dipyramid crystals occurred in all experiments, but other crystal shapes were observed. Figure 6b shows that 1:1 experiments formed crystals that had spikes on a spherical surface, 4:1 had smoother spheres (Figure 6c), and 10:1 had mats of short rods (Figure 6d). There was also a decrease in crystal size with higher fluid:rock ratio.

Fe sulfate was also observed in SEM/EDS measurements of the evaporation products (Figure 6e and Table 3). While Mg sulfate was abundant in EDS measurements, the evaporation products measured by XRD included anhydrite, voltaite (K$_2$Fe$_5^{2+}$Fe$_3^{3+}$Al(SO$_4$)$_2$·18H$_2$O), and rhomboclase ((H$_5$O$_2$)$^+$Fe(SO$_4$)$_2$·2H$_2$O), which may correspond to the observed Fe sulfate. There was no readily apparent Si phase even though this element should be dissolving out of the primary material.

### 3.1.3. Olivine (Forsterite)

Olivine alteration had the greatest visible (Figure 3c) and microscopic surface alteration (Figure 7a). The mineral started as pale green grains and changed rapidly to an orange color. An opaque orange gel overlaid the grains. In addition, the fluid contained orange suspended particles and surface films. Altered olivine grains had visible dissolution pits in petrographic images. Only one experiment, the 3 day 10:1 setup, was visually distinctive from the other olivine experiments. It ended with chalky white grains, rather than the otherwise observed orange grains and gels. However, the XRD and SEM mineralogy was consistent with the other experiments. Trace amounts of oxidized iron controlled the alteration color, but alteration mineralogy...
was mainly amorphous silica with some Mg and Fe sulfates from evaporation of entrained fluid. Amorphous silica was detected by a small bump in the 18–22 2θ region on XRD diffractograms and supported by EDS detections of Si-rich gels. In addition to primary mineralogy, XRD analysis identified hydrated Mg sulfates, probably starkeyite and hexahydrite (MgSO₄ ·4H₂O and MgSO₄ ·6H₂O) (Table 3 and Figure 4c), which were likely an evaporation product. In SEM, virtually every surface was covered by coatings with no discernible shape that may be a mixture of amorphous silica and microcrystalline Mg sulfates. The coatings contained significant amounts of Si. While no distinct crystalline shapes were observed, the coatings did have a Mg sulfate signature in EDS measurements, potentially correlating to the XRD identified sulfates. The thick gels that resulted from these experiments were very difficult to completely rinse away, similar to the plagioclase experiments.

Figure 6. SEM images of pyroxene (augite) reacted with 1 m H₂SO₄ at 65°C. (a) Ca sulfate, identified by XRD as anhydrite (A) from a 4:1 ratio, 9 day experiment. (b) Mg sulfate (Mg) from an experiment with fluid:rock ratio of 1:1 and 12 day. The surface of this sphere has blades, compared to (c) another Mg sulfate sphere with a smoother surface from a 4:1 ratio, 9 day experiment. (d) Third example of Mg sulfate for a 10:1 ratio, 30 day experiments, in the form of a mat of short rods. There is also an increase in size with increasing fluid:rock ratio. (e) Platy Fe sulfate that is observed in evaporation products of the 10:1, 65°C, 60 day experiment. (f) Mg sulfates are products that form during evaporation (65°C, 10:1, 60 day). Later experiments retained and evaporated remaining experimental fluid, which produced numerous and abundant Mg sulfate precipitates. The dipyramid crystal shape is most similar to that of kieserite and hexahydrate.
fluid entrained in the remnant gel contributed Mg sulfate signatures to the analysis of alteration grain products and that Mg sulfates did not precipitate until the evaporation stage of experiments. When experimental fluid from olivine experiments was evaporated, Mg sulfates precipitated, similar to the pyroxene fluid evaporation results. XRD analysis of evaporation products showed pentahydrite (MgSO$_4$ $\cdot$ 5H$_2$O) and kieserite, supporting the general Mg sulfate signatures observed in SEM images (Table 3).

The only distinct forms found in SEM images of these experiments were occasional micron to submicron spheres with an Fe-O EDS signature. These may be an Fe oxide or hydroxide mineral, such as hematite or goethite (Table 3 and Figure 7b). In addition to the more common sphere shape, the Fe-O minerals also formed as a collection of radial spindles, resulting in a star-like form.

3.1.4. Cerro Negro 1999 Cinders

In the final stage of experimental work we reacted whole-rock cinders from the 1999 eruption of Cerro Negro. Since component minerals were reacted individually, those results helped interpret whole-rock reaction pathways. CN basalt is a phenocryst-rich rock composed of basaltic minerals with compositions similar to those of the minerals that were individually reacted, as well as volcanic glass (Table 1). Similar to plagioclase and olivine experiments, a translucent gel layer formed on top of the cinders (Figure 3d). The color and cohesiveness of the gel changed slightly based on the fluid:rock ratio. With increasing fluid:rock ratio it became more cohesive and restricted the degree of iron oxidation that could occur, resulting in a less orange-tinted gel. Alteration products measurable by XRD included gypsum and occasional alunogen (Table 3 and Figure 8a). There was also a minor amorphous Si bump at 18–22 2θ that could have been caused by the gel layer present or amorphous silica replacing phenocrysts (Figure 4d). This is the only silica secondary product and may represent weathering of volcanic glass. Microscopic examination with SEM/EDS identified Fe sulfate and more complex sulfates with Al-Na (natroalunite) and Mg-Al as the cations (Table 3 and Figures 8b–8d).

Evaporation products analyzed with XRD were composed of alunogen and hexahydrite. Hexahydride formation may be related to pyroxene dissolution and subsequent fluid evaporation (Table 3). SEM images of the evaporitic products from the 10:1 ratio experiments showed crystalline forms, which consisted of a Mg-Na sulfate that we could not identify. The models (see section 3.4.4) predicted the formation of mirabilite (Na$_2$SO$_4$ $\cdot$ 10H$_2$O), which could suggest that the Na portion of this unknown sulfate was a similar mineral.

3.2. High-Temperature Experiments at 150 and 200°C

To investigate the influence of formation temperature on alteration mineralogy, we ran experiments at three temperatures: 65, 150, and 200°C. Due to experimental and equipment limitations for high-temperature acidic experiments, we completed fewer 150 and 200°C experiments. This set of experiments was further abbreviated, because the first high-temperature experiments completed resulted in alteration products similar to those within the 65°C experiments. The most noticeable difference between the 65°C experiments and high-temperature experiments occurred in the olivine alteration, in which light green grains altered to a
dark purple color, rather than orange. This color change was an effect of Fe oxidation and likely attributable to the differences between the Parr and Savillex container seals.

Additional 15 day experiments were completed for pyroxene and olivine. GWB models predicted that these would have different alteration patterns at greater reaction progress, including phyllosilicates. However, the family of residual and evaporitic products again matched both shorter- and lower-temperature reactions. Microscopic changes in mineral crystal form, size, and abundance were observed in SEM images, similar to the changes seen due to duration and fluid:rock ratio at 65°C. For pyroxene experiments, the evaporitic Mg sulfates present at higher temperatures were spherical forms and often clumped. The Ca sulfate in these experiments was larger and blade-like in structure compared to the rectangular crystals of 65°C. Natroalunite crystals, formed in the plagioclase alteration experiments, increased in abundance in the higher-temperature experiments (Figure 5d). Corollary thermodynamic models predicted products that matched the experimental results.

3.3. Fluid Composition

Based on ICP-AES fluid analysis data, the species abundances for in situ experimental fluid composition were very similar for a given mineral and largely corresponded to the composition of the primary mineral (Table 4 and Tables S3 and S4 in the supporting information). Essentially, the minerals dissolve congruently, but some fractionation likely happens as indicated by the silica in gels. The general order of cation abundances for the fluids involved in the pyroxene experiments were Ca > Mg > Fe > Si > Al (due to trace impurities in the primary minerals there were minor amounts of Na > Mn > K that did not play a significant role in fluid speciation). Fluids in the olivine experiments followed a similar pattern for the elements that overlap: Mg > Fe > Si (with trace amounts of Ca > Mn > Na from impurities in starting material). The fluids from the plagioclase experiments yielded the following element pattern, from greatest to least concentration, Al > Si > Na > Ca (Mg > Fe > Mn from impurities). Finally, the CN 99 chemical trend was dominated by a combination of plagioclase and olivine: Al > Mg > Fe > Na > Ca > Si > Mn, in general. Notably, the Si
contents of the CN experiments were much lower than those of plagioclase or olivine experiments. Observable in Table 4 are drops in the concentrations of sulfate, Na, and Al in fluid for the plagioclase and CN 99 cinders experiments, which are likely related to the rapid saturation and precipitation of natroalunite mineral family phases. While the plagioclase experiment pH decreased, the CN cinders experiment pH increased. This may have been due to a thicker Al-Si gel that formed in the plagioclase experiments, cutting off dissolution which would continue to neutralize fluid acidity.

The fluid speciation was used to determine the saturation states of minerals (Tables S5 and S6). Saturation state is an indication of whether a fluid is concentrated enough to precipitate a given mineral. In general, the saturation states and minerals were comparable within a given fluid:rock ratio between plagioclase and CN 99 cinder experiments, and the lower fluid:rock ratios had overall higher saturation indices, including many phyllosilicates. Pyroxene and olivine experiments had similar mineral saturation indices for sulfates and silica polymorphs. In the 12 to 60 day, 1:1 ratio CN 99 experiments, Na and K were below the detection limit, so no

### Table 4. Experimental Fluid Compositiona

|                | Day 3 | Day 12 | Day 40 | Day 3 | Day 60 | Day 3 | Day 60 | Day 1 | Day 15 |
|----------------|-------|--------|--------|-------|--------|-------|--------|-------|--------|
| **Pyroxene**   |       |        |        |       |        |       |        |       |        |
| Al3+           | 4.22  | 5.89   | 6.38   | 39.5  | 38.3   | 4.53  | 8.84   | 13.9  | 17.8   |
| Ca2+           | 52.3  | 47.4   | 42.6   | 29.4  | 15.2   | 8.20  | 48.5   | 44.9  | 16.0   |
| Fe2+           | 18.3  | 29.1   | 38.5   | 45.8  | 93.4   | 5.65  | 23.5   | 41.7  | 65.2   |
| K+             | 0.422 | 0.367  | 0.219  | 0.692 | n.d.   | n.d.  | n.d.   | 0.878 | 0.959  |
| Mg2+           | 42.2  | 63.7   | 82.4   | 163   | 311    | 19.7  | 69.8   | 112   | 176    |
| Mn2+           | 0.464 | 0.78   | 1.05   | 0.845 | 3.77   | 0.101 | 0.625  | 1.08  | 1.71   |
| Na+            | 2.39  | 3.25   | 4.50   | 3.94  | 11.4   | 0.764 | 2.77   | 5.64  | 8.69   |
| SO42−          | 883   | 895    | 875    | 992   | 606    | 940   | 925    | 621   | 471    |
| SI2(aq)        | 5.88  | 5.60   | 5.64   | 3.25  | 4.58   | 4.40  | 5.12   | 11.3  | 19.9   |
| pH             | 0.256 | 0.28   | 0.322  | 0.379 | 1.627  | 0.145 | 0.264  | 0.659 | 0.698  |
| **Plagioclase**|       |        |        |       |        |       |        |       |        |
| Al3+           | 491   | 471    | 410    | 287   | 51.4   | 358   | 525    | 243   | 74.2   |
| Ca2+           | 16.1  | 15.0   | 13.2   | 7.82  | 5.83   | 21.6  | 16.7   | 9.81  | 8.19   |
| Fe2+           | 4.90  | 4.63   | 6.24   | 3.82  | 0.64   | 3.30  | 2.22   | 1.13  | 0.344  |
| Mg2+           | 6.45  | 6.31   | 6.24   | 9.84  | 11.5   | 3.71  | 4.52   | 10.4  | 9.24   |
| Mn2+           | 0.09  | 0.089  | 0.088  | 0.083 | 0.129  | 0.059 | 0.082  | 0.155 | 0.123  |
| Na+            | 79.6  | 72.7   | 56.8   | 71.3  | 0.147  | 60.9  | 78.0   | 11.5  | 0.756  |
| SO42−          | 807   | 767    | 668    | 447   | 95.0   | 706   | 851    | 420   | 186    |
| SI2(aq)        | 97.3  | 18.1   | 4.66   | 2.32  | 2.13   | 14.4  | 4.47   | 14.5  | 14.3   |
| K+             | n.d.  | n.d.   | n.d.   | 0.883 | n.d.   | n.d.  | n.d.   | n.d.  | n.d.   |
| pH             | 2.994 | 3.063  | 3.057  | 3.812 | 3.27   | 2.007 | 3.007  | 2.501 | 1.826  |
| **Olivine**    |       |        |        |       |        |       |        |       |        |
| Ca2+           | 1.59  | 1.77   | 2.5    | 2.67  | 1.67   | 1.02  | 1.19   | 2.11  | 1.81   |
| Fe2+           | 71.7  | 17.1   | 0.47   | 4.43  | 0.32   | 85.9  | 13.6   | 68.3  | 30.2   |
| Mg2+           | 916   | 1040   | 1060   | 941   | 834    | 856   | 1080   | 1020  | 784    |
| Mn2+           | 1.37  | 1.56   | 1.46   | 1.38  | 1.04   | 1.30  | 1.69   | 1.77  | 1.21   |
| SO42−          | 993   | 1060   | 1060   | 950   | 838    | 1020  | 1100   | 1170  | 830    |
| SI2(aq)        | 35    | 3.08   | 3.08   | 2.41  | 1.80   | 19.6  | 3.60   | 13.7  | 14.1   |
| pH             | 3.634 | 3.289  | 4.149  | 4.105 | 5.196  | 1.913 | 3.429  | 1.965 | 2.665  |
| **CN 99 Cinder**|      |        |        |       |        |       |        |       |        |
| Al3+           | 254   | 278    | 320    | 203   | 9.57   | 182   | 240    | --    | --     |
| Ca2+           | 12.6  | 13.0   | 12.6   | 12.0  | 8.25   | 22.1  | 17.8   | --    | --     |
| Fe2+           | 69.3  | 33.5   | 7.77   | 34.5  | 0.55   | 384   | 51.5   | --    | --     |
| Mg2+           | 184   | 194    | 165    | 181   | 181    | 81.5  | 82.6   | --    | --     |
| Mn2+           | 1.31  | 1.41   | 1.22   | 1.36  | 1.37   | 0.62  | 0.804  | --    | --     |
| Na+            | 16.2  | 2.71   | 0.219  | 2.99  | n.d.   | 16.0  | 29.1   | --    | --     |
| SO42−          | 659   | 660    | 661    | 535   | 206    | 576   | 687    | --    | --     |
| SI2(aq)        | 4.87  | 4.48   | 4.44   | 7.93  | 7.74   | 3.52  | --     | --    | --     |
| K+             | n.d.  | n.d.   | n.d.   | n.d.  | 0.616  | 0.851 | --     | --    | --     |
| pH             | 3.054 | 3.083  | 3.162  | 3.125 | 3.57   | 1.631 | 1.707  | --    | --     |

aUnits in mmolality.
b“n.d.” (no data) represent measurements of experimental fluids where that ion was not detected.
natroalunite or alunite were predicted to form. The 10:1 plagioclase and CN 99 experiments had measurable K and thus alunite was a potential mineral phase, in addition to natroalunite. Alunite and natroalunite form a solid solution. Measureable K in higher fluid:rock ratios may be a result of the fluid's ability to retain acidity and continue dissolving primary minerals. Overall, the plagioclase and CN 99 cinder experiments had more than twice the number of possible minerals based on fluid chemistry than pyroxene and olivine experiments. This suggests that plagioclase was responsible for greater secondary mineralogy diversity in whole-rock experiments. Additionally, fluids from the plagioclase and CN 99 cinder experiments were more saturated for a number of phyllosilicates and, unexpectedly, natroalunite, with respect to the pyroxene and olivine experiments. For all experiments, silica phases and Ca sulfates (gypsum, anhydrite, and bassanite (CaSO₄ · 0.5H₂O)) were close to equilibrium. Mg sulfates, hexahydrite, epsomite, and kieserite were undersaturated in all experiments and would not precipitate until the fluid became more concentrated.

Because Mg²⁺ was a relatively conservative element and stayed in fluid until evaporation began, the amount of primary mineral dissolved can be estimated by the accumulation of Mg²⁺ in the fluid. However, plagioclase had trace to no Mg²⁺ or other conservative element; therefore, an amount of dissolution (by weight) was not calculated for plagioclase. The dissolution calculation did not take into account all elements or potential chemical interactions and should only be considered relative to each other. Mass loss from dissolution was estimated using the Mg²⁺ trends in fluid concentrations. Assuming no Mg²⁺ in the initial acidic fluid, all Mg²⁺ measured in fluid was a direct result of mineral dissolution. As an example calculation, if there was a 300 mm (mmol/kg water) increase in Mg²⁺ concentration and in a solution with 2.7 g of water, then there were 0.81 mmol of Mg²⁺ added to the entire fluid. This Mg²⁺ abundance was related to mineral weight using the mole fraction of Mg in the mineral and the mineral formula weight. For example, 0.87 mol Mg/mol pyroxene (augite) with a formula weight of 220.75 g/mol resulted in 0.21 g of dissolution, or 7% for the original 3 g of pyroxene. The calculations were most informative for pyroxene and olivine experiments that had abundant Mg²⁺. Overall, the most dissolution occurred in the highest fluid:rock ratio experiments and increased with temperature (Figure 9a). However, CN fluid tended to have a small decrease in the degree of dissolution between the longest and middle duration experiments. Olivine dissolved the least at highest temperature. Among the primary reactants with Mg, olivine had the relatively greatest dissolution, demonstrated by the high fluid concentration of Mg²⁺ relative to its abundance in the olivine mineral.

The change in sulfate anion concentration due to the precipitation of sulfate minerals was used to estimate the amount of precipitation of secondary minerals. This was a rough estimate that only takes sulfate into account and does not consider multiple mineral classes that form. The numbers presented here should only be taken relative to each other. This sulfate change cannot be directly correlated to a mass amount of precipitated secondary sulfate minerals because the calculation only used the change in sulfate concentration, ignoring other species that would contribute to the final precipitated weight (e.g., water and metal cations). Regardless, the calculated quantity of sulfate deposition was of the same order of magnitude as the weight of precipitated minerals, and it provided a means to compare the relative amounts of mineral precipitation. Since the olivine experiments did not precipitate sulfate during the experimental stage, the sulfate anion could not be used to estimate the amount of secondary products produced. The initial sulfate concentration in the fluid is equivalent to 1 m and the decrease in the concentration at the end of the experiments was determined using ICP-AES measurements. The difference was converted into a weight using the amount of fluid used. As an example, in the pyroxene 65°C and 1:1 fluid:rock ratio experiment, there was a difference of 413 mm in sulfate concentration and there was 2.7 g of water in that experiment then that equates to 1.12 mmol of sulfate. Using the formula weight of sulfate, the moles were converted to 0.107 g of overall sulfate loss from concentration and there was 2.7 g of water in that experiment then that equates to 1.12 mmol of sulfate.

3.4. Geochemical Models of Alteration
3.4.1. Plagioclase (Bytownite)

Geochemical models representing each experiment were created to aid in the interpretation of experimental and field results [Marcucci et al., 2013]. Plagioclase models were set up in the “React” modules of GWB to react 1 m H₂SO₄ with the pure plagioclase mineral, as in the experiments. For example, the model that replicated
the 4:1 plagioclase experiments consisted of 3 g of solid reactants in the “Reactant” tab and sulfuric acid and temperature in the “Basis” tab. O₂ fugacity was set to the atmospheric level to represent the air in the sealed reaction vessels. The chemical formulas of primary minerals were used to determine oxide weight percent (Table 1). This composition was used to represent the oxide proportions of the solid mineral. For this example, out of a total of 3 g of plagioclase, the proportion of oxides we used was 1.48 g of SiO₂, 0.98 g of Al₂O₃, 0.46 g of CaO, and 0.08 g of Na₂O. The sulfuric acid was added as a solution of water and sulfuric acid (sulfate anion and protons) for a total molality of 1. For this example, to represent 12 g of sulfuric acid, there was 10.8 g of water with a pH of 0.075 and the sulfate ion was the charge balancing element.

The concentration of sulfate (or Mg²⁺ for olivine) in the experimental fluids at the termination of each experiment as measured by ICP-AES was compared to the predicted sulfate consumption (Mg²⁺ accumulation) in models. This was used as a tracer to compare the extent of reaction progress between the models and experiments. In essence we compared the consumption of sulfate according to the simulation model and the experimental fluid. This comparison also indicated that reactions have not reached equilibrium at any temperature (Table S1). In the above example for 65°C, the final experimental sulfate concentration measured was approximately 700 mM, which matched the model concentration after 30% of the equilibrium reaction had taken place or reaction progress of 0.3. The first approximately 20% and 60% of

Figure 9. (a) Plot that demonstrates the degree of primary mineral dissolution for each mineral over duration and (bottom right) over temperatures. Dissolution was estimated from Mg²⁺ fluid data. Error bars represent a 5% error determined from duplicate instrument measurements. (b) Plot that demonstrates the trend of secondary sulfate mineral precipitation for each mineral over duration and (bottom right) over temperatures calculated from the change in SO₄²⁻ fluid data. Error bars represent a 1% error. The x axis represents experimental duration such that the shortest experiment length (i.e., 3 days) is on the left and the longest is on the right (40 days for 4:1 ratio or 60 for 1:1 and 10:1).
the models were representative of the 65°C 1:1 and 10:1 experiments, respectively. For 150 and 200°C, the reaction progresses were 50% and 70%, respectively (Table S1). The model products matched the experimental results, with the two main phases being amorphous silica and natroalunite (Figure 10a). Inconsistent with experiments, the Ca sulfate anhydrite was predicted in the weathering reaction models; however, gypsum was formed in experimental products, which may be a remnant of fluid evaporation under ambient conditions. Some production of diaspore occurs at the end of the predicted reaction progress, which may be related to the Al-rich gels in experimental observations.

3.4.2. Pyroxene (Augite)
Pyroxene models were set up in the same manner as above, but with pyroxene composition replacing the plagioclase ones. Based on the measured sulfate component, the first 10%, 20%, and 30% of the models were representative of the 1:1, 4:1, and 10:1 65°C experiments, respectively (Table S1). Matching steps for higher temperatures were 10% for 150°C and 50% for 200°C. Anhydrite was observed in experimental results and was also predicted to form in the models (Figure 10b). Amorphous silica was predicted to form in the models, but silica phases were not observed in experimental results. They may be present in concentrations too low for detection or mixed with crystalline phases. Consistent with the determination that Mg sulfate was an evaporitic mineral in the experiments, models were unsaturated with respect to this mineral.

3.4.3. Olivine (Forsterite)
The olivine alteration models were set up the same ways as previously discussed. These were the only experiments in which sulfates did not form during the actual alteration progression; therefore, sulfate could
not be used as a reaction progress tracer. Mg\(^{2+}\) was a conserved element until evaporation. The increase in Mg in the fluid as olivine was dissolved was used as a tracer in these models and indicated reaction progresses of 10%, 30%, and 70% for 1:1, 4:1, and 10:1 at 65°C experiments, respectively. The reaction progress was 30% for both 150 and 200°C experiments. The iron in this system was particularly sensitive to the presence of O\(_2\)(g). Models taking Earth atmospheric oxygen fugacity into account predicted the formation of hematite, possibly correlating to the Fe-O spheres observed in experiments (Figure 10c). Also, predicted to form were amorphous silica, talc, and antigorite. Amorphous silica could be related to the Si-rich gel seen in experiments. The phyllosilicates talc and antigorite were not observed in experiments, which was likely due to a kinetic inhibition or lack of maturation time.

3.4.4. Cerro Negro 1999 Cinders

GWB models designed to represent CN 1999 cinders were based on its oxide composition data (Table 1). Typical products included anhydrite and a silica phase, as well as smaller quantities of jarosite, alunite, natroalunite, and hematite (Figure 10d). Distribution and quantities were dependent on the fluid:rock ratio and temperature. As the fluid:rock ratio decreases, the solution becomes saturated after reacting with less solid material then needed for a higher fluid:rock ratio, allowing earlier mineral formation. Phyllosilicates were predicted to form at lower fluid:rock ratios and more advanced reaction progress for higher ratios, similar to individual plagioclase experiments. Phyllosilicates were not observed in experiments despite model predictions. At higher temperatures, fewer secondary minerals were predicted to form.

Figure 10. Plots of model reaction progress, representing sulfuric acid and mineral reactions, produced using data from Geochemist’s Workbench models. These are stacked plots with the colored area representing the amount of minerals formed. pH is presented as a red line with a numerical right axis. Determination of reaction progress is explained in the text. (a) Example of thermodynamic reaction between 3 g of plagioclase and 12 g of sulfuric acid at 65°C. (b) Similar reaction for pyroxene. (c) GWB model for olivine. (d) Model for the alteration of Cerro Negro basalt cinders.
4. Summary of Experimental Results

The experiments and model simulations collectively provided insights into basaltic acid-sulfate alteration. At the start of experiments, the fluid was speciated with H\(^+\), H\(_2\)SO\(_4\), HSO\(_4\)^{−}, and SO\(_4\)^{2−}. The weathering reactions dissolved the primary minerals, releasing cations into solution. After the Fe\(^{2+}\) was released, it oxidized to Fe\(^{3+}\) and minor amounts of iron oxides formed in the olivine experiments. Over time, cation (Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\), etc.) concentrations increased until they reached a saturation state with the sulfate ion, and began to precipitate secondary sulfate minerals. In our experiments, these were anhydrite in pyroxene experiments and natroalunite in plagioclase experiments. At the end of the experiments, evaporation increased the saturation of the remnant fluid and Mg sulfates and gypsum formed evaporitic deposits.

4.1. Effects of Duration

All secondary minerals observed in the longest time step were also observed in the shortest. Differences in duration manifested in much subtler ways evident in SEM images, including crystal morphology, size, and abundance of secondary minerals. This can be observed in the continued decrease of SO\(_4^{2−}\) in the fluid as sulfate minerals precipitate (Figure 9b) and the buildup of conservative elements, like Mg\(^{2+}\), as reactants dissolved (Figure 9a). As duration increases, minerals have a longer time to form and grow as more material becomes available. The 7.5 month long experiments at 65°C and 4:1 fluid:rock ratio continued to follow this trend (Figures 3b and 2f). The Ca sulfate minerals changed morphology in addition to size and abundance. Shorter experiments produced rectangular prism crystals; the longer experiments had larger, blade-like ones. During this longer time, new secondary minerals such as phyllosilicates did not appear to form, indicating that even longer maturation times, nucleation, or an increase in pH from rock buffering was needed.

4.2. Effects of Fluid:Rock Ratio

The crystal size, abundance, and shape variations observed in the SEM images hold true for fluid:rock ratio changes. The fluid saturated more easily at lower fluid:rock ratios, resulting in mineral precipitation. This is demonstrated in Table 4, where ionic concentration increased more quickly at the lower fluid:rock ratios than at higher ones. However, a lower ratio also means the fluid was more easily buffered and lost its ability to dissolve the primary minerals. Changes in crystal morphology were most evident in the Mg sulfates formed in pyroxene evaporation experiments (Figures 6b–6d). This shape change could be a modification in the specific hydration state of the Mg sulfate. Although it has not been specifically identified, the phase diagram for the evaporation temperature suggests kieserite. The macroscopically observed gels in plagioclase, olivine, and CN basalt experiments increased in thickness with increasing fluid:rock ratio from less than ~0.5 cm for 1:1 to between 0.5 and < 1 cm for 10:1 (Figures 3d and 2g).

4.3. Effects of Temperature

As with duration and fluid:rock ratio, changes in temperature resulted in size, shape, and abundance differences based on SEM images. In the plagioclase experiments, the abundance of natroalunite crystals increased with temperature, although their size was about the same. The stability fields of natroalunite and anhydrite cross into lower sulfate activities as temperature increases. This, in essence, allows these minerals to begin precipitating at lower sulfate concentrations in the fluid and earlier in the experiment duration. In the pyroxene experiments, the size and form of Ca sulfate crystals changed with temperature. The lowest temperature produced thick, prismatic crystals that were hundreds of microns long and tens of microns thick. At 150 and 200°C, the crystals were shorter, less than 100 microns. However, there were differences even between these two temperatures. The 150°C crystals were layered and wide (rectangular prismatic); whereas, at 200°C they were much thinner acicular crystals, possibly due to crystal growth kinetics.

4.4. Fluid Saturation

The lack of phyllosilicates in our experiments despite thermodynamic model predictions indicated that they were kinetically inhibited, had not had time to mature, or were present but difficult to detect using XRD and SEM. We favor a combination of the first two. Fluid composition showed the fluid was supersaturated with respect to phyllosilicates (Table S6) and model results predicted their formation. This is consistent with results from McCollom et al. [2013]. The Al-rich amorphous silica gel present in the plagioclase, olivine, and CN rock alteration experiments may be a precursor for phyllosilicates. This is supported by the fact that the experiments had not reached equilibrium and the infrequent but measureable quantities of phyllosilicates...
formed naturally at Cerro Negro [Hynek et al., 2013; Marcucci et al., 2013]. Geochemical models of Berger et al. [2009] also showed a progression of amorphous silica and jarosite transitioning to other sulfates and then to phyllosilicates. Al-phyllosilicates, such as kaolinite and montmorillonite, can form in acidic volcanic environments and are generally more resistant to acidic and thermal weathering than Fe/Mg-smectites [Fialips et al., 2000; Ece et al., 2008; Altheide et al., 2010; Gavin and Chevrier, 2010], although these are still not present in these experiments. The other possibility is that the phyllosilicates formed a thin layer on grains, which was undetectable with our methods of analysis.

A discrepancy between the fluid chemistry saturation states and the observed experimental products lies in the supersaturation of natroalunite in the plagioclase and Cerro Negro cinder experiments. Natroalunite was observed in both cases; therefore, it should have been in equilibrium with the fluid. This could be explained by the fluid chemistry changing as a result of temperature-dependent reactions (i.e., precipitation) as it cooled prior to analysis or that the thermodynamic data used was invalid under these conditions. Plagioclase experimental fluid had a much higher silica concentration than the other experiments. This may have been due to some of the amorphous Si gel being accidentally taken up during fluid sampling.

In general, the low fluid:rock ratio and high-temperature experiments became saturated most quickly and subsequently consumed elements through precipitation. The 10:1 fluid:rock ratio had the most dissolved species based on Mg$^{2+}$ calculations (Figure 9). The larger quantity of acid had a greater ability to prevent against pH increases due to dissolution, resulting in prolonged dissolution of the primary mineral. Increased temperature also increased the amount of dissolution in all cases except for olivine (Figure 9). This may be related to rapid silica precipitation that inhibits further surface reactions [Jonckheere, 1998]. This may also explain why CN basalt experimental fluid concentrations had a slight peak in dissolution at an intermediate experimental duration.

Pyroxene and olivine had fewer mineral phases that were kinetically inhibited, as indicated by the lower saturation indices. This may be due to the ability of plagioclase and CN 99 cinders to buffer the fluid chemistry to higher pH, which created a stability field for a greater number of minerals like phyllosilicates, as well as those primary materials having more elements available. Based on the rate at which sulfate was consumed, plagioclase and CN 99 cinders precipitate more sulfates because their chemistry supports the formation of multiple sulfates, i.e., complex sulfates like natroalunite and Ca sulfates (Figure 9b).

### 4.5. Cerro Negro Basalt Weathering

In our experiments, we found that plagioclase and olivine weathered faster than pyroxene, which showed very little alteration even though pH remained less than 1. This was contrary to the preferential dissolution of pyroxene over plagioclase found in the models of Zolotov and Mironenko [2007] and McAdam et al. [2008] but similar to the dominant plagioclase weathering seen in Hurowitz et al. [2005] experiments. There were two key differences between the studies that showed dominant plagioclase alteration and those that did not: (1) temperature and (2) experimental versus model method. The experiments conducted in this study and those of Hurowitz et al., [2005] used a high temperature, 65°C and 75°C respectively, while the thermodynamic models used 0°C [Zolotov and Mironenko, 2007; McAdam et al., 2008]. This may indicate that temperature played a role in the dissolution rate of plagioclase, in addition to pH. A second point to consider was the different methods used for the studies, modeling versus experimentation. Modeling often uses far from equilibrium thermodynamics (i.e., very undersaturated or supersaturated) so that kinetic relationships represent either dissolution or precipitation but not both. The experiments presented here had simultaneous dissolution and precipitation, which was constantly changing the fluid chemistry.

At the start of our weathering experiments, plagioclase dissolved and released the cations Ca, Al, and Na, which lead to formation of anhydrite (Ca) and natroalunite (Al-Na), consistent with other whole-rock experiments on Cerro Negro basalt [McCollom et al., 2013]. Mg and Fe were freed from pyroxene and olivine. Fe contributed to sulfates, either as the dominant cation or trace element in more complex sulfates, as well as Fe oxides. Fe oxide spheres were not abundant, likely due to inadequate maturation time and kinetic inhibition or the low concentrations of Fe in primary minerals. Mg accumulated in fluid, but did not reach a point of saturation until evaporation began, at which point Mg sulfates precipitated. A Mg-Al sulfate was also observed with EDS data. We suspect this is a combination of an evaporitic Mg sulfate from entrained fluid on top of fans of Al sulfate from the gel, which cannot be distinguished in the SEM images.
Si was released from all primary minerals; it was most noticeable in noncrystalline surface coatings from plagioclase and olivine weathering. While a Si-rich gel was prevalent in experiments, phyllosilicates were not observed, although they were predicted in models. Phyllosilicates are not very crystalline, which can make them hard to detect with methods such as XRD. Conversely, they may not have formed yet due to kinetic inhibition and the gel material may be a precursor material, which develops into phyllosilicates by increasing temperature and/or pressure. With even longer experiment durations, the gels could transform into more stable phyllosilicates phases through Ostwald ripening [Steefel and Van Cappellen, 1990]. Over time, phases that initially precipitated can transform into more thermodynamically stable phases as the fluid continues to evolve. The models presented in this paper were used as a comparison tool to examine reaction pathways of experiments and related field observations; therefore, phyllosilicates were not suppressed. However, similar models that did suppress phyllosilicates had alteration mineralogies that to first order matched the results presented here [McCollom et al., 2013]. The main difference was the presence of kieserite in the McCollom et al. [2013] models, which was likely a result of a low fluid:rock ratio.

4.6. Comparison to Previous Studies

The Ca, Al, and Mg sulfates and amorphous silica detected in this series of experiments and models are similar to those seen in previous experiments by Banin et al. [1997], Tosca et al. [2004], Golden et al. [2005], and Hurwitz et al. [2005]. However, one restriction of previous studies was the influence of evaporation. Hurwitz et al. [2005] separated phases formed during the experiments and during fluid evaporation and found that sulfates only formed in the evaporitic deposits. Our study showed that Ca sulfate and natroalunite could form during alteration in the closed system (Table 3), although this may be due to the enrichment of Ca and Al in our primary materials. Similarly, Tosca et al. [2004] and Banin et al. [1997] considered evaporation but evaporated experimental fluid on top of the grains and the sulfate was considered evaporitic. Based on the experiments completed in our study, the assumption that sulfates only form during evaporation is not valid. To understand the full reaction process, the alteration mineralogy must be separated from the minerals precipitated during evaporation.

Additionally, the thermodynamic models presented previously [Tosca et al., 2005; Zolotov and Mironenko, 2007] differ from our own models and experimental results in some ways. Low pH alteration models have a dominant amorphous silica component, which was consistent with our results [Zolotov and Mironenko, 2007]. However, those models produced little sulfate. Additionally, the Na released from plagioclase formed Na-saponite and montmorillonite, whereas our experiments and models formed natroalunite. The Meridiani evaporation model is consistent with our experimental evaporation with the formation of Ca, Fe, and Mg sulfates, but we argue that some sulfates form during acid-sulfate alteration and both alteration and evaporation need to be considered for this site [Tosca et al., 2005]. A second Meridiani Planum model was most similar to our own and simulated the reaction of Martian basalt with pure sulfuric acid at low fluid:rock ratios and pH [Berger et al., 2009]. Despite being run under the temperature and atmospheric conditions of Mars, their result of amorphous silica and jarosite followed by Ca, Mg, and Fe sulfates is mostly consistent with the experiments and models presented here, as well as trends in the field site alteration mineralogy [Hynek et al., 2013; Marcucci et al., 2013]. Our work did not produce jarosite, but this may be related to compositional differences and high temperatures, see section 5.

The most common iron oxide morphology observed in olivine experiments was a sphere, but radial star growths were also observed. Golden et al. [2008] examined the growth of hematite spheres analogous to Meridiani Planum under hydrothermal conditions and observed that they had a radial growth pattern in a similar size range, ~1 micron, as seen in our experiments. They further suggested that the larger size of Martian spheres could be due to high temperatures, thus faster kinetics, or longer growth times. Crystals once nucleated would continue to grow as long as material, namely, Fe$^{3+}$, was available. The two populations in our olivine experiments could represent different stages of mineral growth with the star forms being an earlier stage compared to the spheres.

5. Applications to Mars

The combined suite of experimental minerals matched closely with model predictions, Cerro Negro minerals, and Mars observations (Table 5). Investigation into the polyhydrated sulfate forms in Valles Marineris has suggested that the starkeyite and hexahydrite spectra best fit remote sensing data [Bishop et al., 2009]. These were two of the most abundant minerals detected by XRD in our olivine evaporation experiments. Similarly,
Table 5. Comparison of Experiments, Models, Field, and Martian Secondary Mineralogy

| Sulfate/salts          | Experiments\(^a\) | Geochemical Models\(^b,c\) | Cerro Negro\(^d\) | Mars\(^d\) |
|------------------------|-------------------|-----------------------------|------------------|------------|
| Gypsum, anhydrite, Mg sulfates, Al sulfate, natroalunite | Alunite (KAl\(_3\)(SO\(_4\))\(_2\)(OH\(_6\))), anhydrite, Mg sulfate, natroalunite | Alunite, anhydrite, gypsum, Mg sulfate, natroalunite | Gypsum, kieserite, polyhydrated sulfates, halite | Gypsum, kieserite, polyhydrated sulfates, halite |
| Fe minerals            | hematite          | Bernalite (Fe\(^{3+}\)(OH\(_3\))), jarosite | Hematite, jarosite, unidentified Fe3D3 | Hematite, jarosite, unidentified Fe3D3 |
| Clay minerals          | None observed     | Phylllosilicates, smectites | Amorphous clays, smectites | Phylllosilicates, smectites |
| Silica                 | Amorphous silica  | Amorphous silica             | Opaline, amorphous silica | Opaline, hydrated silica |

\(^a\)This study
\(^b\)McCollom and Hynek [2005].
\(^c\)Hynek et al. [2011].
\(^d\)Gendrin et al. [2005], Bibring et al. [2006], Squyres et al. [2007], Mustard et al. [2008], and Ehlmann et al. [2009].

hexahydrite was seen in the CN 99 whole-rock experiments, although a more hydrated Mg sulfate, pentahydrite, was seen instead of starkeyite. These hydrated Mg sulfates may be indicative of weathering from olivine-rich basalt, which is prevalent on Mars [e.g., Hamilton and Christensen, 2005; Edwards et al., 2008]. Kieserite was also a possible mineral form in pyroxene experiments based on the dipyramid crystal shape, which had been detected in many locations on the Martian surface, such as the Juventae, Ius, Hebes, and Capri Chasmata in Valles Marineris [Gendrin et al., 2005; Bishop et al., 2009].

The fact that Mg sulfates formed solely through evaporation in our experiments and models may imply that Mg sulfate on Mars likely formed by similar processes. Other possibilities include very low fluid:rock ratios or in reactions over enough time for Mg sulfates to saturate fluid. The presence of Mg sulfates in the Mars observations suggests that precipitation or rewetting by flowing water is unlikely, since their highly soluble nature would have made them sensitive to the presence of liquid water. For example, the Mg sulfates at the MER landing sites may mean that these areas had no rain; in contrast, an area that lacks Mg sulfates, but has other sulfates, may be an area that had experienced rain or rewetting. It is also possible that subsequent precipitation did occur and the original Mg sulfate deposits were larger than currently observed. Mg sulfates were also largely missing at CN with some exceptions, specifically they were often found in drainage areas [Hynek et al., 2013; Marcucci et al., 2013]. This was explained by terrestrial precipitation transporting and concentrating these materials in topographic lows.

Jarosite was not detected in our experiments, but natroalunite, a Na end-member of the alunite family that is structurally related to the jarosite family, was common. This could be because the chemistry of Cerro Negro, and thus the chemistry of our experiments, was lower in Fe and higher in Al compared to Martian basalt (Figure 1). An alternative explanation is that the jarosite detected on Mars was actually an Fe-rich alunite [McCollom et al., 2013]. McCollom et al. [2013] analyzed jarosite/alunite family minerals with varying compositions using Mössbauer spectroscopy and determined that jarosite and Fe-rich alunites have similar spectra, suggesting the possibility that rover Mössbauer detections identified as jarosite may be an Fe-rich alunite instead.

Ruff et al. [2011] and Arvidson et al. [2010] suggested possible hydrothermal origins for the Home Plate area of Gusev crater based on the presence of Si-rich material and geological context. As seen in the experiments and models, in situ alteration formed sulfate and abundant Si material. The highly soluble nature of sulfates, particularly Mg sulfates, meant they were easily removed even with small amounts of water, resulting in deposits primarily composed of Si, as seen at Home Plate and Cerro Negro. Alternatively, Si could have precipitated as siliceous sinter from steam condensate; also seen at Cerro Negro in limited locales [Hynek et al., 2013].

A hydrothermal origin has also been suggested for the Paso Robles soil class detailed by the Spirit rover [Yen et al., 2008]. These deposits were identified as light toned and sulfur rich. Mineral deposits were rich in ferric sulfates; among the suggested phases were ferricopiapite, rhomboclase, hydronium jarosite, and fibroferrite [Johnson et al., 2007; Lane et al., 2008]. Additional silica, Mg sulfates, Ca sulfates, hematite, and Ca phosphates made up the mineral assemblages of this soil class and mixtures varied on a meter to several hundred meter scale [Johnson et al., 2007; Yen et al., 2008]. Fumarolic activity in volcanic centers has pH and temperature variations at these scales, which can result in mineralogical differences [Hynek et al., 2013; Marcucci et al., 2013]. Our experiments suggest that mineral deposits in the Paso Robles soils could also vary due to differences in primary minerals.
6. Conclusions

In this study, we performed a series of experiments and model simulations to understand acid-sulfate alteration processes occurring in a volcanic environment. The experiments were conducted in sealed reaction vessels at varying fluid:rock ratios (1:1, 4:1, and 10:1), temperatures (65, 150, and 200°C), and durations (1 day to 7.5 months). We broke down the reaction pathways further by reacting individual basalt minerals and a whole-rock basalt with sulfuric acid. The "React" module of GWB was used to replicate the experiments in simulation form.

Multiple sulfate-rich deposits have been observed globally on Mars. Their widespread distribution leads to the possibility of different formation environments, although the general weathering mechanism is acid-sulfate alteration. Being able to distinguish between the different environments is useful for understanding the paleoconditions and evolution of an area. Additionally, understanding these conditions, in particular water and chemical disequilibrium, will provide data to assess the habitability of early Mars. Our work contributes to the research identifying characteristics unique to a hydrothermal, volcanic weathering system.

Our results from laboratory experiments closely match predicted mineralogy from the thermodynamic models when evaporation is taken into consideration (Table 5). Contrary to previous experimental studies, we find that some sulfates, such as anhydrite and natroalunite, do form during the actual alteration process, in addition to forming during evaporation. Our experiments and models also match the mineralogy sampled at Cerro Negro, Nicaragua and detected on Mars by the orbiters and landers. However, defining characteristics of different formation parameters lay in the minute details. With these types of changes in mind, it may be impossible to distinguish formation environments on Mars using orbiter data alone. Instead, microscopic detail and abundances will be necessary to identify the paleoenvironmental conditions for similar geochemical conditions on past Mars.

Below we highlight the results of this work.

1. Plagioclase altered to natroalunite, Ca sulfate, and an amorphous Al-Si-rich gel. Pyroxene altered to Ca sulfate, and olivine altered to crystalline ferric oxides/hydroxides and amorphous gels. Major alteration of whole-rock experiments included Ca, Mg, and Fe sulfate plus natroalunite and amorphous Si-rich material.
2. Comparison of the whole-rock experiments to individual mineral experiments showed that plagioclase, followed by olivine and pyroxene were responsible for alteration assemblages.
3. Evaporation played an important role in forming the final mineral assemblage, forming abundant Mg sulfates and additional Ca sulfates. However, it cannot be assumed that sulfates form solely during evaporation.
4. Secondary mineralogy was consistent for a given starting material regardless of changes in reaction duration, fluid:rock ratios, and temperatures. These parameter variations resulted in secondary products with different size, abundance, and morphology.

To directly respond to the key questions guiding the research:

1. It has yet to be shown that different acid-sulfate weathering environments produce drastically different and distinguishing mineralogical suites. Based on experiments, microscopic imaging may be critical in determining paleoconditions present during formation.
2. Understanding the entire reaction processes that occurred on Mars is vital. The presence or lack of (un)expected minerals may be key to understanding the history. Thermodynamic models assist in the interpretation of experiments.
3. In order to determine specific formation conditions in hydrothermal environments on Mars, future measurements will have to rely on microscopic imaging and a thorough understanding of contributions from various processes including precipitation and evaporation.

References

Altheide, T. S., V. F. Chevrier, and E. Noe Dobrea (2010), Mineralogical characterization of acid weathered phyllosilicates with implications for secondary Martian deposits, Geochim. Cosmochim. Acta, 74(21), 6232–6248, doi:10.1016/j.gca.2010.08.005.

Arvidson, R. E., et al. (2006), Overview of the Spirit Mars Exploration Rover Mission to Gusev Crater: Landing site to Backstay Rock in the Columbia Hills, J. Geophys. Res., 111, E02S01, doi:10.1029/2005JE002499.

Arvidson, R. E., et al. (2010), Spirit Mars Rover Mission: Overview and selected results from the northern Home Plate Winter Haven to the side of Scamander crater, J. Geophys. Res., 115, doi:10.1029/2010JE003633.

Banin, A., F. X. Han, I. Kan, and A. Cicelis (1997), Acidic volatiles and the Mars Soil, J. Geophys. Res., 102(E6), 13,341–13,356.
McCollom, T. M., M. Robbins, B. Moskowitz, T. S. Bergou, N. Jüns, and B. M. Hynek (2013), Experimental study of acid-sulfate alteration of basalt and implications for sulfate deposits on Mars, J. Geophys. Res. Planets, 118, 577–614, doi:10.1002/jgre.20044.

McLennan, S. M., et al. (2005). Provenance and diagenesis of the evaporite-bearing Burns formation, Meridiani Planum, Mars, Earth Planet. Sci. Lett., 240(1), 95–121, doi:10.1016/j.epsl.2005.09.041.

Milliken, R. E., et al. (2008). Opaline silica in young deposits on Mars, Geology, 36(11), 847–850, doi:10.1130/G24967A.1.

Morrison, D. A., L. D. Ashwal, W. C. Phinney, C.-Y. Shih, and J. L. Wooden (1983). Pre-Keweenawan anorthosite inclusions in the Keweenawan Beaver Bay and Duluth Complexes, northeastern Minnesota, Geol. Soc. Am. Bull., 94(2), 206–221, doi:10.1130/0016-7606(1983)94<206:PAKTBZ>2.0.CO;2.

Murchie, S. L., et al. (2009). Compact Reconnaissance Imaging Spectrometer for Mars investigation and data set from the Mars Reconnaissance Orbiter's primary science phase, J. Geophys. Res., 114, E00D07, doi:10.1029/2009JE003344.

Mustard, J. F., et al. (2008). Hydrated silicate minerals on Mars observed by the Mars Reconnaissance Orbiter CRISM instrument, Nature, 454(7202), 305–309, doi:10.1038/nature07097.

Niles, P. B., and J. Michalski (2009). Meridiani Planum sediments on Mars formed through weathering in massive ice deposits, Nat. Geosci., 2(3), 215–220, doi:10.1038/ngeo438.

Rieder, R., et al. (2004). Chemistry of rocks and soils at Meridiani Planum from the alpha particle X-ray Spectrometer, J. Geophys. Res., 114, E00F23, doi:10.1029/2010JE003767.

Ruff, S. W., et al. (2011). Characteristics, distribution, origin, and significance of opaline silica observed by the Spirit rover in Gusev crater, Mars, J. Geophys. Res., 116, E00E03, doi:10.1029/2010JE003767.

Schmidt, M. E., et al. (2009). Spectral, mineralogical, and geochemical variations across Home Plate, Gusev crater, Mars indicate high and low temperature alteration, Earth Planet. Sci. Lett., 281(3–4), 258–266, doi:10.1016/j.epsl.2009.02.030.

Squyres, S. W., et al. (2004). In situ evidence for an ancient aqueous environment at Meridiani Planum, Mars, Science, 306(5702), 1746–1749, doi:10.1126/science.1104358.

Squyres, S. W., et al. (2011). Photosynthesis within Mars' volcanic craters?: Insights from Cerro Negro Volcano, Nicaragua, AGU Fall Meeting Abstracts, 33, 1768.

Roggensack, K., R. L. Hervig, S. B. McKnight, and S. N. Williams (1997). Explosive basaltic volcanism from Cerro Negro volcano, Nicaragua, AGU Fall Meeting Abstracts, 33, 1768.

Rogers, K. L., B. M. Hynek, and T. M. McCollom (2011). Photosynthesis within Mars’ volcanic craters?: Insights from Cerro Negro Volcano, Nicaragua, AGU Fall Meeting Abstracts, 33, 1768.

Walker, J. A., and M. J. Carr (1986). Compositional variations caused by phenocryst sorting at Cerro Negro volcano, Nicaragua, AGU Fall Meeting Abstracts, 33, 1768.

Wray, J. J., S. L. Murchie, S. W. Squyres, F. P. Seelos, and L. L. Tornabene (2009a). Diverse aqueous environments on ancient Mars revealed in the southern highlands, Geology, 37(11), 1043–1046, doi:10.1130/G30331A.1.

Wray, J. J., E. Z. N. Dobrea, R. E. Arvidson, S. M. Wiseman, S. W. Squyres, A. S. McEwen, J. F. Mustard, and S. L. Murchie (2009b). Phyllosilicates and sulfates at Endeavour crater, Meridiani Planum, Mars, Geophys. Res. Lett., 36, L21201, doi:10.1029/2009GL040734.

Yen, A. S., et al. (2008). Hydrothermal processes at Gusev crater: An evaluation of Paso Robles class soils, J. Geophys. Res., 113, E06510, doi:10.1029/2007JE002978.

Zolotov, M. Y., and M. V. Mironenko (2007). Timing of acid weathering on Mars: A kinetic-thermodynamic assessment, J. Geophys. Res., 112, E07006, doi:10.1029/2006JE002882.