1 **Dissolution of Nontronite in Chloride Brines and Implications for the Aqueous**
2 **History of Mars**

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18 **Abstract:**

19 Increasing evidence suggests the presence of recent liquid water, including
20 brines, on Mars. Brines have therefore likely impacted clay minerals such as the Fe-
21 rich mineral nontronite found in martian ancient terrains. To interpret these
22 interactions, we conducted batch experiments to measure the apparent dissolution
23 rate constant of nontronite at 25.0 °C at activities of water ($a_{\text{H}_2\text{O}}$) of 1.00 (0.01 M

CaCl₂ or NaCl), 0.75 (saturated NaCl or 3.00 mol kg⁻¹ CaCl₂), and 0.50 (5.00 mol kg⁻¹ CaCl₂). Experiments at $a_{H_2O} = 1$ (0.01 M CaCl₂) were also conducted at 4.0 °C, 25.0 °C, and 45.0 °C to measure an apparent activation energy for the dissolution of nontronite.

Apparent dissolution rate constants at 25.0 °C in CaCl₂-containing solutions decrease with decreasing activity of water as follows: $1.18 \times 10^{-12} \pm 9 \times 10^{-14}$ moles mineral m⁻² s⁻¹ ($a_{H_2O} = 1$) > $2.36 \times 10^{-13} \pm 3.1 \times 10^{-14}$ moles mineral m⁻² s⁻¹ ($a_{H_2O} = 0.75$) > $2.05 \times 10^{-14} \pm 2.9 \times 10^{-15}$ moles mineral m⁻² s⁻¹ ($a_{H_2O} = 0.50$). Similar results were observed at 25.0 °C in NaCl-containing solutions : $1.89 \times 10^{-12} \pm 1 \times 10^{-13}$ moles mineral m⁻² s⁻¹ ($a_{H_2O} = 1$) > $1.98 \times 10^{-13} \pm 2.3 \times 10^{-14}$ moles mineral m⁻² s⁻¹ ($a_{H_2O} = 0.75$). This decrease in apparent dissolution rate constants with decreasing activity of water follows a relationship of the form: $\log k_{diss} = 3.70 \pm 0.20 \times a_{H_2O} - 15.49$, where k_{diss} is the apparent dissolution rate constant, and a_{H_2O} is the activity of water. The slope of this relationship (3.70 ± 0.20) is within uncertainty of that of other minerals where the relationship between dissolution rates and activity of water has been tested, including forsteritic olivine ($\log R = 3.27 \pm 0.91 \times a_{H_2O} - 11.00$) (OLSEN et al., 2015) and jarosite ($\log R = 3.85 \pm 0.43 \times a_{H_2O} - 12.84$) (DIXON et al., 2015), where R is the mineral dissolution rate. This result allows prediction of mineral dissolution as a function of activity of water and suggests that with decreasing activity of water, mineral dissolution will decrease due to the role of water as a ligand in the reaction.

Apparent dissolution rate constants in the dilute NaCl solution ($1.89 \times 10^{-12} \pm 1 \times 10^{-13}$ moles mineral m⁻² s⁻¹) are slightly greater than those in the dilute CaCl₂

solutions ($1.18 \times 10^{-12} \pm 9 \times 10^{-14}$ moles mineral $\text{m}^{-2} \text{s}^{-1}$). We attribute this effect to the exchange of Na with Ca in the nontronite interlayer. An apparent activation energy of 54.6 ± 1.0 kJ/mol was calculated from apparent dissolution rate constants in dilute CaCl_2 -containing solutions at temperatures of 4.0 °C, 25.0 °C, and 45.0 °C: $2.33 \times 10^{-13} \pm 1.3 \times 10^{-14}$ moles mineral $\text{m}^{-2} \text{s}^{-1}$ (4.0 °C), $1.18 \times 10^{-12} \pm 9 \times 10^{-14}$ moles mineral $\text{m}^{-2} \text{s}^{-1}$ (25.0 °C), and $4.98 \times 10^{-12} \pm 3.8 \times 10^{-13}$ moles mineral $\text{m}^{-2} \text{s}^{-1}$ (45.0 °C).

The greatly decreased dissolution of nontronite in brines and at low temperatures suggests that any martian nontronite found to be perceptibly weathered may have experienced very long periods of water-rock interaction with brines at the low temperatures prevalent on Mars, with important implications for the paleoclimate and long-term potential habitability of Mars.

1. Introduction:

Liquid water is a necessary ingredient for life on Earth and its history on Mars is therefore essential to understanding the potential habitability of that planet. High ionic strength solutions like brines (up to ~ 6.15 m) are also able to host life at a wide range of temperature and water activities (JONES AND LINEWEAVER, 2010). While current surface conditions on Mars are not able to sustain pure liquid water, brines may exist temporarily (HENDERSON-SELLERS AND MEADOWS, 1976; BRASS, 1980; HABERLE et al., 2001; JONES AND LINEWEAVER, 2010; McEWEN et al., 2011; CHEVRIER AND RIVERA-VALENTIN, 2012; MARTÍN-TORRES et al., 2015; OJHA et al., 2015). Chloride and chloride plus sulfate brines could be stable at present day temperatures on Mars (BRASS, 1980) and increasing evidence points to their presence. Recurring Slope Lineae (RSL) growth observed by the Mars Reconnaissance Orbiter are attributed to

seasonal flow suggestive of liquid brines (McEWEN et al., 2011; MARTÍNEZ AND RENNO, 2013; OJHA et al., 2015). Correlation of Mg with S and enrichment of S, Cl, and Br measured by the MER Spirit at Gusev Crater suggest transport by saline solutions through soils (HASKIN et al., 2005; WANG et al., 2006; MING et al., 2008). Relative humidity and temperature measurements from the Rover Environmental Monitoring Station on the Curiosity Rover have also detected conditions capable of supporting perchlorate brines (MARTÍN-TORRES et al., 2015), and perchlorate measurements at the Phoenix landing site suggest thin films of perchlorate solutions (CULL et al., 2010). Ice excavated by the Phoenix Lander has been argued to have formed from a frozen brine because of its relative softness (RENNÓ et al., 2009; SMITH et al., 2009). Obliquity-driven climate change is proposed to have deposited then removed ice over large swaths of the Martian surface, and periodically made liquid water more available (WORDSWORTH, 2016). Therefore, over the course of martian history even long after the inferred wetter epochs ending ~ 3.5 Ga, a significant proportion of the exposed land surface may have been affected by interaction with small quantities of liquid water, and that water is likely to have been a brine.

The Fe-rich smectite nontronite has been detected on the surface of Mars, particularly in ancient terrains (POULET et al., 2005). Nontronite has been found intimately mixed with sulfates at Gale Crater (MILLIKEN et al., 2010; THOMSON et al., 2011) and it has also been found beneath Al-rich silicates at Mawrth Vallis (BIBRING et al., 2006; BISHOP et al., 2008; WRAY et al., 2008; McKEOWN et al., 2009; LOIZEAU et al., 2010; NOE DOBREA et al., 2010), at Nili Fossae (EHLMANN et al., 2009); Valles Marineris (ROACH et al., 2010); and Terra Sirenum (WRAY et al., 2011). Fe-Mg-rich

93 phyllosilicates have also been documented in multiple locations on the surface of
94 Mars by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) on
95 the Mars Reconnaissance Orbiter and the Observatoire pour la Minéralogie, l'Eau,
96 les Glaces et l'Activité (OMEGA) spectrometer on the Mars Express orbiters (POULET
97 et al., 2005; BISHOP et al., 2008; MUSTARD et al., 2008; MURCHIE et al., 2009). If brines
98 have been active on the martian surface, it is likely that at least some of the
99 observed nontronite deposits have interacted with brines since their formation. A
100 key question is whether these ancient, nontronite-bearing terrains would record
101 evidence of such interaction.

102 Few studies have examined mineral dissolution rates in brines (HAUSRATH
103 AND BRANTLEY, 2010; PRITCHETT et al., 2012; DIXON et al., 2015; OLSEN et al., 2015), and
104 none that we know of have analyzed nontronite dissolution rates in brines. Previous
105 work suggests that mineral dissolution slows significantly in high-ionic strength
106 brines (HAUSRATH AND BRANTLEY, 2010; PRITCHETT et al., 2012; DIXON et al., 2015;
107 OLSEN et al., 2015), and we therefore tested the importance of that effect on
108 nontronite, derived apparent dissolution rate constants, determined which
109 parameters influenced them, and calculated an apparent activation energy.
110 Apparent dissolution rate constants of nontronite were measured as a function of
111 activity of water ($a_{\text{H}_2\text{O}}$) at $a_{\text{H}_2\text{O}} = 1.00, 0.75$ and 0.5 , and temperature at $4^\circ, 25^\circ$, and
112 45.0°C . Experiments were performed at a pH of 2, chosen to be relevant to later,
113 colder and drier time periods, assumed to be acidic (BIBRING et al., 2006), when
114 brines are likely to have been important. Reacted material was examined to
115 determine the nature of alteration resulting from interaction with the brines. The

results of this work can help interpret past aqueous conditions on Mars, thereby providing a better understanding of the habitability of martian environments.

2. Materials and Methods:

2.1 Materials:

The Clay Mineral Society nontronite standard NAu-1 ($Na_{1.05}$) [$Si_{6.98}$ $Al_{0.95}Fe_{0.07}$]/[$Al_{0.36}Fe_{3.61}Mg_{0.04}$] $O_{20}(OH)_4$ (GATES et al., 2002) was used in all mineral dissolution experiments. NAu-1 was mined from the Uley Graphite Mine, Australia (KEELING et al., 2000) and has been previously characterized as predominantly nontronite with traces of kaolin, quartz, biotite and goethite totaling approximately 10% (KEELING et al., 2000). Naturally occurring clay minerals such as NAu-1 commonly include trace mineral phases which are very difficult to remove without altering the main phase (MILLER et al., 2012). However, pure, synthetic clay minerals produced in the laboratory may not be representative of bulk clays formed in nature. Therefore, we chose to use the natural NAu-1 nontronite standard to study dissolution rates in this study both for direct comparison with previous work (GAINEY et al., 2014), and as a natural analog for bulk clay mineral deposits which have been observed on Mars. In order to analyze the trace phases in the nontronite NAu-1 used in our experiments we performed synchrotron XRD analyses described below in Section 2.4.

We gently hand-crushed the well-indurated NAu-1 bulk sample in small batches in an agate mortar and pestle to produce 40-120 micron-sized aggregates which were separated by sieving. We sonicated the 40-120 micron aggregates in ethanol at two minute intervals to remove fine particles on the surfaces of the larger

nontronite aggregates, thus minimizing the effects of fine grains and individual particles on the initial reactive surface area within the experiment and ensuring that all experiments had both similar initial mass and surface area of NAu-1 available for reaction. Crushing, sieving, washing and ultrasonication of minerals prior to dissolution in kinetic studies is a standard method of preparation used in previous studies of clay mineral dissolution (DEVIDAL et al., 1992; WIELAND AND STUMM, 1992; GANOR et al., 1995) to control the surface area of the materials.

A significant decrease in fine particles was observed when aggregate surfaces were examined by Scanning Electron Microscopy (SEM) using a JSM-5610 Scanning Electron Microscope after washing, although occasional fine particles remained. Surface area of the bulk material was determined using a Quantachrome NOVA 2000e Surface area and Pore Size Analyzer. Nontronite was outgassed under vacuum at 50 °C for 24 hours before measuring a six-point BET (Brunauer-Emmett-Teller) nitrogen adsorption isotherm (BRUNAUER et al., 1938). Apparent dissolution rate constants were normalized to the measured nontronite initial surface area ($30.9 \pm 1.5 \text{ m}^2 \text{ g}^{-1}$). It should be noted that nontronite is prone to swelling when in water which could result in a different surface area compared to dry nontronite (BERGAYA AND LAGALY, 2013). However, normalization to BET surface area is a standard method very commonly used in previous experiments reporting clay mineral dissolution rates (CARROLL-WEBB AND WALTHER, 1988; CARROLL AND WALTHER, 1990; CHIN AND MILLS, 1991; HUERTAS et al., 1998; METZ AND GANOR, 2001; CAMA et al., 2002; CAMA AND GANOR, 2006) and so we utilize it here to allow comparison of dissolution rates between different minerals. We also provide dissolution rates

normalized to mass (Table 1).

2.2 Batch Dissolution Experiments:

Experiments were designed to test the effect of water activity, solution chemistry, and temperature on nontronite dissolution. Batch experiments were performed using CaCl_2 - and NaCl -containing solutions with $a_{\text{H}_2\text{O}}$ equal to 1.00, 0.75 and 0.5, and 1.00 and 0.75, respectively. The 1.00 dilute solutions contained 0.01M NaCl or 0.01M CaCl_2 , which had an activity of water = 0.999 calculated using PHREEQC (PARKHURST AND APPELO, 1999), which is similar to terrestrial soil waters (HARTER AND NAIDU, 2001). Dissolution experiments are commonly performed in low ionic strength solutions rather than pure water to prevent rapid changes in the activity of water as the mineral dissolves. The 0.75 $a_{\text{H}_2\text{O}}$ CaCl_2 brine was made by adding 166.66 g of anhydrous CaCl_2 to 500 g of 18.2 M Ω water, and the 0.50 $a_{\text{H}_2\text{O}}$ CaCl_2 brine was made by adding 360.68g of anhydrous CaCl_2 to 500 g of 18.2 M Ω water (RARD AND CLEGG, 1997). The NaCl brine was made by adding 150 g of NaCl to 356 g of 18.2 M Ω water (CHIRIFE AND RESNIK, 1984).

All solutions were adjusted to an initial pH = 2.0 using high purity HCl . Previous measurements of pH in brines have employed multiple techniques, and double junction fast flow pH electrodes have been commonly used (BOWEN AND BENISON, 2009; HAUSRATH AND BRANTLEY, 2010). In order to compare apparent dissolution rate constants across activities of water, it was necessary to ensure that the initial pH was the same in all conditions. To do this, all pH measurements were made with the same Mettler Toledo InLab® Expert Pro pH electrode. This electrode has a double junction and temperature sensor, both of which increase accuracy

when measuring pH in brines. We also measured the starting pH of the brines with a VWR symPHony™ High-flow pH electrode designed for hard-to-measure samples and measured values within 0.1 pH units of the target pH of 2. We therefore make the assumption that although uncertainties on pH measurements are higher in brines, these measurements are sufficiently precise to allow comparison between activities of water and with previous data.

For each experimental condition except the 0.50 *a*H₂O experiments which contained 5.0g of nontronite to increase solution concentrations, 0.5-1.0g of crushed, sieved and washed nontronite was combined with 200ml of solution in an acid-washed Low Density Polyethylene (LDPE) batch reactor. To test the effect of temperature and calculate an apparent activation energy of dissolution, experiments were performed in 0.01M CaCl₂ solutions at 4.0 °C, 25.0 °C, and 45.0 °C on an orbital shaker in a temperature-controlled cold-room (4.0 ± 0.1 °C), or in temperature-controlled shaking water baths (25.0±0.1 °C and 45.0 ±0.1 °C). All solutions were equilibrated to the correct temperature for 24 hours prior to the addition of nontronite. The experiments were agitated in a shaker bath to keep the solution well-mixed and ensure that dissolution was not transport-limited. In all cases, batch reactors were agitated at 100 strokes per minute.

To sample the reactors, ten ml of solution only (no mineral grains) were removed at regular time intervals that varied depending on the temperature and solution composition and were based on preliminary experiments. Because the removal of the solution changed the water: mineral ratio throughout the experiments, this changing ratio was accounted for after WELCH AND ULLMAN

(2000) as described below. A minimum of 13 solution samples were collected during the initial period of the experiments, and then batch reactors were allowed to react for an additional 1-4 months to collect long term points under steady conditions. Samples were taken at different time intervals to accommodate the different dissolution rates. The 25 °C and 45 °C experiments were sampled 2-3 times a day for one week while the 4 °C experiments were sampled daily for three weeks. The 1.00 aH₂O and 0.75 aH₂O experiments were sampled 2-3 times a day for one week while the 0.50 aH₂O experiments were sampled daily for three weeks. The pH of each sample was measured on a separate aliquot of unfiltered solution at room temperature, with the remainder of the solution sample filtered through a 0.45 µm polypropylene syringe filter and acidified to 1% v/v with high purity HNO₃. Each condition was run in duplicate with at least one blank for each condition. A complete list of experimental conditions, including duplicates, is shown in Table 1.

2.3 Analytical Methods:

Silica concentrations were measured with a Thermo Genesys 10S UV-Vis spectrophotometer at a wavelength of either 700nm (dilute solutions and NaCl brines) or 400 nm (CaCl₂ brines) using methods slightly modified from the ASTM and USGS methods to optimize analysis in high ionic strength solutions (ASTM D859-10; FISHMAN AND FRIEDMAN, 1989). The silica analysis consisted of two steps: 1) the addition of an acid and ammonium molybdate to form silicomolybdate which produces a yellow color, the intensity of which reflects the concentration of available silica (ASTM D859-10) and 2) the reduction of silicomolybdate which produces a blue color the intensity of which reflects the concentration of available

silica (FISHMAN AND FRIEDMAN, 1989). Performing both steps increases the measurement range to 0.1-100 ppm SiO₂ measured at 700 nm, compared to a measurement range of 0.1-1.0ppm SiO₂ when only performing the first step measured at 400nm (ASTM D859-10; GOVETT, 1961). We used a hybrid method, combining the first step from ASTM D859-10 and the second step from the USGS test method I-1700-85 to avoid interference caused by precipitation of Ca sulfites within the brines, which occurs during the second reducing step of the ASTM D859-10 method due to the addition of an amino-naphthol-sulfonic acid solution (ASTM D859-10; FISHMAN AND FRIEDMAN, 1989). Both steps were used for samples from all dilute experiments at all temperatures and NaCl brines with $a_{H_2O} = 0.75$. Only the first step was used for $a_{H_2O} = 0.75$ CaCl₂ and $a_{H_2O} = 0.50$ CaCl₂ brines because precipitation occurred when adding sodium sulfite as a reducing agent in step two. In order to match the solution matrices for the standards and the samples, standards were prepared in 18.2 MΩ water and then combined with a solution matching the composition of the sample solution in a 1:1 ratio, and samples were diluted 1:1 with 18.2 MΩ water. The average standard error of thirteen silica calibration curves measured on the Thermo Genesys 10S UV-Vis spectrophotometer was found to be $4 \pm 3\%$, with the highest value = 8%. Based on that, we assume a conservative uncertainty of 10% on silica measurements.

The colorimetric silicomolybdate method is commonly believed to measure monomeric silica (H₄SiO₄) (ICOPINI et al., 2005). ILER (1979) has argued that the colorimetric silicomolybdate method also measures concentrations of dimeric (H₆Si₂O₇), and possibly trimeric (H₈Si₃O₁₀) silica, and TANAKAA AND TAKAHASHIB

(2001) have suggested that the method may also detect linear and cyclic tetramers. Previous work has indicated that the rate of oligomerization from molybdate reactive silica to silica nanoparticles or amorphous silica is slow under acidic conditions such as those used here, as well as under low silica concentrations (ICOPINI et al, 2005). For example, ICOPINI et al., (2005) observed very little oligomerization at any pH in solutions of 4.2 mmol silica, orders of magnitude above the highest concentration of silica solutions measured in our brine experiments. In previous work, silica concentrations in equilibrium with amorphous silica decreased from an average of 3.76 mmol SiO₂ in dilute solutions to 3.43 mmol SiO₂ in the presence of Na-K-Ca-Cl-HCO₃⁻-H₂O solutions ranging from 0.01 molal to 0.24 molal (ICOPINI et al., 2005). Forsterite, fayalite and basaltic glass dissolution in Ca-Na-Cl solutions also resulted in decreased steady silica concentrations at higher concentrations, with steady concentrations in near eutectic brines at 22.1 °C ranging from 0.17 to 0.45 mm (HAUSRATH AND BRANTLEY, 2010). We therefore make the assumption here that these measurements are representative of silica release from the nontronite surfaces.

Iron concentrations were measured using a Thermo Scientific iCE 3000 series Atomic Absorption spectrometer for all samples for which sufficient solution remained after silica measurements. All samples were treated with a CaCO₃ solution to reduce interference, following the method described by EATON et al. (2005). Samples from experiments with α H₂O = 1.00 were analyzed for iron concentrations without dilution. Brine samples required a 1:8 dilution to prevent damage to the AA spectrometer (PRITCHETT et al., 2012). The detection limit for Fe concentrations was

measured as 0.05 ppm using the method described by the Perkin-Elmer Analytical Methods for Atomic Absorption Spectroscopy manual (CORPORATION, 1964), resulting in a practical quantitation limit of 0.20 ppm. Because solution samples were filtered through a 0.45 μm filter and then acidified, any iron-rich nanoparticles or colloids that passed through the filter and then dissolved upon acidification would also have been measured. However, low (non-stoichiometric) iron concentrations suggest such nanoparticles or colloids did not contribute significantly to measured Fe concentrations.

2.4 Characterization of the solid:

After collection of the long-term solution chemistry point(s) for each experiment ($\sim 3\text{-}6$ months), solutions were decanted and the remaining material was rinsed with 18.2 M Ω water. Rinsed reacted material was frozen for at least 24 hours, and then freeze dried for 24 hours to remove all ice. Reacted material and unreacted N_{Au}-1 for comparison were carbon coated, and observed using a JEOL field-emission SEM JSM-6700F. Samples were also analyzed using Visible/Near-Infrared (VNIR) and Infrared (IR) reflectance spectroscopy to further constrain alteration and to be able to make a direct comparison to Mars. VNIR spectra were measured over the range 0.4 - 2.5 μm using an ASD FieldSpec3 and IR spectra were measured over the range 2.5 to 25 μm using a iS50 FTIR spectrometer with all spectra measured at the California Institute of Technology. ENVI version 4.7 was used to remove the continuum and to identify the absorption wavelengths. FE-SEM, VNIR, and IR analysis also included reacted nontronite removed from a set of experiments within a saturated CaCl₂ brine. Those experiments provided sufficient

reacted material for analysis but had aqueous Fe and Si concentrations below detection for all solution samples and were not included in the kinetic portion of this study.

Unreacted and reacted nontronite were also examined by synchrotron XRD. Unreacted NAu-1 was measured at the synchrotron beamline 16-ID-B at the Advanced Photon Source in transmission mode with a rotating sample and collimated primary beam with a spot size of approximately 150x150 μm^2 . A Pilatus 1M area detector was used for data acquisition, and details on experimental set up can be found in KUNZ et al. (2005). The use of an unfocused beam allows analysis of a larger area than a focused beam. NAu-1 reacted in the presence of 0.01 M NaCl was examined at the synchrotron beamline 12.2.2 at the Advanced Light Source using a focused beam with a spot size of approximately 30x40 μm^2 . For the reacted NAu-1, two grains were examined, one representative of the majority of the bulk reacted material, and the other a whitish grain that was also common. In each case samples were analyzed on capillary tubes.

3. Results:

3.1 Solution chemistry:

The pH of each experiment typically remained relatively steady, increasing somewhat over time (see Supplemental Material). In general, experiments in dilute solutions remained the most stable with measured pH values for $a_{\text{H}_2\text{O}} = 1.00$ conditions ranging from 1.98 to 2.08 at 4.0 °C, 1.84 to 2.54 at 25.0 °C, and 1.92 to 2.43 at 45.0 °C. Experiments performed in lower water activity solutions had larger

changes, with measured pH values for $a_{\text{H}_2\text{O}} = 0.75$ ranging from 1.90 to 3.05 and $a_{\text{H}_2\text{O}} = 0.5$ ranging from 1.78 to 2.6 (see Supplemental Material).

Moles released of silica and iron were corrected for solution volume removed during sampling and therefore changing water: mineral ratios after WELCH AND ULLMAN (2000):

$$m_{(t)} = m_{(t-1)} + (c_{(t)} - c_{(t-1)})V_{(t-1)} \quad (\text{Eq. 1})$$

where $m_{(t)}$ and $m_{(t-1)}$ are moles of silica or iron released to solution at time t and $t-1$ (the preceding time interval), $c_{(t)}$ and $c_{(t-1)}$ are the concentrations of silica or iron in moles•liter⁻¹ at time intervals t and $t-1$, and V is the volume of solution in liters remaining at time $t-1$.

Silica concentrations in samples collected during the initial period of the experiments showed a non-linear relationship with time indicative of an approach to steady state or equilibrium where an opposing precipitation reaction is important (Supplementary Material figures 1-14).

All samples with sufficient solution remaining after measurement of silica were analyzed for Fe concentrations but only experiments at $a_{\text{H}_2\text{O}} = 1.0$ had detectable concentrations. Similar to silica concentrations, Fe release increased over time, approaching steady conditions (Supplemental Materials Figures 15-33). In all cases, Fe: Si ratios in solution were below the Fe: Si ratio in nontronite, indicating incongruent dissolution and/or precipitation of Fe-bearing phases in experiments at $a_{\text{H}_2\text{O}} = 1.00$ (Figure 1). This is consistent with previous work (METZ et al., 2005; GAINEY et al., 2014), which concluded that Fe is not released

stoichiometrically during smectite dissolution because of preferential Fe reabsorption and precipitation.

3.2 FE-SEM Results:

No observations by FE-SEM indicated significant alteration or secondary mineral precipitation. Similar surfaces were observed in both reacted and unreacted nontronite, with nontronite with rounded, rough edges being more common than nontronite with smooth sharp surfaces. No observable difference with changing activity of water and temperature was observed (Figure 2).

3.3 IR Results:

Changes in the VNIR spectra due to interaction with liquid water or brines are slight if present (Figure 3). A slight shift shortward of about 10nm can be seen in the 2.43 μm Fe-OH absorption in samples exposed to saturated CaCl_2 brines compared to all other brine and dilute experiments. This shift could be explained by an extra absorption caused by differences in water content, crystallinity or occupancy of octahedral cation sites. VNIR spectra are, however, largely invariant.

FTIR spectra have more noticeable spectral changes. The Si-O stretch near 1000 cm^{-1} becomes narrower for all reacted samples. A reflectance maximum/emission minimum at 1220 cm^{-1} and a feature at 790 cm^{-1} disappear in reacted samples compared to the unreacted NAu-1 spectra. The Al/Si-O-Si deformations between 600 and 400 cm^{-1} change in shape for all 25.0°C and 45.0 °C experiments. The spectra of the reacted samples are more typical of dioctohedral

smectites (MICHALSKI et al., 2005) and some observed spectral changes could be caused by the removal or transformation of the minor phases in N Au-1.

3.4 Synchrotron XRD results:

Synchrotron XRD analyses of unreacted N Au-1 indicate the presence of bulk nontronite along with small amounts of kaolinite, quartz, anatase and a 10 Å phase in the glauconite-illite series (Figure 4a). This is consistent with previous analyses of N Au-1 indicating trace amounts of other phases (KEELING et al. 2000). Observations of representative reacted N Au-1 indicate bulk nontronite along with goethite and the 10 Å phase in the glauconite-illite series (Figure 4b). The 10 Å phase in the glauconite-illite series, and the biotite that has been previously detected in N Au-1 (KEELING et al., 2000) are likely to be the same or very similar, given their similarity by X-ray diffraction. The representative reacted nontronite also shows a shift in the 001 peak to lower angles, possibly due to cation exchange between the Ca originally in the interlayer, and the Na present in solution, as well as an increase in peak width due to weathering of nontronite, either due to a reduction in grain size or intra-lattice (stacking) disorder. This is relevant to smectites at Gale which also show a smaller basal spacing (VANIMAN 2014). The goethite in the reacted material is fine scale, with an average grain size likely 100-300 nm.

Synchrotron XRD analyses did not detect anatase, kaolinite, or quartz in the reacted sample, in contrast to the untreated nontronite. This could be due to either 1) the inherent variability that comes with fine scale micro XRD analyses that sample a very small volume of each aggregate of grains or 2) more significant dissolution of these minerals relative to nontronite. The loss of anatase is consistent with the results of

GAINEY et al. (2014) who showed steady state concentrations of Ti below detection. The loss of quartz is also not surprising, due to the very crystalline nature of that mineral, which means that very small concentrations can be detected by XRD. Due to the very small concentrations of quartz, and the much higher surface area of the bulk nontronite, we anticipate that the dissolution of quartz was minor relative to the dissolution of the bulk nontronite. In addition, dissolution trends are consistent with previous observations of dissolution of clay minerals, and not with what would be expected if dissolution of quartz were an important factor, which is discussed below. Similarly, the small amounts of kaolinite, and the fact that it has a significantly slower dissolution rate at the pH of our experiments than nontronite (GAINEY et al., 2014) suggest that its dissolution was also minor relative to the dissolution of the bulk nontronite. The detection of significant goethite in the reacted material (Figure 4b) is consistent with the low stoichiometric release of Fe relative to silica throughout the experiments (Figure 1), although goethite has also previously been detected in unreacted N Au-1 (Keeling et al. 2000). We note, however, that all of these trends are observed in the mineralogy of the material sampled at the end of the experiment after the final, steady concentration measurement, rather than throughout the experiment.

In a separate synchrotron experiment, a single whitish reacted N Au-1 grain which was also observed to be common was examined by synchrotron-X-ray diffraction. The obtained diffraction pattern indicates the presence of a highly disordered or nanocrystalline phyllosilicate that can be interpreted as disordered nontronite (Figure 4c). This observation suggests the potential dissolution of nontronite and reprecipitation of disordered nontronite or a phase similar to it.

3.4 Dissolution Rates

Silicon occupies 90% of the tetrahedral sites in nontronite (VELDE, 1995; KEELING et al., 2000; GAINNEY et al., 2014), and dissolution of the tetrahedral site is assumed to represent the rate-limiting step in smectite dissolution (MARTY et al., 2011). We therefore calculated apparent dissolution rate constants from silica release.

Several approaches were followed to ensure that at least one steady point was measured for all experiments. Unless steady conditions were obviously reached during the first measured 13 points ($a_{\text{H}_2\text{O}} = 0.50$ conditions only (see Supplementary Material and Figures 5 and 6)), at least one point was measured after a significantly longer time period (1-4 months) than the duration of the initial experiments. For experiments in solutions with activity of water = 1.00 and 0.75, that point, or the average of multiple such points, was used as the steady condition for calculation of apparent dissolution rate constants. For the $a_{\text{H}_2\text{O}} = 0.50$ experiments, steady conditions were defined as unchanged concentrations for three or more days during the initial experiments, and the average of the last 5 points was used as the steady value. The fact that steady conditions in the $a_{\text{H}_2\text{O}} = 0.50$ brines were reached within the first 13 sampling points is not unexpected as silica solubility is lower in brines than in dilute solutions and silica precipitation rates increase with increasing ionic strength (ILER, 1979; ICOPINI et al., 2005).

In all cases but the experiments performed at 4.0 °C, silica release had clearly approached steady conditions by the long-term point (Supplementary Material figures 1-14). In experiments performed at 4.0 °C, silica release less obviously reaches

steady conditions. However, the measured silica concentrations display curvature over time (Figure 5 and Supplementary Material), and since long term silica concentrations at 4.0 °C are only slightly lower than the long term points measured at 25.0 °C and 45.0 °C, they therefore likely represent a good estimate of steady conditions.

The presence of steady conditions (Supplementary Material figures 1-14) could be due to either steady state conditions, in which Si release from one phase is equal to Si precipitation to another, or true chemical equilibrium with a Si-containing phase, in this case, nontronite. In order to model either behavior, we calculate the rate of change in moles of silica released at any time (m) as resulting from the apparent dissolution rate constant (k_{diss}) multiplied by the surface area of the primary mineral, A (m²), minus the loss due to precipitation, with k_{ppn} (s⁻¹) defined as the precipitation rate constant of the secondary phase multiplied by the moles released at any point (m) (HAUSRATH and BRANTLEY 2010).

$$\frac{dm}{dt} = Ak_{diss} - k_{ppn}m \quad . \quad (2)$$

Manipulating this equation results in an equation that reduces at steady state to

$$0 = Ak_{diss} \left(1 - \frac{k_{ppn}}{Ak_{diss}} m_{ss} \right) \quad , \quad (3)$$

where m_{ss} is moles released at steady state. Rewriting this equation to isolate m_{ss} results in the following equation

$$m_{ss} = \frac{Ak_{diss}}{k_{ppn}}, \quad (4)$$

where after substitution, separating variables and integrating, the resultant equation can be used to calculate the apparent dissolution rate constant (k_{diss}) if moles released at any given time period, moles released at steady state, and surface area are known (see HAUSRATH and BRANTLEY 2010 for more detail):

$$-m_{ss} \ln \left(1 - \frac{m}{m_{ss}} \right) = Ak_{diss}t + C \quad (5)$$

where m is moles released of silica at each point calculated as described in equation 1, m_{ss} is moles released at steady state based on the long term point(s) measured after 5-179 days as described above, A is the surface area measured by BET analysis as described above, k_{diss} is the apparent dissolution rate constant in $\text{mol m}^{-2} \text{s}^{-1}$ calculated over the entire duration of dissolution, t is time in seconds, and C is the constant of integration. The uncertainty on the apparent dissolution rate constant was estimated from the standard error on the regression (mol s^{-1}) with the 5% uncertainty of the BET surface area (m^2) propagated through, and divided by the stoichiometric coefficient (6.98 mol Si per 1 mol nontronite). Apparent dissolution

rate constants decreased with decreasing activity of water and temperature (Table 1; Figure 7 and 8).

An apparent activation energy was calculated by plotting the natural log of the apparent dissolution rate constant versus $1000/T$, where T is the temperature in K. The apparent activation energy is the negative slope of that line multiplied by the universal gas constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$). In these experiments, apparent dissolution rate constants from batch reactors with $a_{\text{H}_2\text{O}} = 1.00$ containing CaCl_2 were used to calculate an apparent activation energy (Figure 8) of $54.6 \pm 1.00 \text{ kJ/mol}$.

4. Discussion:

4.1 The effect of brines on nontronite dissolution:

In these experiments, dissolution of nontronite was slower in lower water activity brines than in dilute solutions (Figure 7). Apparent dissolution rate constants of nontronite in $a_{\text{H}_2\text{O}} = 0.75$ CaCl_2 solutions were 0.20 times as fast when compared to apparent dissolution rate constants of nontronite in $a_{\text{H}_2\text{O}} = 1.00$ CaCl_2 solutions, while apparent dissolution rate constants of nontronite in $a_{\text{H}_2\text{O}} = 0.50$ CaCl_2 solutions were 0.017 times as fast when compared to apparent dissolution rate constants in $a_{\text{H}_2\text{O}} = 1.00$ CaCl_2 solutions. Apparent dissolution rate constants for nontronite in $a_{\text{H}_2\text{O}} = 0.75$ NaCl solutions were 0.11 times as fast when compared to apparent dissolution rate constants of nontronite in $a_{\text{H}_2\text{O}} = 1.00$ NaCl solutions.

Previous studies examining mineral dissolution rates in the presence of brines have similarly shown that dissolution rates decrease with decreasing water activity (HAUSRATH AND BRANTLEY, 2010; PRITCHETT et al., 2012; DIXON et al., 2015;

OLSEN et al., 2015). HAUSRATH AND BRANTLEY (2010) documented a decrease in olivine dissolution of an order of magnitude in CaCl_2 - NaCl - H_2O near-eutectic brines compared to dilute solutions. OLSEN et al. (2015) suggested that dissolution rates of forsteritic olivine are slowed in Mg-sulfate, Na-sulfate, Mg-nitrate, and K-nitrate brines due to decreases in the available water participating as a ligand in the dissolution reaction. PRITCHETT et al. (2012) documented a decrease in jarosite dissolution rates in early experiments of almost two orders of magnitude in an $a_{\text{H}_2\text{O}} = 0.35$ brine compared to dilute solutions. The early decrease in jarosite dissolution was then followed by an increase in jarosite dissolution rates following gypsum precipitation allowing Cl^- complexation, although rates were still slower than in dilute solutions. DIXON et al. (2015), who performed batch jarosite dissolution experiments similar to PRITCHETT et al. (2012) but also performed experiments in flow-through reactors, confirmed the decreased dissolution rates in brines in general, as well as the increase in jarosite dissolution rates in saturated calcium chloride brines over time. Both OLSEN et al. (2015) and PRITCHETT et al. (2012) show a linear decrease in log dissolution rates with decreasing activities of water.

Our results also show a linear decrease in log apparent dissolution rate constants with decreasing activities of water, which is the same within uncertainty as that measured by OLSEN et al. (2015) and PRITCHETT et al. (2012) (Figure 9). Solutions used by OLSEN et al. (2015) at $\text{pH} = 2$ covered activities from 1.0 to 0.91, and the slope of the decreasing log dissolution rates of forsteritic olivine with decreasing activity of water was 3.27 ± 0.91 . In PRITCHETT et al. (2012), dissolution of jarosite was measured in CaCl_2 and NaCl brines ($a_{\text{H}_2\text{O}} = 1.0$ -0.35) using ultrapure

deionized water with a pH of ~ 3 -4. These jarosite experiments showed a linear decrease in log dissolution rates of jarosite with decreasing activity of water with a slope of 3.85 ± 0.43 (Figure 9). Our results, which have a slope of the decreasing log apparent dissolution rate constant of nontronite with decreasing activity of water of 3.70 ± 0.20 , are within uncertainty of OLSEN et al. (2015) and PRITCHETT et al. (2012). They are therefore also consistent with decreased activity of water decreasing dissolution, likely due to the water acting as a ligand during nontronite dissolution (OLSEN et al., 2015).

Apparent dissolution rate constants for nontronite in the CaCl_2 and NaCl $a_{\text{H}_2\text{O}} = 0.75$ brines were within uncertainty of each other (Table 1), but apparent dissolution rate constants in the $a_{\text{H}_2\text{O}} = 1.00$ CaCl_2 solutions were 0.62 times as fast as in the $a_{\text{H}_2\text{O}} = 1.00$ NaCl solution. Multiple factors could be contributing to the difference between dissolution in the 0.01 M NaCl and CaCl_2 solutions, including differences in the ionic strength and the ions in the solution, as well as the identity of the ions (Ca versus Na) present within the interlayer of the clay mineral.

The 0.01 M solutions of CaCl_2 and NaCl have different ionic strengths (0.01 mol for the NaCl solution and 0.02 mol for the CaCl_2 solution calculated using PHREEQC (PARKHURST AND APPELO, 1999). DOVE AND NIX (1997) have shown that the presence of cations enhanced dissolution of quartz by modifying rates of solvent motion, exchange, or orientation at the mineral – solution interface at concentrations that bracket those used in our $a_{\text{H}_2\text{O}} = 1.00$ experiments (0.0001-0.2 molal). However, they also showed that the effects of Ca and Na are approximately equal. If the effect observed in these experiments were based solely on the ionic

549 strength, then the difference between the ionic strengths of the two solutions would
550 likely cause enhanced dissolution in the CaCl_2 solution. Since enhanced dissolution
551 is instead observed in the presence of the NaCl solution, the difference in ionic
552 strengths between the two solutions is likely not the controlling factor in the
553 differences in dissolution measured in $a\text{H}_2\text{O} = 1.00$ solutions.

554 The exchange of the Na ion in solution with the Ca ion in the nontronite
555 interlayer is shown in the synchrotron microXRD results (Figure 4) where the
556 reacted nontronite has a 001 peak shifted to lower angles due to the smaller sodium
557 ion. This ion exchange may cause dissolution of nontronite to be faster in the
558 presence of solutions in which the ion in solution is different from that in the
559 interlayer. In previous work, MYLLYKYLA et al. (2013) performed dissolution
560 experiments of either Na- or Ca-containing montmorillonite in a low ionic strength
561 solution ($I = 0.005\text{m}$) that contained $\sim 10\times$ as many moles of Na as Ca. They
562 observed slightly enhanced dissolution of the Ca-containing montmorillonite over
563 the Na-containing montmorillonite at 25°C . Since the solution they were using
564 contained predominantly Na ions, their results are similarly consistent with faster
565 dissolution of smectites when the interlayer cation differs from that in solution,
566 leading to ion exchange. This effect therefore likely explains the observations of our
567 low ionic strength experiments.

568 Dissolution of nontronite in dilute 0.01M CaCl_2 and NaCl solutions in our
569 batch reactors was faster than nontronite dissolution rates previously measured
570 using flow-through reactors at a similar pH (Figure 7) (GAINEY et al., 2014). The
571 nontronite used in the GAINEY et al. (2014) study was the same NAu-1 as the

nontronite used in this study, with the same size fraction (40-125 μm). However, GAINEY et al. (2014) used the final surface area rather than the initial surface area used in this study. When the GAINEY et al. (2014) rates are normalized to the initial surface area of washed nontronite used in this study, flow-through dissolution rates were approximately 0.11-0.35x as fast as the dissolution measured here (Figure 7). This is consistent with previous studies which have shown that dissolution rates of smectite measured in batch reactors were three times faster than smectite dissolution rates in flow-through reactors (FURRER et al., 1993). The difference in rates measured in batch and mixed flow reactors can be caused by different particle aggregation as a result of the difference in mixing methods (FURRER et al., 1993). In addition, GAINEY et al. (2014) calculated rates from the last five data points of each steady state condition, whereas in this study we used the solution chemistry over the entire duration of the experiments.

Both the apparent dissolution rate constants measured in this study as well as the rates measured by GAINEY et al. (2014) are similar to previous measurements of clay mineral dissolution rates in the literature (WIELAND AND STUMM, 1992; CAMA et al., 2002; ROZALÉN et al., 2008). WIELAND AND STUMM (1992) measured dissolution rates for kaolinite using Si release of $9.73 \times 10^{-13} \pm 1.1 \times 10^{-13} \text{ mol m}^{-2} \text{ s}^{-1}$ at a pH of 2.00 and CAMA et al. (2002) measured dissolution rates for kaolinite based on silica of $3.61 \times 10^{-14} \pm 5.8 \times 10^{-15} \text{ mol m}^{-2} \text{ s}^{-1}$ at pH 2.04, both in flow-through reactors. ROZALÉN et al. (2008) measured a montmorillonite dissolution rate based on Si of $3.30 \times 10^{-14} \text{ mol m}^{-2} \text{ s}^{-1}$ (error <15%) at pH 1.98. Dissolution measured in our study was faster than kaolinite dissolution measured by WIELAND AND STUMM (1992) and CAMA et al.

(2002) and montmorillonite dissolution measured by ROZALÉN et al. (2008). The dissolution of nontronite is likely impacted by substitution occurring within the mineral structure: increasing amounts of ferric Fe relative to Al in the octahedral site is likely to decrease the solubility of the mineral based on previous measurements that showed that the solubility of smectites decreased with the composition of the octahedral layer in the following order: $\text{Mg} > \text{Fe}^{2+} > \text{Al} > \text{Fe}^{3+}$ (TARDY AND GARRELS, 1974; TARDY AND FRITZ, 1981). With substitution of Fe in the tetrahedral layer, we anticipate that dissolution will increase due to the disruption of the mineral structure (KOMADEL, 2003). However, this effect was not tested in this study due to the use of only one mineral composition. Relative dissolution can also be difficult to compare due to differences in experimental setup and surface area measurements between laboratories.

The precipitation of a secondary phase similar to disordered nontronite during our experiments is not surprising. Our experiments were intentionally run to steady conditions (see Figures in SOM), and our kinetic modeling incorporates the increasingly important back reaction (precipitation of a silica-containing phase) throughout the experiments. The indication by synchrotron XRD that the proposed secondary phase is disordered and nanocrystalline is also not surprising – it precipitated relatively rapidly during our low temperature experiments, which would lead to a more disordered state. In addition, the interactions between surface enthalpy and phase transformation energetics mean that materials that would be metastable at larger grain sizes can be stabilized at the nanophase (NAVROTSKY et al., 2008), which may have been important in stabilizing the nanocrystalline material observed in our experiments.

Although the presence of other trace phases with the bulk nontronite in N Au-1 detected by synchrotron analyses is not ideal, their presence does not affect the main conclusion of this work, which is that decreases in the activity of water decrease the dissolution rate in a very similar manner for very divergent minerals. As discussed above, our results also do not show the effects that would be expected if dissolution of trace phases were an important factor. We also note that although the use of synchrotron microXRD is ideal for this purpose of potentially detecting small amounts of poorly crystalline material present, it also is inherently not a bulk measurement, and therefore captures variability at a very fine scale.

4.2 Effect of Temperature and Activation Energy:

Brines remain liquid at lower temperatures than dilute solutions, including the low temperatures on present day Mars (BRASS, 1980; HABERLE et al., 2001). Nontronite dissolution as a function of temperature is therefore relevant to interpreting past aqueous interactions on Mars. Using apparent dissolution rate constants measured in dilute CaCl_2 solutions at 4.0 °C, 25.0 °C, and 45.0 °C, an apparent activation energy of 54.6 ± 1.0 kJ/mol was calculated. To the best of our knowledge, this is the first measured activation energy for nontronite dissolution.

This apparent activation energy for nontronite dissolution is similar to previously measured apparent activation energies for clay mineral dissolution. Apparent activation energies for smectite dissolution have been reported as 87 kJ/mol (no error reported, although the error on the rate is reported at 15%) for K-montmorillonite when measured in flow-through and batch reactors over a pH

range of 1.0-5.8 and a temperature range of 25° - 70 °C (ROZALÉN et al., 2008). AMRAM AND GANOR (2005) measured an apparent activation energy of 71.1 ± 8.4 kJ/mol (for a temperature range of 25 °-70 °C) for smectite. CAMA et al. (2002) report an apparent activation energy of 78.4 kJ/mol for kaolinite dissolution at pH 2.0 in flow-through reactors at temperatures ranging from 25° - 70 °C (CAMA et al., 2002). PALANDRI AND KHARAKA (2004) calculated an apparent activation energy of dissolution of smectite of 23.6 kJ/mol, kaolinite of 65.9 kJ/mol and montmorillonite of 48.0 kJ/mol using dissolution data from CARROLL AND WALTHER (1990); NAGY et al. (1991); SOONG (1993); GANOR et al. (1995); HUERTAS et al. (1999a); HUERTAS et al. (1999b) for kaolinite, NAGY (1995) for montmorillonite, and SVERDRUP (1990); ZYSSET AND SCHINDLER (1996); BAUER AND BERGER (1998); HUERTAS et al. (2001) for smectite. The activation energy measured in our experiments is also more consistent with the activation energy of the mineral interface reaction (~60 kJ/mol) rather than the activation energy of diffusion (~20 kJ/mol) (Brantley 2008), suggesting interface control in our experiments.

4.3 Implications for Mars:

Though evidence for clay mineral formation by extensive interaction with liquid water early in Mars history is widespread, the low temperatures of the present-day martian surface make aqueous alteration by brines the most probable form of recent water-rock interaction on Mars. These brines could be habitable environments. Although rare, life on Earth has been found at activities of water as low as 0.61 in a high-sugar food and also in saturated NaCl brines with an $a_{H_2O} = 0.75$ (GRANT, 2004). Gale Crater has been shown to have the potential for

environmental conditions that keep perchlorate brines liquid (MARTÍN-TORRES et al., 2015). These brines would have temperatures and activities of water that are too low to support terrestrial life, but areas with higher humidity and temperatures could allow brines of other compositions to exist. NaCl and CaCl₂ brines are habitable on Earth and would be stable on Mars at higher temperatures and humidities.

Dissolution of nontronite in high ionic strength solutions and at low temperatures is significantly slower than in dilute solutions at room temperature, suggesting that clay minerals reacted with brines on Mars may display much less dissolution than clay minerals interacting with dilute solutions for the same duration of time. In order to quantify this effect, using dissolution data from this study and GAINEY et al. (2014), we have modeled nontronite dissolution under a range of pH, temperature, and activity of water conditions that are relevant to Mars (Figure 10). Results indicate that dissolution of nontronite on Mars may be very slow, and that the activity of water effect examined in this study has a larger impact on dissolution than the temperature or pH range examined. Observable dissolution of nontronite may therefore indicate potentially habitable conditions occurring on Mars over very long timescales.

The indications of interaction with brines are subtle in collected data. Infrared spectra show little to no systematic variability in the nontronite due to treatment over the timescales of this study. XRD data do show a modest shift in the 001 peak due to cation exchange in the interlayer. Thus, in a martian geologic unit, nearby nontronite samples with different layer spacings may indicate interaction

with brines of different fluid cation compositions at a later time in some locales. Indeed, such 001 peak shifts have been found in inferred paleolake sediments at Gale crater and attributed to variable interactions with later diagenetic fluids (Vaniman et al., 2014).

An additional tracer of later alteration of nontronite might be the presence of silica. Spectral evidence exists for widespread silica on the surface of Mars (MICHALSKI et al., 2003) which has been attributed to surficial aqueous activity (KRAFT et al., 2003). Martian silica coatings may be similar to coatings found on Earth in cold and dry environments (DORN, 1998; DIXON et al., 2002; HAUSRATH et al., 2008). Equilibrium with amorphous silica is reached faster and at lower concentrations at lower activities of water (ICOPINI et al., 2005). The decreased release of silica from the dissolution of nontronite over time in these experiments could be due to the precipitation of amorphous silica, which has been detected in previous dissolution experiments of nontronite (GAINEY et al., 2014). Precipitated silica would be expected to form a silica-rich coating on the nontronite mineral surfaces. On these samples, however, silica-rich coatings were not detected using either FE-SEM, VNIR or FTIR spectroscopy, possibly due to the relatively short duration of the experiments (85-179 days for the final time point), and the low total amount of dissolution (~2-5% for dilute solutions at all temperatures, and < 1% for all brines). FTIR observations show only subtle differences (Figure 3), likely due to the alteration of trace phases.

Low Fe/Si ratios in solution samples (Figure 1) indicate that Fe is less mobile than silica. Low iron release was also observed in nontronite dissolution by GAINEY

et al. (2014) at pH 0.9 and 1.7. METZ et al. (2005) observed lower than expected Fe release compared to Al in smectite dissolution, which was caused by preferential Fe reabsorption or precipitation. Our results may result from non-stoichiometric dissolution, Fe sorption, or precipitation of Fe-bearing phases. A combination of precipitated Fe-bearing phases and possible formation of reprecipitated disordered nontronite (Figure 4) could also explain the similarities between reacted and unreacted nontronite. XRD results suggest goethite formation, although goethite has also been found in unreacted NAu-1 (KEELING et al., 2000). The breakdown of iron silicates, including iron-bearing clays, by partial, low temperature alteration has also been proposed to explain the ubiquity of nanophase Fe(III) oxides in Martian dust eg (GOETZ et al., 2005).

5. Conclusions:

A saturated NaCl brine with $a_{\text{H}_2\text{O}} = 0.75$, like the one used in this study, can remain liquid down to -21 °C (BAUER et al., 1988) and has hosted life for a few eukaryotes on Earth (GRANT, 2004). Environments on Mars that contain brines may therefore be currently habitable environments.

Nontronite has been detected on the surface of Mars, particularly in ancient terrains that have been exposed at the surface for billions of years (POULET et al., 2005; BIBRING et al., 2006; BISHOP et al., 2008; EHLMANN et al., 2009; MILLIKEN et al., 2010; THOMSON et al., 2011). To interpret interactions between nontronite and potential solutions on Mars, we measured dissolution of nontronite in solutions

with activities of water ranging from 1.00 to 0.50 and temperatures ranging from 4.0° - 45.0 °C.

Results indicate that nontronite dissolution decreases in brines with decreasing activity of water, and that the relationship between log dissolution rates and the activity of water in multiple brines (NaCl, CaCl₂ and MgSO₄) for multiple minerals (jarosite, nontronite and olivine) is both linear and the same within uncertainty (OLSEN et al., 2015; DIXON et al., 2015). This result strongly supports the proposed mechanism that water behaves as a ligand during dissolution. Cation exchange in the interlayer has been shown to slightly increase dissolution in $a_{H_2O} = 1.00$ solutions. Nontronite dissolution also decreased with decreasing temperature and an apparent activation energy of 54.6 ± 1.0 kJ/mol was calculated, similar to other apparent activation energies of smectite dissolution. Our results clearly demonstrate that nontronite dissolves more slowly in the presence of brines than in dilute solutions. If evidence of nontronite dissolution (such as nontronite depletion in a soil that had a nontronite-rich parent material, for example) were observed on the martian surface, it would therefore reflect a much great period of dissolution if the altering solutions were brines than if they were dilute solutions. Deposits in which nontronite has been perceptibly leached may therefore indicate potentially habitable conditions occurring over very long timescales on Mars.

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773 **Figures and Tables**

774 **Table 1. Apparent dissolution rate constants**

T (°C) ¹	Salt	aH ₂ O ²	Duration (days)	k _{diss} (mol mineral m ⁻² s ⁻¹)	Uncertainty ³	k _{diss} (mol mineral g ⁻¹ s ⁻¹)	Uncertainty ³
25.0	CaCl ₂	1.00	179	1.23x10 ⁻¹²	1x10 ⁻¹³ (8%)	3.78x10 ⁻¹¹	2.2x10 ⁻¹² (6%)
25.0	CaCl ₂	1.00	179	1.13x10 ⁻¹²	9x10 ⁻¹⁴ (8%)	3.50x10 ⁻¹¹	2.2x10 ⁻¹² (6%)
25.0	CaCl ₂	0.75	179	2.13x10 ⁻¹³	3.2x10 ⁻¹⁴ (15%)	7.99x10 ⁻¹²	9.1x10 ⁻¹³ (8%)
25.0	CaCl ₂	0.75	179	2.59x10 ⁻¹³	2.9x10 ⁻¹⁴ (11%)	6.58x10 ⁻¹²	8.4x10 ⁻¹³ (8%)
25.0	CaCl ₂	0.50	15	1.41x10 ⁻¹⁴	1.7x10 ⁻¹⁵ (12%)	4.36x10 ⁻¹³	4.8x10 ⁻¹⁴ (8%)
25.0	CaCl ₂	0.50	15	2.69x10 ⁻¹⁴	4.0x10 ⁻¹⁵ (15%)	8.3x10 ⁻¹³	1.2x10 ⁻¹³ (8%)
25.0	NaCl	1.00	105	1.74x10 ⁻¹²	9x10 ⁻¹⁴ (5%)	5.35x10 ⁻¹¹	3x10 ⁻¹³ (8%)
25.0	NaCl	1.00	105	2.06x10 ⁻¹²	1.0x10 ⁻¹³ (5%)	6.35x10 ⁻¹¹	5x10 ⁻¹³ (8%)
25.0	NaCl	0.75	147	1.94x10 ⁻¹³	2.4x10 ⁻¹⁴ (12%)	5.97x10 ⁻¹²	5.8x10 ⁻¹³ (8%)
25.0	NaCl	0.75	147	2.04x10 ⁻¹³	3.5x10 ⁻¹⁴ (17%)	6.29x10 ⁻¹²	6.7x10 ⁻¹³ (8%)
45.0	CaCl ₂	1.00	85	5.22x10 ⁻¹²	3.8x10 ⁻¹³ (7%)	1.61x10 ⁻¹⁰	9x10 ⁻¹² (8%)
45.0	CaCl ₂	1.00	85	4.73x10 ⁻¹²	3.9x10 ⁻¹³ (8%)	1.46x10 ⁻¹⁰	9x10 ⁻¹² (8%)
4.0	CaCl ₂	1.00	105	2.39x10 ⁻¹³	1.3x10 ⁻¹⁴ (5%)	7.37x10 ⁻¹²	1.7x10 ⁻¹³ (8%)
4.0	CaCl ₂	1.00	105	2.28x10 ⁻¹³	1.2x10 ⁻¹⁴ (5%)	7.04x10 ⁻¹²	1.0x10 ⁻¹³ (8%)

775 ¹Temperature measured to 0.1 °C using the internal thermometer on the water bath and cold-room.

776 ²aH₂O from RARD AND CLEGG (1997) for CaCl₂ brines, CHIRIFE AND RESNIK (1984) for NaCl brine, and calculated using PhreeqC
777 (PARKHURST AND APPELO (1999)) for all 0.01 M solutions.

778 ³The uncertainty on the apparent dissolution rate constant was estimated from the standard error on the regression (mol s⁻¹)
779 with the 5% uncertainty of the BET surface area (m²) propagated through, and divided by the stoichiometric coefficient (6.98
780 mol Si per 1 mol nontronite) to obtain the uncertainty in mol mineral m⁻² s⁻¹.

Figure 1. Fe: Si ratios for experiments at 25 °C where [Fe] was above detection. The solid line represents the stoichiometric ratio of Fe: Si in the unreacted nontronite (0.52). Experiments at 25 °C remain relatively stable near 0.20 over time. Analytical uncertainty on solution chemistry is smaller than all points.

795 Figure 2. FE-SEM images of unreacted and reacted surfaces of N Au-1. (A) Unreacted
796 sieved and washed N Au-1 observed before dissolution experiments, compared to reacted
797 N Au-1 removed from dissolution experiments conducted at (B) 25.0° C $a_{\text{H}_2\text{O}} = 1.00$
798 CaCl_2 , and (C) 25.0° C $a_{\text{H}_2\text{O}} = 1.00$ NaCl. Surface textures appear similar for all
799 experiments as well as the unreacted material. In each case, the scale bar is 10 micron.

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802 Figure 3. Top: FTIR spectra of unreacted and reacted nontronite, with the spectra from
803 wavenumber 2500 – 3900 cm^{-1} top left, and the spectra from wavenumber 1400 – 350
804 cm^{-1} top right. The Si-O stretch near 1000 cm^{-1} becomes narrower for all reacted samples.
805 A reflectance maximum/emission minimum at 1220 cm^{-1} and a feature at 790 cm^{-1}
806 disappear in reacted samples compared to the unreacted N Au-1 spectra. The Al/Si-O-Si

807 deformations between 600 and 400 cm^{-1} change in shape for all 25.0° C and 45.0 °C
808 experiments. The spectral properties of the 25-NaCl-0.75 sample near 3600 cm^{-1} may be
809 due to an initial trace phase or precipitated iron oxides and oxyhydroxides. In each case,
810 the sample analyzed was the first of the duplicates (Table 1), and the label indicates that
811 the sample was either the unreacted N Au-1, or the conditions of alteration, with the
812 temperature listed first, followed by the salt, followed by the activity of water in the
813 solution.

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815 Bottom: VNIR spectra of unreacted and reacted nontronite at wavelengths from 0.5-2.5
816 μm , offset for clarity, enlargement from 2.10 μm to 2.45 μm shown to the right. Little
817 change is noted with reaction - for samples treated with the 0.75 aH₂O CaCl₂ brine, there
818 is a slight change in the absorption near 2.43 μm with a subtle shift of about 10nm
819 shortward. In each case the sample analyzed was the first of the duplicates (Table 1), and
820 the label indicates that the sample was either the unreacted N Au-1, or the conditions of
821 alteration, with the temperature listed first, followed by the salt, followed by the activity
822 of water in the solution.

Figure 4. Synchrotron XRD analyses of a) unreacted N_{Au}-1 b) a representative sample of N_{Au}-1 reacted in 0.01M NaCl solution, and c) a grain of whitish N_{Au}-1 that had been reacted in a 0.01M NaCl solution and was also common. Results indicate that unreacted N_{Au}-1 can be fit as bulk nontronite containing small amounts of kaolinite, quartz, anatase and a 10 Å phase in the glauconite-illite series. This is consistent with previous analyses of N_{Au}-1 that indicate that it contains traces of kaolinite, quartz and a 10 Å phase (previously identified as biotite) along with ~ 90% nontronite (KEELING et al. 2000). Representative reacted N_{Au}-1 can be fit as a mixture of bulk nontronite also containing goethite, and the 10 Å phase in the glauconite-illite series. The 10 Å phase in the glauconite-illite series and the biotite that has been previously detected in N_{Au}-1 (KEELING et al., 2000) are likely to be the same or very similar, given their similarity by X-ray diffraction. The representative reacted nontronite also shows a shift in the 001 peak to lower angles, possible due to cation exchange between the Ca originally in the interlayer, and the Na in the solution, as well as an increase in peak width due to weathering of nontronite, either due to a reduction in grain size or intra-lattice (stacking) disorder. This is relevant to smectites at Gale which also show a smaller basal spacing (VANIMAN 2014), and may also enhance dissolution. MicroXRD analyses of whitish grains of reacted N_{Au}-1 indicate significant changes in grain size, and suggest the formation of disordered nontronite (c). The presence of a material comparable with disordered nontronite (c) is consistent with potential dissolution of nontronite and reprecipitation of a disordered phase. The modeled pattern is that of bulk nontronite that does not take into account the shape of the crystallites, and assumes that the bulk structure of the nanocrystalline material is the same as that of the bulk nontronite.

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856 Figure 5. Moles silica released as a function of time at temperatures of 4.0 °C, 25.0 °C,
857 and 45.0 °C at $a_{\text{H}_2\text{O}} = 1.00$. Steeper slopes indicate faster dissolution, and these
858 experiments therefore indicate that dissolution increased with increasing temperature.
859 Analytical uncertainty on solution chemistry is smaller than all points.

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863 Figure 6. Moles silica released as a function of time at $a_{\text{H}_2\text{O}} = 1.00, 0.75, \text{ and } 0.50$ at 25
 864 °C. Steeper slopes indicate faster dissolution. These experiments indicate dissolution
 865 decreased with decreasing activity of water, and that in very dilute solutions, nontronite
 866 dissolution is increased in the presence of 0.01 M NaCl solutions relative to 0.01 M
 867 CaCl_2 solutions. Samples were taken at different time intervals to accommodate different
 868 dissolution rates. The 1.00 $a_{\text{H}_2\text{O}}$ and 0.75 $a_{\text{H}_2\text{O}}$ experiments were sampled 2-3 times a
 869 day for one week while the 0.50 $a_{\text{H}_2\text{O}}$ experiments were sampled daily for three weeks.
 870 Analytical uncertainty on solution chemistry is smaller than all points.

Figure 7. Log dissolution as a function of activity of water for dilute and brine experiments at 25.0° C and pH 1.8-2.0 show a decrease in dissolution with decreasing activity of water. Rates from GAINNEY et al. (2014) were measured at a flow rate = 0.1609 ml/h and pH = 1.8 using the same size fraction N Au-1 as that used in this study. The rate plotted here is the rate reported in GAINNEY et al. (2014) normalized to the initial surface area ($30.9 \pm 1.5 \text{ m}^2 \text{ g}^{-1}$) used in this study ($4.18 \times 10^{-13} \pm 2.8 \times 10^{-14} \text{ moles mineral m}^{-2} \text{ s}^{-1}$) to better compare the results.

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884 Figure 8. Arrhenius plot of nontronite dissolution at pH = 2.0 Measured uncertainties are
 885 smaller than all points. The apparent activation energy is 54.6 ± 1.0 kJ/mol

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Figure 9. Comparison of dissolution of nontronite, jarosite and forsteritic olivine as a function of activity of water. Activities cover a range of 1.0-0.5 for nontronite, 1.0-0.35 for K- and Na-jarosite, and 1.0-0.91 for forsteritic olivine. All experiments were performed at temperatures from 23-26° C; forsteritic olivine and nontronite dissolution experiments were performed at pH = 2.0 For jarosite experiments with $a_{H_2O} < 1.00$ the pH is ~ 3-4.

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898 Figure 10. Nontronite dissolution as a function of pH, temperature and activity of water
 899 likely relevant to martian conditions. Lines show k_{diss} from this study at pH = 2 with a
 900 linear pH dependence under acidic conditions from GAINEY et al. (2014), with the line
 901 indicating the dissolution at 25.0 °C at 0.75 activity of water overlying the line indicating
 902 dissolution at 4.0 °C activity of water = 1.00. Changes to nontronite dissolution caused by
 903 changes in activity of water have a larger impact than temperature and pH under the
 904 range of conditions examined here. Dissolution likely on Mars in brines at low
 905 temperatures is indicated with the arrow.

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