Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 126 (2014) 192–211

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Nontronite dissolution rates and implications for Mars

S.R. Gainey [a,*], E.M. Hausrath [a], J.A. Hurowitz [b], R.E. Milliken [c]

[a] Department of Geoscience, University of Nevada, 4505 S. Maryland Parkway, Las Vegas, NV 89154-4010, United States
[b] Department of Geosciences, Stony Brook University, 255 Earth and Space Sciences Building (ESS), Stony Brook, NY 11794-2100, United States
[c] Geological Sciences, Brown University, 324 Brook Street, Box 1846, Providence, RI 02912, United States

Received 31 May 2013; accepted in revised form 31 October 2013; available online 15 November 2013

Abstract

The Fe-rich smectite nontronite $M^{+}_{1.05}[Si_{6.98}Al_{1.02}][Al_{0.29}Fe_{3.68}Mg_{0.04}]O_{20}(OH)_4$ has been detected using orbital data at multiple locations in ancient terrains on Mars, including Mawrth Vallis, Nilli Fossae, north of the Syrtis Major volcanic plateau, Terra Meridiani, and the landing site of the Mars Science Laboratory (MSL), Gale Crater. Given the antiquity of these sites (>3.0 Ga), it is likely that nontronite has been exposed to the martian environment for long periods of time and therefore provides an integrated record of processes in near surface environments including pedogenesis and diagenesis. In particular, nontronite detected at Mawrth Vallis is overlain by montmorillonite and kaolinite, and it has been previously suggested that this mineralogical sequence may be the result of surface weathering. In order to better understand clay mineral weathering on Mars, we measured dissolution rates of nontronite in column reactors at solution pH values of 0.9, 1.7, and 3.0, and two flow rates (0.16 ml/h and 0.32 ml/h). Solution chemistry indicates stoichiometric dissolution at pH = 0.9 and non-stoichiometric dissolution at pH = 1.7 and 3.0. Mineral dissolution rates based on elemental release rates at pH = 1.7 and 3.0 of Ca, Si and Fe follow the order interlayer > tetrahedral > octahedral sites, respectively. The behavior of all experiments suggests far from equilibrium conditions, with the exception of the experiment performed at pH 3.0 and flow rate 0.16 ml/h. A pH-dependent dissolution rate law was calculated through Si release from experiments that showed no dependence on saturation (far from equilibrium conditions) under both flow rates and is $r = 10^{-12.06\ (\pm 0.123)} \cdot 10^{-0.297\ (\pm 0.058)\cdot \mathrm{pH}}$ where r has the units mol mineral $m^{-2}\,s^{-1}$. When compared to dissolution rates from the literature, our results indicate that nontronite dissolution is significantly slower than dissolution of the primary phases present in basalt under acidic conditions, suggesting that once nontronite forms it could remain stable at or near the surface of Mars for extended periods of time. Nontronite dissolution rates are faster than dissolution rates of montmorillonite (Rozalén et al., 2008) and kaolinite (Huertas et al., 1999), suggesting that chemical weathering of a mixed clay deposit would enrich the proportions of montmorillonite and kaolinite through the preferential dissolution of nontronite. Vis–NIR analyses of our reacted products and thermodynamic modeling of our experimental conditions both indicate the precipitation of amorphous silica within columns, and amorphous silica has also been observed in association with phyllosilicates on the martian surface (Mustard et al., 2008; Ehlmann et al., 2009; Murchie et al., 2009a). Therefore, chemical weathering of strata containing mixtures of montmorillonite, nontronite and kaolinite provides a potential formation mechanism for the mineralogic stratigraphy observed at Mawrth Vallis and other locations on Mars.

* Corresponding author.
E-mail addresses: gaineys@unlv.nevada.edu (S.R. Gainey), elisabeth.hausrath@unlv.edu (E.M. Hausrath), joel.hurowitz@stonybrook.edu (J.A. Hurowitz), Ralph_Milliken@brown.edu (R.E. Milliken).

0016-7037/$ - see front matter
http://dx.doi.org/10.1016/j.gca.2013.10.055

1. INTRODUCTION

Spectral observations from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) and the Observatoire pour la Mineralogie, L'Eau, les Glaces et l'Activite (OMEGA) spectrometer on board the Mars Reconnaissance and Mars Express orbiters, respectively, have detected spectral signatures indicative of clay minerals at numerous locations across the martian surface (Bibring et al., 2005; Poulet et al., 2005; Bibring et al., 2006; Michalski and Noe Dobrea, 2007; Loizeau et al., 2007; Bishop et al., 2008; Ehlmann et al., 2008; Mustard et al., 2008; Murchie et al., 2009b; Wray et al., 2009; Ehlmann et al., 2011). These phyllosillicate detections occur throughout the ancient martian crust, including the Mawrth Vallis region, Nilli Fossae region, north of the Syrtis Major volcanic plateau, and the landing site of the Mars Science Laboratory (MSL), Gale Crater, as well as others (Bibring et al., 2005, 2006; Michalski and Noe Dobrea, 2007; Clark et al., 2007; Ehlmann et al., 2008; Mustard et al., 2008; Murchie et al., 2009b; Wray et al., 2009; Milliken et al., 2010). Clay minerals generally form from the hydrolysis of silicate minerals through hydrothermal alteration, metamorphism and/or weathering and some have speculated that the presence of clay minerals indicate long term water–rock interactions on Mars (Ehlmann et al., 2011). Liquid water is one of the essential requirements for life as we know it; constraining the duration and amount of water on Mars will enable the scientific community to make more accurate predictions regarding the paleo-environmental conditions and past habitability of Mars. Clay minerals may also act as a catalyst in the formation of organic chemical compounds, with clay minerals therefore having a direct impact on possible habitability of Mars (Ferris, 2005).

Stratigraphic relationships and age estimates from crater counting suggest that clay minerals detected from orbit on Mars are ancient (Bibring et al., 2006; Mustard et al., 2008; Murchie et al., 2009a; Ehlmann et al., 2011) and are therefore likely to have been altered by diagenetic and pedogenic processes subsequent to their formation. Exposed stratigraphic units in the Mawrth Vallis region indicate a transition from an Fe- and Mg-rich clay with a spectral signature consistent with nontronite to an Al-rich smectite, potentially montmorillonite mixed with kaolinite and silica (Loizeau et al., 2007; Bishop et al., 2008; Wray et al., 2009; Michalski et al., 2010; Noe Dobrea et al., 2010). The landing site of the Mars Science Laboratory *Curiosity* rover, Gale Crater, also contains deposits of clay minerals that include a thick (tens of meters) deposit of Fe-rich smectite, possibly nontronite (Fig. 1) (Milliken et al., 2010; Thomson et al., 2011). At Gale, the clay minerals are overlain by mixed beds of clay and sulfate minerals and/or sulfate cemented nontronite, which grade upward into sulfate-rich deposits (Milliken et al., 2010). The mineralogical variation within the stratigraphy at these locations and others could indicate changes in depositional environments, diagenetic processes, as well as global changes in martian climate (Milliken et al., 2010). However, few studies have examined nontronite dissolution kinetics and clay-to-clay alterations under Mars-relevant conditions, which could provide a better understanding of the processes that affected the minerals observed at the martian surface.

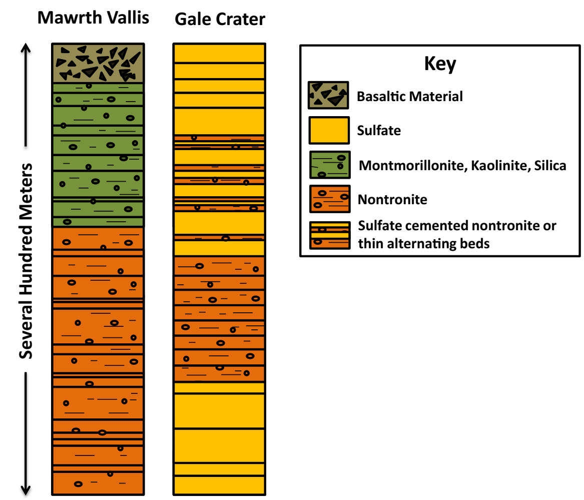

Fig. 1. (A) Stratigraphy of the Mawrth Vallis region, constructed from spectra taken by the Mars Reconnaissance and Mars Express Orbiters (Michalski et al., 2010). (B) Stratigraphy of lower mound Gale Crater, constructed from CRISM data (Milliken et al., 2010). Note the depicted stratigraphy for Gale Crater underlies several kilometers of unidentified dust covered materials (Milliken et al., 2010). ***Strata are not to scale.

Here we report the results of experiments designed to determine the proton-promoted dissolution rates of nontronite and identify secondary precipitates formed during nontronite dissolution. These experimental results allow us to constrain the stability of nontronite at the martian surface and address whether pedogenic alteration can produce the spectral and mineralogical heterogeneity observed in the Mawrth Vallis region and other localities on Mars.

2. MAWRTH VALLIS

The Mawrth Vallis region contains extensive deposits of phyllosilicate-bearing rock (Loizeau et al., 2007, 2010; Michalski et al., 2010). Mawrth Vallis is a valley that transects the region and is believed to have formed through fluvial processes. The rocks in which the clays reside pre-date the incision of the valley, placing their deposition in the early-middle Noachian (3.8–4.1 Gya) (Michalski and Noe Dobrea, 2007; Bishop et al., 2008; Michalski et al., 2010). However, whether the clays are detrital or authigenic is not known, thus the age of the clays is poorly constrained. The stratigraphy is generally characterized by a Fe- and Mg-rich nontronite-bearing unit overlain by an Al-rich montmorillonite-bearing unit mixed with kaolinite and amorphous silica (Fig. 1) (Loizeau et al., 2007; Bishop et al., 2008; Wray et al., 2009; Michalski et al., 2010). Several hypotheses exist addressing the origin and chemical composition of the Mawrth Vallis stratigraphy, including formation under volcanic, sedimentary and pedogenic conditions (Wray et al., 2009; Loizeau et al., 2010; Michalski et al., 2010; Noe Dobrea et al., 2010; Gaudin et al., 2011).