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NASA Proposal Number

13-MFRP13-0072

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SECTION V - Certification and Authorization

Certification of Compliance with Applicable Executive Orders and U.S. Code

By submitting the proposal identified in the Cover Sheet/Proposal Summary in response to this Research Announcement, the Authorizing Official of the proposing organization (or the individual proposer if there is no proposing organization) as identified below:

- certifies that the statements made in this proposal are true and complete to the best of his/her knowledge;
- agrees to accept the obligations to comply with NASA award terms and conditions if an award is made as a result of this proposal; and
- confirms compliance with all provisions, rules, and stipulations set forth in the two Certifications and one Assurance contained in this NRA (namely, (i) the Assurance of Compliance with the NASA Regulations Pursuant to Nondiscrimination in Federally Assisted Programs, and (ii) Certifications, Disclosures, and Assurances Regarding Lobbying and Debarment and Suspension.

Willful provision of false information in this proposal and/or its supporting documents, or in reports required under an ensuing award, is a criminal offense (U.S. Code, Title 18, Section 1001).

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Date

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Proposal Title : Experimental Constraints on Mineralogical and Compositional Changes during Basalt Alteration and Phyllosilicate Formation under Mars-Relevant Conditions	

SECTION VII - Project Summary

Orbiter and rover operations have detected widespread occurrences of clays in the Noachian-aged crust of Mars, primarily Fe(III)-Mg smectites. The processes that formed these clays are the subject of ongoing debate. However, an often overlooked aspect is the lack of ferrous iron-bearing clays and the near universal occurrence of ferric clays. The formation of such phases requires oxidation of iron which is inconsistent with the anoxic conditions present in the early- to mid-Noachian. This suggests ferric clays observed today may be oxidation products of ferrous clays that formed during the Noachian.

Reconstructing past Martian conditions associated with aqueous alteration of the basaltic crust to clays and interpreting modern orbital and rover observations of these deposits requires an understanding of how clay formation and stability varies with redox conditions. Work on the PI's existing grant from this program has shown through geochemical modeling that weathering and hydrothermal alteration in the absence of oxidants produces ferrous clays that are predicted to convert into nontronite/Mg-saponite assemblages upon oxidation. This ongoing project has also shown experimentally that ferrous smectites can be directly oxidized into ferric smectites but that this requires mineral recrystallization and is affected by the oxidant species. Together, these studies have shown that plausible routes exist for temporally decoupled iron-bearing clay formation and the oxidation of iron.

This proposal seeks to place additional fundamental constraints on clay formation via basalt alteration that are needed to better relate mineralogical occurrences on Mars to past conditions. Our prior work has shown that complete conversion of ferrous smectites to nontronites requires a coupling of iron oxidation to recrystallization in order to accommodate the excess charge and strain produced from converting Fe(II) to Fe(III). This affects the rate at which ferrous smectites may undergo oxidation; preliminary data further suggests that this process is affected by clay composition. This project will synthesize Fe(II)- smectites over a compositional range representative of expected Martian clays and characterize their oxidative transformations. In addition, Fe/Mg smectites and other clays on Mars often exist in complex mineral assemblages, sometimes including carbonates, formed through the alteration of basalt. Oxidation of such assemblages may produce different products than when Fe(II) clays oxidize isochemically because mass transfer of chemical components may occur among minerals in an assemblage. This project will produce clay-bearing assemblages through hydrothermal alteration of mafic rocks and then determine the mineral transformation that results from iron oxidation. Finally, APXS instruments on MER and MSL rovers can detect variations in trace element compositions of clay-bearing units in comparison to unaltered mafic rocks on Mars. These elements are known to substitute in the octahedral sheets of clays and measurements on Mars suggest these elements redistribute during basalt alteration. This project will investigate the repartitioning of trace elements that occurs upon oxidation of Fe(II)-smectites and clay-bearing mafic rock alteration assemblages. Identifying the mineralogical and compositional changes associated with basalt alteration and phyllosilicate will be aided by advanced analytical methods, including X-ray absorption, Mössbauer, and visible-near infrared spectroscopies performed on sealed samples or in a glovebox to prevent oxidation. The proposed work will improve our understanding of geochemical processes that operated on Mars in the Noachian by establishing the mineralogical and compositional changes associated with decoupled basalt alteration and iron oxidation. It will also aid in the interpretation of data from current and planned rover and orbital missions and directly addresses a number of goals set by MEPAG.

Experimental Constraints on Mineralogical and Compositional Changes during Basalt Alteration and Phyllosilicate Formation under Mars-Relevant Conditions

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SCIENTIFIC/TECHNICAL MANAGEMENT

1. PROJECT MOTIVATION

Orbiter and rover operations have widespread occurrences of phyllosilicates in the Noachian-aged crust of Mars [1-11]. These phases are most commonly Fe(III)/Mg phyllosilicates, likely nontronite and saponite, but aluminous clays like montmorillonite, kaolinite, and beidellite and hydrothermal phases like serpentine and chlorite have also been detected. Ongoing debate centers on the extent of phyllosilicate production via near-surface alteration versus hydrothermal or magmatic processes [6,7,12]. However, a separate issue that has been less frequently addressed is the near-universal occurrence of iron-bearing phyllosilicates containing oxidized ferric iron rather than the reduced ferrous iron that exists in the mafic crust. Formation of ferric smectites requires oxidation of iron, which can only occur through the addition of an atmospherically-derived oxidant. Such oxidation is inconsistent with the anoxic conditions believed to have been present during the early- to mid-Noachian [13-16] and that dominated the early Earth until ~2.4 Ga [17-22]. The observed stratigraphic association of Al-clays, largely free of iron oxides, above Fe/Mg clays in a number of locations on Mars [5,23,24] is also consistent with an early reducing environment [25], as abundant iron oxides would coexist with the Al-clays if leaching occurred under oxidizing conditions [25,26]. This suggests that widespread iron oxidation post-dates the major clay forming events. A proposal that ferric sulfate deposits in Meridiani Planum, which postdate most clay deposits [3,10], formed through iron oxidation contemporaneous with either deposition or diagenesis [27] is consistent with iron oxidation not occurring until late in the Noachian. The recent observation by the Mars Science Laboratory (MSL) of a blue-gray clay-bearing unit a few centimeters beneath an oxidized surface layer [2] suggests that ferrous iron clays may be widespread on Mars today but are largely undetectable from orbit because of ongoing oxidation of the planet's surface.

Reconstructing past Martian conditions associated with aqueous alteration of basalt to phyllosilicates and interpreting modern orbital and rover observations of these deposits requires an understanding of how phyllosilicate formation and stability varies with redox conditions. Work on the PI's existing grant from this program (see section 4) has shown through geochemical modeling that hydrothermal alteration and low-temperature weathering in the absence of oxidants produces ferrous phyllosilicates that are predicted to convert into nontronite/Mg-saponite assemblages upon oxidation. This ongoing project has also shown experimentally that a ferrous smectite can be directly oxidized into a ferric smectite but that this requires mineral recrystallization and is affected by the oxidant species. Together, these studies demonstrate that iron-bearing clay formation and the oxidation of iron need not have been coeval and that plausible routes exist for these processes to have been temporally decoupled.

Additional fundamental constraints on clay formation via basalt alteration under Mars-relevant (or Mars-plausible) conditions are needed in order to better relate mineralogical occurrences on Mars to past conditions. Our prior work has shown that complete conversion of ferrous smectites to nontronites requires a coupling of iron oxidation to recrystallization in order to accommodate the excess charge and strain produced from converting Fe(II) to Fe(III). This affects the rate at which ferrous smectites may undergo oxidation. Preliminary data suggests that this process is affected by clay composition (see section 4.2.). *The role of clay composition and recrystallization in controlling the rate and extent of iron oxidation needs to be determined in order to establish the conditions under which such processes occur(red) on Mars.* In addition, Fe/Mg smectites and other phyllosilicates on Mars often exist in complex mineral assemblages, sometimes including carbonates, formed through the alteration of basalt (see section 3). Oxidation of such assemblages may produce different products than when ferrous phyllosilicates oxidize isochemically because mass transfer of chemical components may occur among minerals in an assemblage. *The transformations that occur*

upon oxidation of such assemblages need to be determined in order to interpret observations of altered mafic rocks on Mars. Finally, Alpha Particle X-ray Spectrometer (APXS) instruments on Mars Exploration Rover (MER) Opportunity and MSL can detect variations in trace element (e.g., Cr, Mn, Ni, Zn) compositions of phyllosilicate-bearing units in comparison to unaltered Martian basalts. These elements are known to substitute in the octahedral sheets of phyllosilicates [28]. Measurements of sulfate deposits in Meridiani Planum and phyllosilicate units in the rim of Endeavor Crater suggest that trace element redistribution has occurred during basalt alteration [29,30]. The behavior of trace elements during basalt alteration to phyllosilicate-bearing assemblages and the oxidation of phyllosilicates need to be established in order to use APXS trace element data to gain insight into past aqueous processes on Mars.

2. OBJECTIVES

The primary objective of this proposal is to ***determine the mineralogical and chemical signatures of mafic rock alteration and oxidation of the resulting phyllosilicate-bearing assemblages***. Specific objectives include:

- 1. Characterizing the effect of Fe(II)-smectite composition on its susceptibility to oxidation and the resulting mineral product(s).*
- 2. Evaluate the mineral phases that result from oxidation of phyllosilicate-bearing assemblages produced by anoxic isochemical mafic rock alteration*
- 3. Investigate the oxidation products of mafic rocks hydrothermally altered under high-CO₂ conditions.*
- 4. Determine the repartitioning behavior of trace elements during the oxidation of Fe(II)-smectites and phyllosilicate-bearing assemblages produced by anoxic mafic rock alteration.*

3. BACKGROUND INFORMATION

3.1. Occurrences of Phyllosilicates on Mars

Phyllosilicates and other secondary silicate minerals are widely distributed in Noachian-aged terrains [3,5-7,10] and provide insight into near-surface conditions and thus the potential habitability of early Mars. Fe/Mg smectites, primarily identified as nontronite and Mg-saponite, are the most commonly observed and abundant phases, occurring in basin fill, stratigraphic sections with multiple clay-bearing units, and crustal material exposed in impact craters. Multiple formation processes have been proposed for the origins of Fe/Mg phyllosilicates. Near-surface weathering/pedogenesis were considered upon initial detection of these phases [3,11] because of the widespread formation of clays in soils on Earth, but such open system formation processes should produce substantial depth-dependent leaching that cannot explain expansive, thick stratigraphies dominated by Fe/Mg smectites. Many Fe/Mg phyllosilicate deposits are now believed to have formed in the subsurface [3,6,7,12,24,31] through hydrothermal groundwater circulation, diagenesis/low-grade metamorphism, and precipitation from residual fluids during late stages of magma cooling.

Kaolinite and Al-smectites, (montmorillonite and beidellite), are observed less frequently [6]. They show limited occurrence in craters but, when present, often appear in stratigraphic sections in layers above Fe/Mg smectites [5-7]. These Al smectite units in stratigraphic sections are generally free of substantial Fe/Mg smectites and iron oxides. Their composition requires that extensive leaching of Fe and Mg has occurred based on simple mass balance considerations. Given the low solubility of Fe(III), this leaching likely occurred under anoxic conditions. A similar conclusion was reached in a recent study comparing these capping Al smectite units to weathering profiles formed under oxidizing conditions in the Deccan Traps [26].

Chlorites are frequently observed in material exhumed by impact cratering and are often associated with prehnite, zeolites, serpentine, silica, or illite/muscovite [7,8,31,73]. The detection of prehnite indicates hydrothermal alteration of the basaltic crust at temperatures up to 200-400°C [74,75]; the occurrence of chlorite also suggests hydrothermal alteration at temperatures above 200°C [76]. Other phyllosilicates, including Fe/Mg smectites and interstratified chlorite-smectite [77], are compatible with subsurface, hydrothermal formation at lower temperatures (<100 to 250° C) [76]. The presence of Al-rich hydrous alteration phases also suggests subsurface formation at elevated temperature because feldspars, the primary Al host in mafic rocks, shows limited alteration at temperatures similar to those present on Earth's surface (~0 to 40°C) compared to olivine and pyroxenes [76,78-80].

3.2. Composition of Terrestrial Smectites

Smectites are a major product of silicate rock weathering and hydrothermal alteration [28]. A wide range of smectites are observed on Earth (Fig. 1), with the aluminous smectites (montmorillonite, beidellite) found most extensively in continental settings because of the predominantly highly evolved, felsic continental crust. In oceanic settings and continental settings associated with mafic and ultramafic rocks, nontronites and a wide range of intermediate Fe/Mg smectites are observed. Those forming in anoxic subsurface settings [28,33,34,51,56,57,81,82] consist of trioctahedral Fe^{II}-Mg saponites (Fig. 1) rather than the typical ferric smectites, such as nontronite and Fe^{III}-bearing saponites, that form from in soils and on the ocean floor where O₂ is abundant.

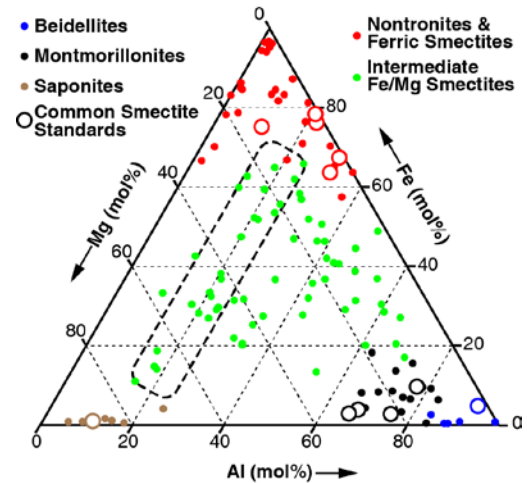


Figure 1. Compositions of smectites observed in continental and marine settings on Earth [28,32-72]. The dashed region outlines the compositional range of trioctahedral smectites (saponites) associated with anoxic basalt alteration. The compositions of commonly-used smectite standards are also shown.

3.3. Mineral Indicators of Noachian Atmospheric Redox State

The redox state of the Noachian atmosphere is poorly constrained but was almost certainly anoxic for much of this time period. Mars' current atmosphere is composed mainly (95.3%) of carbon dioxide [83] with partial pressure of O₂ of about 10⁻⁵ bars [15,84]. Proposed values for P_{O2} in the Noachian include 10⁻⁷⁸ bars as calculated using meteorites [15], to a minimum of 10⁻⁶⁹ bars based on the presence of Fe(III) oxides [14], to between 10⁻¹²-10⁻¹⁵ bars using an estimation method originally applied to early Earth [13]. The study of Martian meteorites clearly supports variable P_{O2} through time, with the oldest meteorite, ALH84001, being the most reduced [16].

Mineral deposits offer important additional constraints on the evolution of the redox state of Mars in the Noachian. The occurrence of widespread ferric oxide and sulfate minerals in late Noachian deposits [3,10,85-88] clearly points to oxidizing conditions around 3.7 Ga. The occurrence of the ferric smectite nontronite in early- to mid-Noachian units has been interpreted to indicate that the atmosphere was capable of oxidizing iron during this earlier period when phyllosilicate formation dominated [89]. This, however, disagrees with established concepts of the redox state of the early Martian atmosphere [13-16]. Modeling and experimental studies by the PI (see section 4) have shown that ferric smectites can be generated through later oxidation of ferrous smectite precursors, phases expected to form during basalt alteration under the anoxic conditions expected in the early- to mid-Noachian [28,84].

Further evidence for an anoxic early- to mid-Noachian atmosphere come from observation of Al phyllosilicate units stratigraphically above Fe/Mg phyllosilicates in many locations [5-7]. These are consistent with subaerial leaching and pedogenesis and are similar to the profiles of phyllosilicates formed on Earth in locales such as the Deccan Traps [26]. However, a major difference between these Martian and terrestrial deposits is that the Al phyllosilicates on Earth are intimately associated with iron oxides, whereas the Martian deposits are largely free of such phases. This difference can only be explained if the Al phyllosilicates on Mars were formed through leaching under anoxic conditions. As these units postdate formation of the more widespread Fe/Mg smectites, this indicates that the atmosphere did not transition to an oxidizing state until after substantial phyllosilicate formation had ceased. It is possible that there was a single major oxidation event on Mars that was coeval [25] with either the initial deposition or later diagenesis of the sulfate-bearing sedimentary rocks at Meridiani Planum from the late-Noachian or Noachian-Hesperian transition, which are younger than the Southern Highland phyllosilicates [3,10]. Recent drilling activities by MSL at Gale Crater show signs of reduced lithified sediments beneath a thin oxidized veneer [2], suggesting that the shallow subsurface of Mars may still contain extensive deposits that predate widespread iron oxidation. Ongoing deposition of oxidants on Mars' surface produced by photochemical and triboelectric processes in the atmosphere [90,91] may continue to oxidize materials exposed on the surface through erosion.

It is now clear that Fe-bearing mineral phases from the early- to mid-Noachian did not require an oxidizing atmosphere to form and more likely were produced under anoxic conditions. The widespread ferric smectites observed today are thus likely later oxidation products of precursor ferrous iron-bearing phases. *Interpreting past Martian environmental conditions using phyllosilicates, the major mineral indicators of aqueous activity in the early- to mid-Noachian, requires an understanding of how these phases change mineralogically and compositionally under oxidation of structural iron from Fe(II) to Fe(III), and how this in turn affect the distribution of other elements associated with these minerals.*

3.4. Occurrence of Carbonate Minerals on Mars

Extensive carbonate deposits like those found on Earth do not exist on Mars [92]. Instead, limited occurrences are found that appear in early- to mid-Noachian units. The most direct evidence for carbonates comes from observations by MER Spirit of the Comanche outcrop, where Mössbauer and thermal emission spectroscopy and X-ray fluorescence identified Mg-Fe carbonates at concentrations of 16 to 34 wt.% [93]. Carbonates have also recently been detected from orbit in this region [94]. Analyses by the Phoenix lander suggest the presence of Ca-bearing carbonate minerals at the 3 to 6 wt.% level [95,96]. Orbital detections in other areas of Mars include Mg-rich carbonates in Noachian-aged olivine-bearing bedrock [97], Mg carbonates in sedimentary deposits associated with Fe/Mg smectites [8,98], and layered Ca and/or Fe carbonate-bearing rocks exposed by large impacts [99]. *The majority of carbonate detections on Mars point to a dominantly subsurface, hydrothermal origin formed through alteration of mafic or ultramafic rocks during the early- to mid-Noachian.*

3.5. Trace Element Behavior on Mars during Basalt Alteration

Unlike mineralogy, the trace element composition of Martian surface materials cannot be determined through remote sensing from orbit. The primary information on trace element behavior on Mars comes from data collected by the APXS instruments on the MER rovers (e.g., [100-102]). Meridiani Planum outcrops show elevated levels of Ni and Zn but similar levels of Cr as compared to unaltered basaltic materials [30]. These trace element distributions are believed to result from iron oxidation and recrystallization processes [30] and cannot be explained by meteorite inputs [103,104]. Data on trace element behavior in phyllosilicate-bearing units is much more limited. Coordinated observations by MER Opportunity and CRISM have identified an area at Cape York in the rim of

Endeavor Crater with clear signatures of Fe smectites formed from basalt alteration. APXS data in this area provides evidence of trace element redistribution; Ni and Zn show evidence of both leaching and accumulation. This data is currently in preparation for publication [1] and is cited solely to demonstrate that trace element redistribution appears to occur during basalt alteration on Mars and that rovers can observe such behavior. Additional trace element data at both Endeavor and Gale Craters should be forthcoming from ongoing and future APXS measurements from MER Opportunity [105] and MSL [106,107].

3.6. Trace Element Behavior during Basalt Alteration and Phyllosilicate Formation in Terrestrial Systems

Trace element behavior in terrestrial systems can provide additional insight into behavior expected on Mars. Trace elements are released to solution during weathering of basalt under oxidizing conditions (e.g., [108]), and greater mobilization is expected under anoxic conditions where high surface area iron oxides that strongly sorb trace elements will not form. Studies of terrestrial paleosols, primarily formed from basalt protoliths, reveal substantial difference in iron distributions under anoxic and oxic conditions across the great oxidation event ca. 2.4 Ga [19,109-116]. The oldest definitive paleosols (pre-2.4 Ga) show relatively uniform Fe and Mg leaching and little Fe oxidation, all consistent with anoxic weathering [25]. Paleosols formed after the ~2.4 Ga rise in atmospheric O₂ show different patterns of element distributions, with substantial iron retention through the formation of iron oxides, consistent with oxic weathering [19,109,113]. Little data is available on trace element behavior but the strong affinity of ferric oxides for adsorbing and incorporating trace elements [117] suggests that their behavior during basalt weathering is also affected by redox conditions.

The formation of phyllosilicates also affects trace element behavior. Fe-rich smectites formed in metalliferous deposits often contain substantial quantities of elements such as Cr, Mn, Ni, and Zn [28,37,118-120]. Reaction of trace elements with phyllosilicates can lead to the incorporation of these elements into clay structure [121-126]. Experimental studies of synthetic smectite have found that trace elements readily incorporate into the octahedral sheet [127-133]. *Together, these studies suggest that trace elements likely repartition during basalt weathering and alteration and likely are incorporated into phyllosilicate clays.*

4. PAST WORK AND PRELIMINARY DATA

Relevant past work and preliminary experiments conducted by the PI is reviewed below.

4.1. Geochemical Modeling of Phyllosilicate Formation and Alteration

Geochemical models were created to explore the thermodynamic and mass balance constraints on phyllosilicate formation from basalt under anoxic and oxic conditions. Equilibrium thermodynamic calculations were made in The Geochemist's Workbench [134] using the LLNL thermochemical database [135] modified to include data for phyllosilicates [25] estimated using published procedures [136-139]. Basalt of the 'Adirondack' composition observed in Gusev Crater [140,141] was used in the rock alteration and weathering calculations. These calculations were performed as a function of water-rock ratio because this is a major control on the types of phyllosilicates produced.

Hydrothermal alteration at 100°C produce assemblages consisting of saponite, serpentine, and zeolites, while 250°C alteration produces chlorite, prehnite, talc, and, occasional serpentine. The phases predicted to form are consistent with observed deep phyllosilicate assemblages on Mars [5,7,8,10,73]. Weathering of basalt at lower temperature conditions (25°C) in the absence of an oxidant produces different mineral assemblages. Uniform whole rock weathering produces primarily

Fe^{II}/Mg saponite-montmorillonite mixtures. However, feldspars weather more slowly than olivines and pyroxenes [76,78-80], and the alteration products should thus be less aluminous than predicted for whole-rock weathering. Calculations where feldspars have reduced reactivity, made simply by allowing only 25% of the feldspars to react, produce assemblages dominated by Fe^{II}/Mg saponites (Fig. 2). Similar weathering calculations performed in the presence of an oxidant (O₂ gas) produce assemblages consisting on nontronite, Mg saponite, and hematite (Fig. 2). At some water-rock ratios nontronite is the sole phase produced. If the active iron oxide in such systems is assumed to be ferrihydrite rather than the less soluble hematite then no iron oxides form. The iron instead partitions into nontronite that coexists with Mg saponite under most conditions.

The nontronite-saponite mixtures produced by oxidative weathering appear to be most consistent with clay assemblage currently observed on Mars [4,5,7-11,73,142,143]. However, later oxidation of assemblages produced by hydrothermal alteration or anoxic weathering may also potentially generate similar final mineral assemblages. Oxidation of hydrothermal assemblages produces nontronite-saponite-montmorillonite mixtures. The montmorillonite originates from breakdown of Al-rich zeolites or prehnite; if these do not alter during oxidation because of slow reaction kinetics then nontronite-saponite assemblages are produced. Oxidative alteration of minerals formed during anoxic weathering is predicted to produce nontronite-saponite assemblages, accompanied by hematite under some conditions (Fig. 3). Both direct oxidative weathering and secondary oxidation of the products of hydrothermal alteration or anoxic weathering can produce smectite assemblages consistent with those currently observed on Mars. A manuscript describing this work is currently in review at the *Journal of Geophysical Research* [25].

4.2. Experimental Studies of Fe(II)-Smectite Oxidation

Experimental studies were conducted to confirm that oxidative alteration of pre-formed Fe^{II}-smectites can yield nontronite-like phases. A synthetic ferrous smectite of composition [Ca_{0.35}](Mg_{0.71}Fe^{II}_{1.20}Al_{0.63})(Si_{3.57}Al_{0.43})O₁₀(OH)₂ was oxidized using H₂O₂ or O₂. Peroxide produced rapid and complete oxidation and was structurally disruptive, ejecting Fe from the clay. However, recrystallization produced a single dioctahedral ferric smectite. X-ray absorption spectra (Fig. 4) show that oxidation by dissolved O₂ was slower, resulting in incomplete oxidation (22% of the Fe(II) was oxidized after 1 day of reaction and 37% was oxidized after 1 week), preserving an apparent trioctahedral structure. Recrystallization resulted in the exsolution of a dioctahedral phase, as indicated by a splitting of the (060) X-ray diffraction peak (Fig. 5). The amount of dioctahedral smectite produced correlated with the extent of Fe oxidation. This work is currently being prepared for submission to the *Journal of Geophysical Research* [144].

Oxidation of Fe^{II}-smectite by nitrate (NO₃⁻) was also investigated. While nitrate has not been clearly identified on Mars, perchlorate has [145-147] and nitrate and perchlorate are deposited

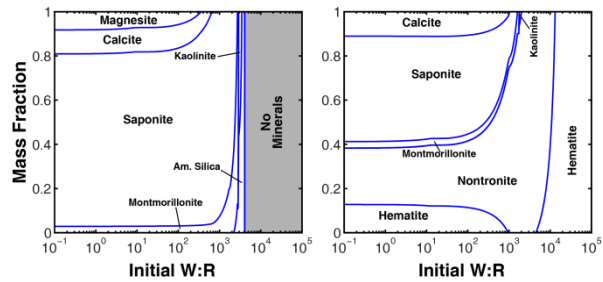


Figure 2. Products of basalt weathering under anoxic (top) and oxic (bottom) conditions by a fluid initially containing 10^{-2.5} molal H₂SO₄ at P_{CO2} = 10⁻³ bar. Oxic conditions were maintained by a 10⁻² bar O₂ gas buffer.

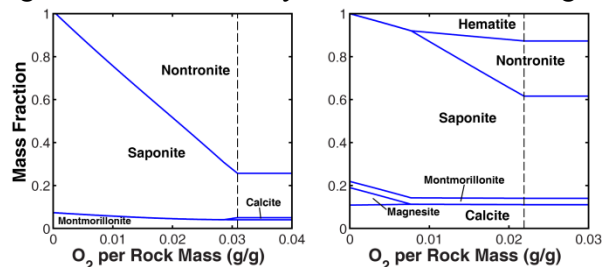


Figure 3. Clay formed by oxidation by O₂ of the products of basalt weathering under anoxic conditions at water-rock ratios of 1000 (left) and 1 (right).

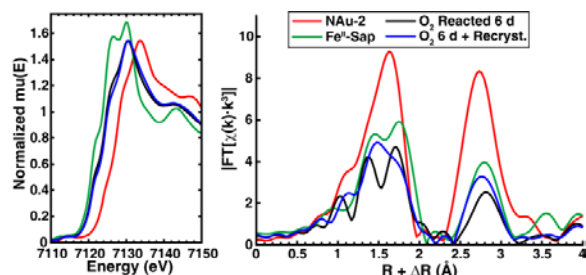


Figure 4. XANES (left) and EXAFS (right) spectra of Fe^{II} -smectite before and after oxidation by O_2 for 1 week. The spectrum of a nontronite is also shown.

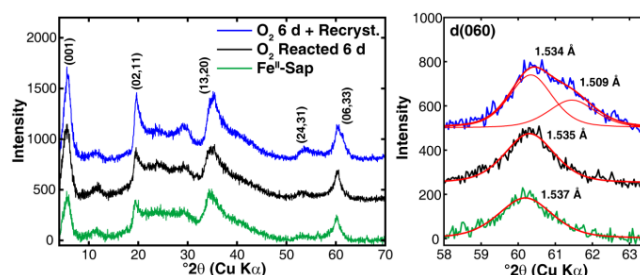


Figure 5. Full indexed powder XRD patterns (left) and fits to (060) peaks (right) of Fe^{II} -smectite after oxidation by O_2 for 1 week.

together in the Antarctic dry valleys [148]. The mechanism responsible for perchlorate deposition on Mars should also deposit nitrate. Only nitrate alone investigated because perchlorate is known to not readily oxidize $\text{Fe}(\text{II})$ [149]; perchlorate also poses a safety hazard. Our studies of Fe^{II} -saponite oxidation by nitrate showed that it is kinetically limited at ambient conditions (22°C) but is rapid and complete under hydrothermal conditions (200°C). The complexity of introducing atmospherically-produced nitrate into a hydrothermal system suggests that nitrate is not a plausible oxidant of $\text{Fe}(\text{II})$ -smectites on Mars. This work is in preparation for submission to *Clays and Clay Minerals* [150].

An additional preliminary experiment has investigated the role of $\text{Fe}(\text{II})$ content on the susceptibility of a $\text{Fe}(\text{II})$ -smectite to oxidation. A smectite of nominal composition $[\text{Ca}_{0.45}](\text{Fe}_{1.41}\text{Al}_{0.78})(\text{Si}_{3.93}\text{Al}_{0.07})\text{O}_{10}(\text{OH})_2$ was synthesized. This had an $\text{Fe}+\text{Mg}:\text{Al}$ ratio similar to the prior $\text{Fe}(\text{II})$ -smectite studied but with only $\text{Fe}(\text{II})$ as the divalent structural cation. A 1 week exposure to dissolved O_2 resulted in 48% of the structural iron being oxidized to $\text{Fe}(\text{III})$, compared to 37% in the previously-studied smectite. Higher Fe contents thus appear to increase the extent of Fe oxidation that will occur without additional recrystallization. *This suggests that composition affects a smectite's susceptibility to oxidation and the rate at which it will oxidize.*

4.3. Isochemical Hydrothermal Mafic Rock Alteration

Many phyllosilicate assemblages on Mars are interpreted to have formed through isochemical alteration of mafic rocks [6,7]. Preliminary experiments have hydrothermally altered the U.S. Geological Survey mafic rock standard DNC-1 [151] into a phyllosilicate-bearing assemblage. DNC-1 is a dolerite (a holocrystalline rock with the same composition as basalt) from North Carolina, USA, composed approximately of 50% plagioclase feldspar, 30% clinopyroxene, 15% olivine, and minor opaques [152]. 5 g of DNC-1 were ground in a micronizing mill in deoxygenated deionized water to produce a grain size $<5 \mu\text{m}$. The material was then placed in PTFE-lined hydrothermal bomb and aged in a vacuum oven backfilled with ultrahigh purity $\text{N}_2(\text{g})$ for 2 weeks at 200°C . A substantial portion of the materials were

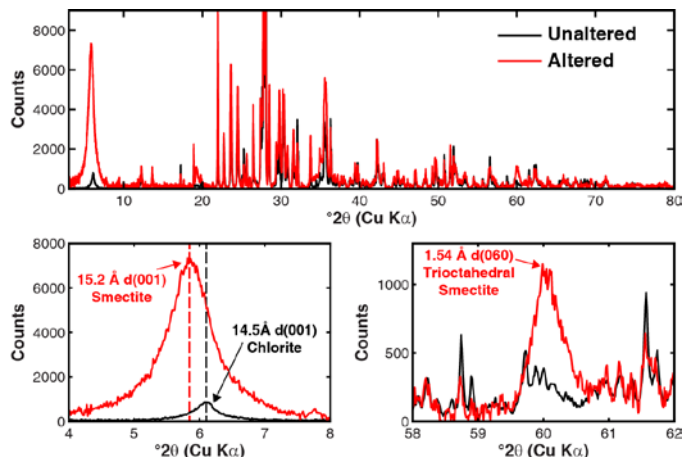


Figure 6. (top) Powder XRD pattern of USGS mafic rock standard DNC-1 as received and after 2 weeks of hydrothermal alteration at 200°C . (bottom left) XRD patterns around 2:1 phyllosilicate basal reflections. (bottom right) XRD patterns around the location of (060) reflections of phyllosilicates.

converted to trioctahedral smectites, as indicated by the appearance of large 15 Å basal reflections and (060) peaks with d-spacings of 1.54 Å (**Fig. 6**). Residual mineral phases consisted primarily of plagioclase feldspar, with a larger portion of the pyroxene and olivine having altered. This assemblage is consistent with the expected mineralogical composition of Fe/Mg smectite units on Mars before they experienced oxidation, as these units lack substantial Al-bearing alteration products [7,8,10,11,73] and contain residual feldspar [153]. We are currently working to determine the clay yield, which we estimate at >40% by weight, as well as the mineralogy of the clay size fraction. Given the high clay yield we are confident that phyllosilicate-bearing assemblages can be produced through isochemical hydrothermal alteration under anoxic conditions.

5. PROPOSED RESEARCH

5.1. Major Hypotheses to be Tested

The proposed research is guided by the following major hypotheses:

1. *Smectite composition affects the rate and extent of iron oxidation because trioctahedral structures may only accommodate the addition of a finite amount of positive charge; recrystallization resets the structure and allows for additional iron oxidation.*
2. *Oxidation of phyllosilicate-bearing assemblages formed from altered mafic rocks causes redistribution of iron and other elements among secondary hydrous silicate phases, producing smectites that differ in composition from those produced by oxidation of single-phase smectites.*
3. *Oxidation of mafic rock alteration assemblages that also contain carbonates produce different phyllosilicate phases than carbonate-free systems because of cation trapping by carbonate minerals.*
4. *Trace element repartitioning upon oxidation of Fe(II) smectites varies systematically with iron content and the extent of exsolution of a dioctahedral Fe(III) smectite.*
5. *Trace element behavior during oxidation of phyllosilicate-bearing mafic rock alteration assemblages differs between carbonate-free and carbonate-bearing systems because cation trapping in carbonate minerals alters the secondary phases that form.*

5.2. Research Approach

Temporally decoupled phyllosilicate formation and iron oxidation on early Mars lacks clear and appropriate terrestrial analog sites. While insight into Martian clay formation has been gained through studies of locales such as the Deccan Traps [26], Iceland [154], and Columbia River Basalts [155,156], the 21% O₂ atmosphere of Earth has resulted in nearly complete iron oxidation in the weathering and alteration products at these sites. Fe mobility during such oxidative alteration is substantially different than under anoxic conditions [113] because of the large difference in the solubilities of Fe(II) and Fe(III). Even the altered lavas of the Mururoa Atoll, a possible example of clay formation during late stages of lava cooling, show substantial interaction with the atmosphere or seawater as they contain abundant nontronite [12,157,158], which requires an external oxidant (likely O₂ from seawater) to have formed. There are limited samples of basalt alteration under anoxic conditions [28,33,34,51,56,57,81,82,159] that can provide insight into possible clay formation process under expected Noachian conditions, but these are difficult to study (e.g., interior of the oceanic crust, bottom of the Red Sea) and do not extend to subaerial conditions. This proposal thus employs a series of laboratory analog studies under controlled redox conditions to explore the connection between alteration, iron oxidation, clay mineralogy, and trace element behavior. It builds on the PI's expertise in iron redox chemistry [160-167] and prior MFRP-funded work on ferrous smectite synthesis and oxidative alteration [25,144,150].

5.3. Research Projects

5.3.1. Effect of Clay Composition on Oxidative Alteration Products

In our prior work, we have investigated various oxidization pathways for a single synthetic Fe(II) smectite (see section 4.2.). This work clearly showed that different oxidants vary in their ability to oxidize an Fe(II) smectites, that oxidation was generally either incomplete or structurally disruptive, and that recrystallization may cause the exsolution of a dioctahedral smectite whose proportion correlated with the fraction of iron that was oxidized. This proposal seeks to determine how the composition of smectites, specifically phases that are less Al-rich and thus more consistent with smectites expected on Mars, affect the reactivity of such phases towards oxidation by dissolved O₂ and the structural constraints they place on the extent of oxidation. This work also seeks to understand how smectite recrystallization affects the ability of these phases to fully oxidize.

Smectite Synthesis: We will synthesize Fe^{II}-bearing smectites with a range of Fe and Mg contents (Fig. 7) that are in line with the compositions of saponites formed through anoxic alteration of terrestrial basalts (Fig. 1). Existing hydrothermal sol-gel synthesis procedures [168-172] have been modified to prevent Fe(II) oxidation by preparing all samples under anoxic conditions in an anaerobic chamber and heating the samples in PTFE-lined bombs at 200°C in a vacuum oven backfilled with ultrahigh purity N₂(g) [144,150]. Following synthesis the Fe^{II}-smectites will be characterized for phase purity by powder X-ray diffraction (XRD); all samples will be measured in an air-tight sample cells to prevent oxidation. Compositions will be determined by total digestions followed by inductively-coupled plasma optical emission spectrometry (ICP-OES). X-ray absorption spectroscopy (XAS) [173] and Mössbauer spectroscopy [174] will characterize the Fe coordination environment in the synthetic clays and the number of sites Fe occupies in the structure and will be used to confirm that Fe did not oxidize during synthesis. In addition, visible-near infrared (VNIR) spectra will be collected to evaluate structural properties of the synthesized clays. All spectra will be collected in sealed cells or a glovebox to prevent oxidation.

Compositional Effects on Susceptibility to and Extent of Oxidation: The synthetic Fe(II)-smectites will each be subjected to oxidation at ambient temperature in an air-saturated 0.01 M CaCl₂ solution for 1 and 7 days. Continuous bubbling with air will buffer the O₂ partial pressure at 0.21 bar. The CaCl₂ electrolyte is used to provide a stable ionic strength, to facilitate accurate pH measurements (pH electrodes have performance problems in highly dilute aqueous solutions), and to Ca-saturate the clay, which aids in later determination of composition. CaCl₂ was also selected because it will not incorporate into the clay structure. Our prior studies [144,150] have found that the presence of CaCl₂ has no effect on iron oxidation or mineralogical transformations. Two reactions times are chosen to assess the rate of oxidation. After reaction, the solids will be returned to the anaerobic chamber to prevent further oxidation and then dried for characterization. A subsample of each smectite oxidized for 7 days will be hydrothermally recrystallized at 200°C under anoxic conditions to allow for structural relaxation. The oxidation of Fe(II) to Fe(III) introduces into the clay structure a smaller cation with higher charge and should introduce substantial strain; the clay structure should thus reequilibrate. This is expected to be relevant on geological time scales but too

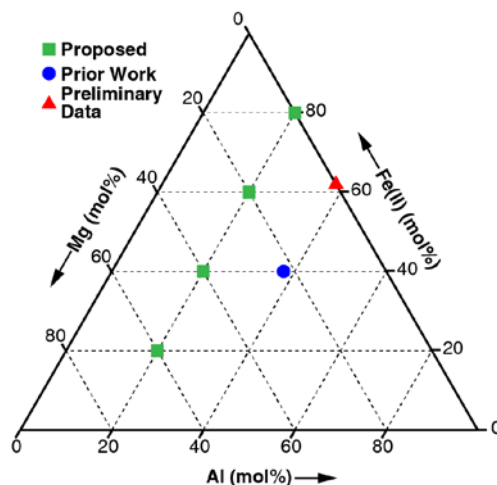


Figure 7. Proposed synthetic Fe(II)-smectite compositions to be used in oxidative alteration experiments. The compositions studied in prior work and in preliminary experiments by the PI (see section 4.2.) are also noted.

slow to practically study in the laboratory; the hydrothermal recrystallization is thus designed to accelerate this process. The recrystallized clays will each then be split, with a portion saved for characterization and the remainder put through a second oxidation. Select samples will be put through multiple cycles of oxidation and recrystallization until complete Fe oxidation is achieved.

The resulting solid materials from these experiments will be characterized by powder XRD in air-tight sample cells to identify structural changes upon oxidation, including the effects on layer stacking and *a*-axis length. The (060) reflections will be analyzed to identify exsolution of multiple smectite phases (e.g., one trioctahedral, one dioctahedral); our prior work observed this behavior after recrystallization. Transmission electron microscopy (TEM) will be used to investigate possible formation of multiple smectites as well as other alteration products. XAS and Mössbauer spectroscopy will be used to characterize the change in Fe coordination upon oxidation and quantify the extent of Fe oxidation and the abundances of the resulting Fe phases. VNIR spectra will be collected to evaluate changes in cation clustering in the clay as well as to document spectral features diagnostic of Fe-smectite in various oxidation states for use in planetary remote sensing applications. The clay compositions will be determined by digestion followed by ICP-OES. Fluid samples collected after each step will also be analyzed by ICP-OES to investigate whether any structural components are lost during reaction.

5.3.2. Oxidation of Hydrothermal Mineral Assemblages

The widespread Fe/Mg phyllosilicate deposits on Mars are generally not single-phase materials; rather, they are a complex mineral assemblages that often include multiple phyllosilicates plus residual feldspar, pyroxene, and olivine [153]. During oxidative alteration the mineralogical products can gain or lose chemical components through reaction with the other minerals present. This possibility of mass transfer among mineral phases during oxidative alteration suggests that different oxidation products may form compared to the single-phase studies described above. In addition, mafic rocks altered in the presence of high CO₂ partial pressures will produce carbonate minerals that will bind phyllosilicate-forming cations, altering the resulting mineral assemblages. This section of the proposed research thus seeks to investigate the mineral products of the oxidation of phyllosilicate-bearing assemblages produced by alteration of mafic rocks.

Bulk Isochemical Alteration of Basalts: Many of the widespread Fe/Mg phyllosilicate-bearing units on Mars are postulated to have formed via isochemical alteration [6,7]. While such alteration may proceed at ambient temperatures in the laboratory, this is likely exceedingly slow and forming phyllosilicate-bearing assemblages in this way is impractical on the timescale of a 3-year research project. We will thus instead isochemically alter mafic rock samples under hydrothermal conditions to increase the reaction rate. Our preliminary work (see section 4.3.) shows that phyllosilicate-bearing assemblages similar to those found on Mars can be produced in two weeks at 200°C. This project will utilize four U.S. Geological Survey (USGS) mafic rock standards (**Table 1**): Columbia River basalt BCR-2, Icelandic basalt BIR-1, North Carolina dolerite DNC-1, and Twin Sisters dunite DTS-2. The basalts and dolerite were selected as they varied in mineralogy and glass content [108,152,175-177]. The dunite was selected as a rock dominated by olivine [178] that would be likely to produce different phyllosilicates (e.g.,

Table 1. Compositions of USGS Mafic Rock Standards.

Oxide/Element*	BCR-2	BIR-1	DNC-1	DTS-2
SiO ₂	54.4	47.96	47.15	39.4
FeO	9.20	8.34	7.32	5.49
Fe ₂ O ₃	3.58	2.06	1.79	1.66
Al ₂ O ₃	13.5	15.5	18.34	0.45
CaO	7.12	13.3	11.49	0.12
MgO	3.59	9.70	10.13	49.4
Na ₂ O	3.16	1.82	1.89	0.01
K ₂ O	1.79	0.03	0.234	0.001
TiO ₂	2.26	0.96	0.48	0.005
P ₂ O ₅	0.35	0.02	0.07	0.002
Cr	17	370	270	15500
Mn	1520	1355	1160	830
Ni	13	170	247	3780
Zn	127	70	70	45

*Oxides reported in wt.%, trace elements in µg/g.

serpentine, talc) during alteration. These rocks also all vary in their trace element content (**Table 1**).

Isochemical alteration will be conducted by placing each ground mafic rock in a PTFE-lined bomb with deoxygenated deionized water. These will be heated in a vacuum oven backfilled with N₂(g) to prevent iron oxidation during alteration. Temperatures of 100°C to 250°C will be used to explore possible different alteration mineralogies (e.g., the temperature dependent transition from smectite to chlorite). After alteration, the fluid composition will be measured by ICP-OES to determine the extent of element leaching during alteration; pH will also be measured. A geochemical model employing the database prepared in the PI's current MFRP project (see section 4.1.) will be used to evaluate the saturation state of various phyllosilicates at the end of alteration. The solid phase will be dried in an anaerobic chamber to prevent iron oxidation. Subsamples will be characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray absorption spectroscopy (XAS), Mössbauer spectroscopy, and visible-near infrared (VNIR) spectroscopy. To prevent sample oxidation during analysis, XRD and XAS measurements will be made using sealed sample cells and Mössbauer and VNIR measurements will be performed in an anaerobic glovebox. Quantitative analysis of mineral abundances will be obtained from the XRD data using a combination of Rietveld [179-181] and reference intensity ratio (RIR) methods [180-183]. The abundances of Fe-bearing phases will be quantified using the XAS and Mössbauer data through fitting procedures [173,174,184,185]. Thin sections will be prepared from select samples and analyzed by electron probe microanalysis (EPMA) to examine the extent of primary mineral alteration and the thickness of any resulting clay films. The clay size fraction will also be separated and characterized using the above methods as well as transition electron microscopy (TEM).

Hydrothermal Alteration to Mixed Phyllosilicate and Carbonate Assemblages: To explore how the presence of carbonates in phyllosilicate-bearing altered mafic rocks affects subsequent oxidation processes, we will prepare a series of mixed carbonate-phyllosilicate assemblages through hydrothermal alteration of the selected USGS mafic rock standards under controlled CO₂ pressures. Each mafic rock sample will be ground and loaded into a hydrothermal high-pressure reactor; these reactors have been applied extensively to the study of rock carbonation by supercritical CO₂ for geological carbon sequestration [186-196]. CO₂ partial pressures of 0.01 to 100 bar will be used to span the range of partial pressures typically found in CO₂-bearing hydrothermal systems [197-202]. These will be set using pure CO₂ gas or a N₂/CO₂ mixture, with pressure held static using a high-pressure syringe pump. Lower final CO₂ partial pressure may also be explored to induce less carbonate mineralization by pressurizing a system with CO₂ but then sealing the reactor, allowing carbonate formation to draw down the CO₂ partial pressure to a lower level at equilibrium. Temperatures will be varied between 50°C and 250°C. The resulting mineral assemblages and associated fluids will be characterized using the same analytical and modeling techniques as in the isochemical alteration studies. XAS and Mössbauer measurements will specifically investigate the fraction of Fe incorporated into siderite. The solid carbonate content will be determined using a total organic carbon (TOC) analyzer, which, despite the name, also measures total inorganic carbon.

Oxidation of Altered Mafic Rocks: To investigate how complex mineral assemblages affect mineralogical changes resulting from iron oxidation, samples of the altered mafic rocks (isochemical and carbonated) will each be suspended in air-saturated water for 1 week. After reaction, the fluid will be collected and the dissolved concentrations of major elements will be measured by ICP-OES and ICP-MS. In addition, the dissolved inorganic carbon content will be measured by TOC analysis; pH will also be measured. The solids will be characterized by XRD and SEM to determine mineralogical changes upon oxidation; select samples will also be characterized by EMPA following preparation as thin sections. The extent of Fe oxidation and changes in Fe mineralogy will be quantified by Mössbauer spectroscopy and XAS. VNIR spectra will be collected to aid in identification of alteration products and to determine how spectral properties of altered mafic rocks change upon oxidation.

5.3.3. Trace Element Repartitioning during Oxidative Alteration

Trace elements such as Cr, Mn, Ni, and Zn are often incorporated into smectites and other phyllosilicates during basalt weathering and alteration [28,37,118-120,203-206]. This promotes their redistribution during alteration and provides a mechanism to retain trace elements added through fluid flow (e.g., hydrothermal circulation) and prevent their leaching. Ni^{2+} , Zn^{2+} , and Mn^{2+} are substantially more soluble than Cr^{3+} and should show distinct redistribution behavior. Oxidizing conditions may change this pattern as Mn^{2+} will convert to the less soluble Mn^{3+} or Mn^{4+} . Trace elements in phyllosilicates and altered basalts may thus provide measureable indicators of past alteration and oxidation processes on Mars. This section of the proposal seeks to establish how these element repartition during oxidation of ferrous smectites and altered mafic rocks.

Synthesis of Trace Element-Substituted Fe(II) Smectites: The Fe(II)-smectite synthesis procedures used above will be modified to include trace levels (~1000 ppm) of Cr, Mn, Ni, and Zn. Synthesis methods for trace metal-bearing smectites are well established [127,128] and in fact formed the basis for the method we developed to synthesize Fe(II)-smectites. These synthetic substituted Fe(II)-smectites will be characterized using the same techniques as the pure Fe(II)-smectites (see section 5.3.1.). In addition, Cr, Mn, Ni, and Zn K-edge XAS measurements will be performed to determine the substitution mechanism of these elements in the smectite structure.

Trace Element Redistribution upon Fe(II) Smectite Oxidation and Recrystallization: The trace element-bearing Fe(II)-smectites will be oxidized and recrystallized as described in section 5.3.1. to determine how trace elements repartition between the initial clay, the aqueous fluid, and the products of oxidation and recrystallization. Similar analytical methods will be used as described above. In addition, XAS will be used to investigate how trace element incorporation into the solid phase changes upon iron oxidation.

Trace Element Behavior during Alteration of Mafic Rocks: The USGS mafic rock standards contain the Cr, Mn, Ni, and Zn at levels ranging from 10 to 15000 ppm (Table 1). The behavior of these trace elements during isochemical and carbonate-forming alteration of the USGS mafic rock standards described in section 5.3.2. will be characterize. Release of these trace elements to the fluid phase will be quantified using ICP-MS. Cr, Mn, Ni, and Zn XAS measurements will be performed on the solids having at least 100 ppm of these elements (the approximate practical detection limit of XAS [173]) to determine how their chemical form changes during alteration (e.g., Ni may repartition from olivine to smectite). The trace element content and chemical form in the clay size fraction will also be determined. In addition, quantification of carbonate-bound trace elements will be performed by extraction using an acetic acid-sodium acetate buffer [207,208] followed by analysis of the resulting fluid by ICP-MS.

An additional experiment will examine the fate of Ni and Zn added to the fluid prior to alteration to determine how trace elements in hydrothermal fluids are incorporated into mineral phases during alteration. These elements were selected because they are relatively soluble and show clear repartitioning behavior at both Meridiani and Endeavor Crater [1,30]. Separate alteration experiments will be conducted with the fluid spiked with NiCl_2 and ZnCl_2 at concentrations that produce 1000 ppm solid phase concentrations. These low levels are not expected to change the major alteration products but are high enough for the fate of these elements to be determined through chemical analysis of the clay size fraction and carbonate minerals and through XAS measurements.

Trace Element Redistribution upon Oxidation of Altered Mafic Rocks: Trace element behavior will be monitored during the oxidation experiments involving the altered mafic rock assemblages described in section 5.3.2. Following oxidation, the trace element contents will be determined for the clay size fraction and carbonate component by ICP-MS; concentrations in aqueous solution will also be monitored. XAS measurements will be used to determine how Cr, Mn, Ni, and Zn are redistributed among mineral phases during oxidation so that changes in trace element content can be directly related to mineralogical transformations. Additional oxidation experiments

will be conducted using the Ni and Zn-spiked alteration assemblages described above; these will be analyzed using the same techniques as in the other oxidation studies.

5.4. Project Personnel

This project will be directed and managed by PI Catalano. Catalano is responsible for overall experimental design, guidance of the graduate students in conducting experiments and analyzing the data, writing proposals to obtain time at synchrotrons for XAS, assisting with the preparation of manuscripts, and managing the thermodynamic databases employed to aid in data analysis. Co-I Morris is responsible for collecting and analyzing Mössbauer and VNIR spectra and for training the graduate student in these methods. Washington University graduate student Ryan Nickerson will conduct the majority of the laboratory experiments under the guidance of PI Catalano and will prepare manuscripts. The proposed work will comprise the majority of his Ph.D. dissertation. Nickerson will also travel to the Johnson Space Center to assist in Mössbauer and VNIR spectroscopic measurements and will receive training from Co-I Morris.

5.5 Project Timeline

Year 1: Synthesis, characterization, oxidation, and recrystallization of Fe(II)-smectites; Isochemical alteration of mafic rocks with and without added trace elements; XAS, Mössbauer, and VNIR analyses of Fe(II)-smectites; Acquisition and setup of the hydrothermal reactor and high-pressure syringe pump.

Year 2: Oxidation of isochemically-altered mafic rocks and associated mineralogical and compositional analyses; Hydrothermal alteration of mafic rocks under high-CO₂ conditions with and without trace elements added; XAS, Mössbauer, and VNIR analyses of isochemically-altered mafic rocks before and after oxidation and high-CO₂ alteration assemblages before oxidation; Preparation of manuscripts on Fe(II)-smectite experiments and isochemical alteration and oxidation experiments.

Year 3: Oxidation of mafic rocks altered under high CO₂-conditions and associated mineralogical and compositional analyses; Synthesis, characterization, oxidation, and recrystallization of trace element-substituted Fe(II)-smectites; XAS, Mössbauer, and VNIR analyses on oxidized, carbonate-bearing altered mafic rocks and on trace element-substituted Fe(II)-smectites; Preparation of manuscripts on high-CO₂ alteration and oxidation experiments and trace element-substituted smectite experiments.

5.6. Plan for Data Sharing

Graduate student Ryan Nickerson and PI Catalano will prepare manuscripts for submission to peer-reviewed scientific journals that traditionally are read by the relevant scientific communities, such as the *Journal of Geophysical Research: Planets* and *Earth and Planetary Sciences Letters*. In addition, research results will be presented by the graduate student and PI annually at the Lunar and Planetary Science Conference or at other relevant geological, geophysical, or geochemical conferences such as the Geological Society of America Annual Meeting, the Fall Meeting of the American Geophysical Union, or specialized NASA-supported conferences. The PI will make sure that all data, methods, and any stable archived samples are made available upon request.

5.7. Relationship to Other Proposals

PI Catalano is participating as a Co-I on two recently-submitted collaborative proposals to NASA led by Dr. Bethany Ehlmann (see Current and Pending Support) that seek to improve the spectral database used to interpret remote sensing data and our ability to interpret such data quantitatively. These proposals are deliberately duplicative, having been coordinated between Ehlmann and the respective program managers, and only one at most would be funded. Catalano's contribution to the proposed work would be synthesizing and characterizing Fe(II)-, Fe(III)-, and

Fe(II)/Fe(III)-bearing smectites. Some would be of similar composition as proposed to be studied in the present proposal; these proposals are thus complimentary. In all proposals Catalano would apply his group's existing knowledge in Fe(II)-smectite synthesis. However, for the Ehlmann-led proposals, Catalano will only synthesize clays; no experiments will be performed on these materials and all material prepared will be dedicated for characterization. In the present proposal, synthesized clays will be used in experiments and will be deliberately reacted and altered.

5.8. Status of Current MFRP Grant

PI Catalano is currently managing a project supported by the Mars Fundamental Research program that investigates iron bearing clay formation and alteration. Major projects include laboratory studies of the oxidation of a ferrous smectite by O₂, H₂O₂, and NO₃⁻ and basalt weathering at ambient temperatures under anoxic and oxic conditions, as well as geochemical modeling of phyllosilicate formation and transformation pathways. This project began in June 2011 and is just now beginning the final year of the project. The current submission has a start date of September 2014 to coincide with the expected depletion of existing funds.

This prior work has results in one paper in review and two in preparation:

Catalano J. G. (2013) Thermodynamic and mass balance constraints on iron-bearing phyllosilicate formation and alteration pathways on early Mars. *J. Geophys. Res.*, submitted.

Beehr A. R. and Catalano J. G. (2013) Ferric smectite formation via oxidation and recrystallization of precursor ferrous saponite by O₂ and H₂O₂. In preparation for the *J. Geophys. Res.*

Beehr A. R. and Catalano J. G. (2013) Oxidation of ferrous saponite by nitrate under ambient and hydrothermal conditions. In preparation for *Clays Clay Miner.*

An additional paper on anoxic and oxic basalt weathering at ambient temperatures and possibly a third paper on Fe(II)-smectite oxidation are expected to be prepared in 2014 before the current grant expired. This existing grant has also supported the PI's involvement in four other publications, one published, one in press, and two in preparation. These publications utilized insight gained on fundamental aspects of clay formation and alteration in the course of this project or the thermodynamic data prepared for the publication by the PI currently in review but did not involve analysis of Mars mission data by the PI:

Liu Y., Arvidson R.E., Wolff M.J., Mellon M.T., Catalano J.G., Wang A., Bishop J.L. (2012) Lambert albedo retrieval and analyses over Aram Chaos from OMEGA hyperspectral imaging data. *J. Geophys. Res.* **117**, E00J11.

Fraeman A. A., Arvidson R. E., Catalano J. G., Grotzinger J. P., Morris R. V., Murchie S. L., Stack K. M., Humm D. C., McGovern J. A., Seelos F. P., Seelos K. D., and Viviano C. E. (2013) A hematite-bearing layer in Gale Crater: Mapping and implications for past aqueous conditions. *Geology*, in press.

Arvidson R. E., Squyres S. W., Murchie S., Clark B. C., Knoll A. H., Catalano J. G., McLennan S. M., and Morris R. V. (2013) Martian clay-mineral bearing outcrops on the rim of Endeavour Crater inferred from spatially oversampled CRISM spectra and Opportunity rover data. In preparation for *Science*.

Liu Y., Arvidson R. E., Catalano J. G. (2013) Spectral and stratigraphic mapping of hydrated minerals associated with interior layered deposits near the southern wall of Melas Chasma, Mars. In preparation for *Geophys. Res. Lett.*

6. IMPACT ON UNDERSTANDING OF MARS

The proposed work will substantially improve our understanding of geochemical processes that likely operated on Mars in the early- to mid-Noachian. Experimental results will address the conditions under which phyllosilicate phases similar to those observed via orbital remote sensing [5-

8,10,31,73,209] form through the alteration and oxidation of mafic rocks. The proposed research will determine the susceptibility of ferrous iron-bearing phyllosilicates to oxidative alteration, the likely origin of ferric smectites found on Mars today **[25]**. This work will also establish how the mineralogy of complex assemblages produced through alteration of mafic rock changes upon later oxidation. As part of these studies, the effect of carbonates on oxidative alteration and the fate of carbonates during this process will be determined. This will document the expected mineralogical changes that occur when carbonate-bearing hydrothermal assemblages are exposed to oxidizing conditions and, in the event that substantial carbonate dissolution occurs upon iron oxidation, may provide new insight into the limited exposure of these phases on Mars' surface.

This project will also address a number of specific goals set by the Mars Exploration Program Analysis Group **[210]**. The expected results will provide new insight into the mechanism through which weathering and alteration processes altered Mars' crust during the Noachian, furthering goal III.A. It will provide a strengthened scientific basis for evaluating whether widespread clay formation was a near-surface or subsurface process and thus help constrain past water availability. It will also provide an improved understanding of rock alteration in hydrothermal systems, potential habitats for past life. This work will lead to new insight into the likely oxidation state of the Martian atmosphere during phyllosilicate-forming periods in the Noachian and may help provide additional mineralogical constraints on the timing of widespread oxidation of the Martian surface, furthering goals II.C and I.C. Finally, these studies will identify mineral phases formed through basalt alteration that contain substantial reducing equivalents. These minerals may have served as electron donors for past microbial life. This work will thus further goal I.A. by identifying new potential energy sources for past life on Mars.

7. IMPACT ON CURRENT AND FUTURE MARS MISSIONS

This work will benefit the current and future exploration of Mars **[211]** by providing an improved scientific basis for interpreting data from landers and orbiters. MER Opportunity has recently investigated phyllosilicate-bearing outcrops in the rim of Endeavor Crater in Meridiani Planum **[1]**. The proposed work will aid in the interpretation of the conditions that formed these deposits by providing an improved understanding of phyllosilicate formation and alteration processes as well as the associated redistribution of trace elements, which can be directly compared to observations made by the APXS. The proposed work will also greatly aid in interpreting observations made by MSL Curiosity in Gale Crater **[107]**. MSL will explore regions that contain substantial Fe/Mg phyllosilicate exposures **[212]** and areas of past redox interfaces **[213]**. In addition, recent drill cuttings by MSL showed a reduced phyllosilicate-bearing layer below a thin oxidized surface layer **[2]**, suggesting that formation of ferrous iron-bearing clay hypothesized by the PI and other to be important basalt alteration products on Mars **[25,84,144,150]** may be widespread and the later oxidation of these materials may be a major route to the formation of nontronites observed from orbit. Understanding iron-bearing clay oxidative alteration processes will thus be essential to interpreting mineralogical observations made by MSL. MSL contains an APXS instrument **[106,107]** and the trace element studies of the present work will also produce results directly comparable to data obtained by MSL. In addition, the proposed work will aid in the interpretation of orbital remote sensing data by Mars Express/OMEGA and MRO/CRISM imaging spectrometers by providing VNIR spectra of phyllosilicates and phyllosilicate-bearing altered mafic rocks for comparison with actual observations as well as refining our understanding of the geological and environmental conditions under which phyllosilicates form and alter. Finally, the proposed research could aid in the planning of future Mars missions, such as the proposed 2020 rover.

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