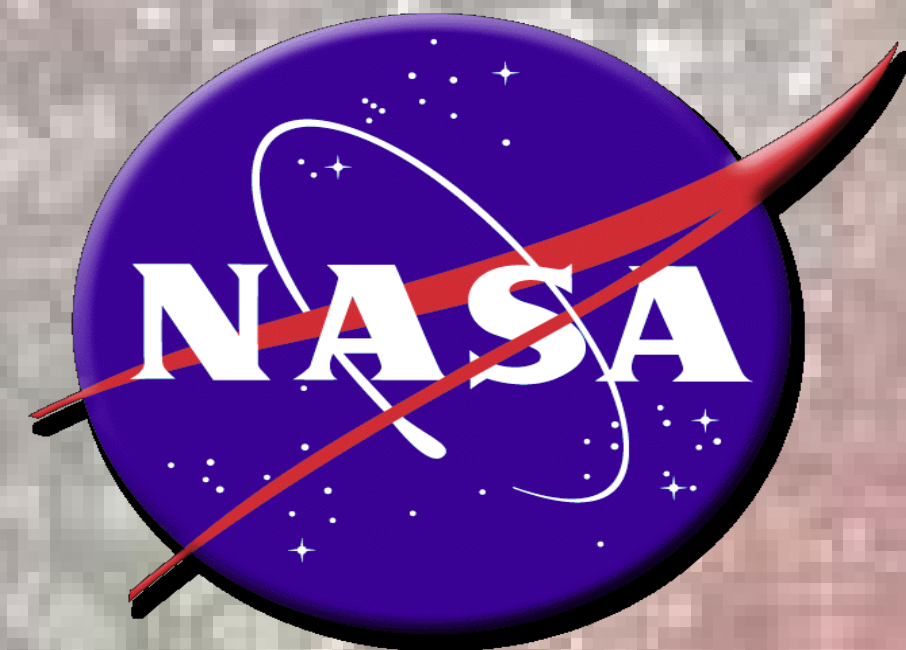


The Formation of Fe/Mg Smectite Under Mildly Acidic Conditions on Early Mars

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INTRODUCTION

•The detection of Fe/Mg smectites and carbonate in Noachian and early Hesperian terrain of Mars suggests that neutral to mildly alkaline conditions prevailed during the early history of Mars.

•If early Mars surface geochemical conditions were neutral to moderately alkaline with a denser CO₂ atmosphere than today, then “large” carbonates deposits should be more widely detected in Noachian terrain.

PROBLEM

•Why have so few carbonate deposits been detected compared to Fe/Mg smectites?

•Fe/Mg smectites on early Mars formed under mildly acidic conditions, which would preclude the extensive formation of carbonate deposits.

GOAL

•The goal of the proposed work is to evaluate the formation of Fe/Mg smectites under mildly acidic conditions

OBJECTIVES

•Examine sources of mild acidity on Mars.

•Evaluate terrestrial examples of smectite formation under mildly acidic conditions

•Propose experiments to test the hypothesis that alteration of basaltic glass parent under mildly acidic conditions (pH 3-5) can yield Fe/Mg smectites.

Noachian Mild Acidity on Mars

•Early CO₂-dominated atmosphere (~1-4 bar) could have contributed to mild acidity caused by carbonate equilibration in water



•Fe-hydrolysis (Hurowitz et al., 2009)

•SO₂ volcanic gasses (Settle, 1979; Fairén et al., 2004)

•These sources of acidity competed with base-forming cations that resulted in mild acidic solutions that were not favorable for carbonate formation but may have allowed for Fe/Mg smectite formation.

Smectite Formation from Glass

•Flow-Through Dissolution Studies pH 2-11 basaltic glass (Berger et al., 1994; Gislason and Oelkers, 2003)

- Alteration layer formed and spalled glass off.
- Leached layers may have contained phyllosilicates but were not examined.
- Difficult to produce significant phyllosilicate due to short experimental times (< 12 days).

•Batch Dissolution Studies

- Batch dissolution studies of basaltic glass in pH 4 synthetic seawater solutions at 260-320° C yielded saponite formation on glass surfaces (Berger et al., 1987; 1988) (Fig. 1).
- Cations are selectively removed while Si and Al become enriched.
- Fe and Mg are lost from **zone II** but become enriched in **zone III**.
- Ca and Na are leached from the glass surface.
- Fe and Mg diffuse from the glass into the rim, while Mg simultaneously diffuses from solution into the rim.
- An amorphous silicate gel forms in **zone III**, which then recrystallizes into stable smectite (**zone IV**) (Berger et al., 1987).
- The added Mg in solution appears to have enhanced the crystallization of phyllosilicate despite the presence of low pH solutions.

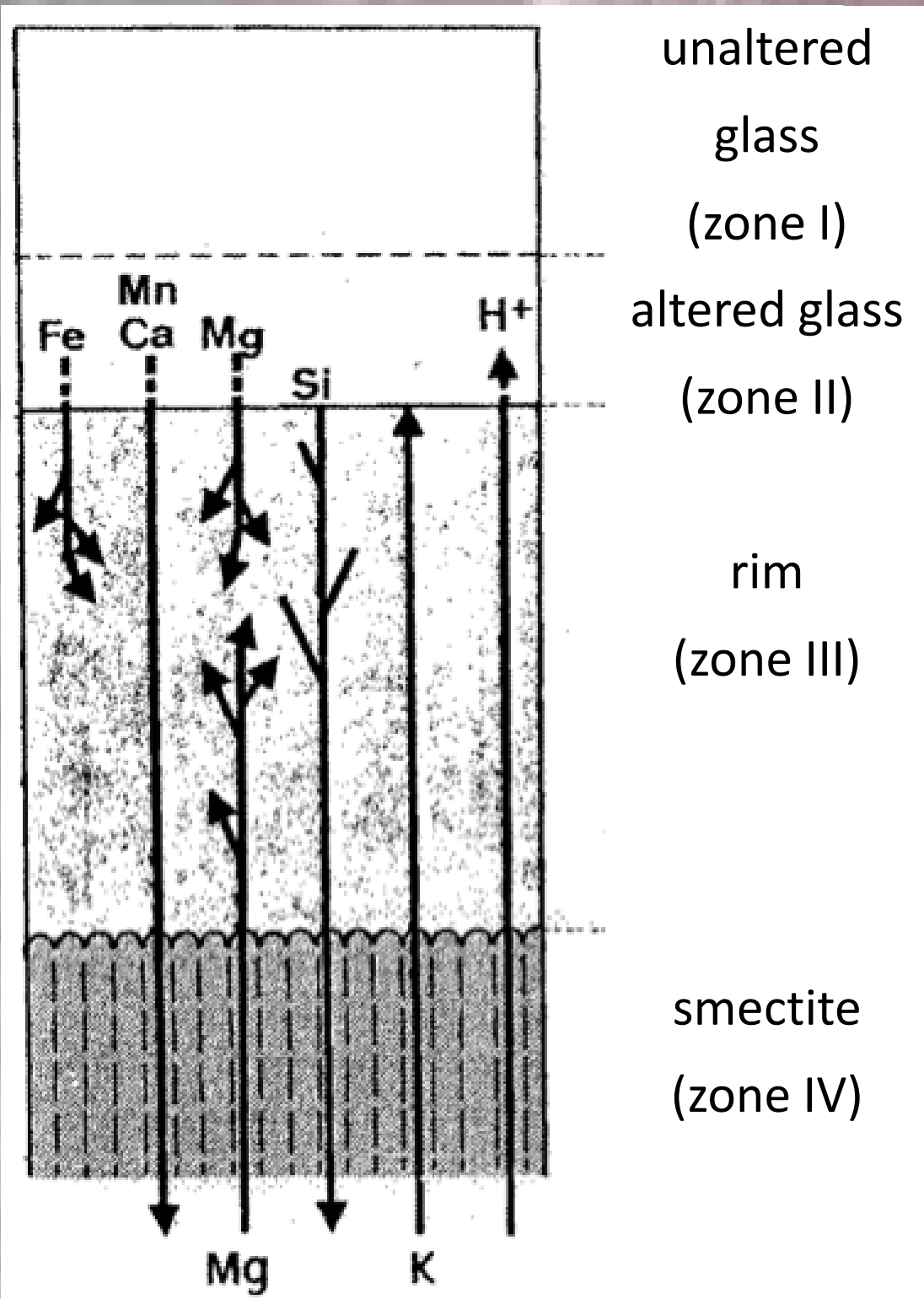


Fig. 1. Model of the formation of Mg²⁺-saponite derived from basaltic glass. Arrows indicate direction of cation movement into and/or out of the glass and altered layered zones (from Berger et al., 1987).

Proposed Experiments

•**Objective 1: Determine the Fe and Mg solution concentrations required for Mg²⁺-saponite and Fe²⁺-saponite formation from alteration of basaltic glass at low pH and high pH.**

- The formation of Mg²⁺- and Fe²⁺-saponite at low pH is hypothesized to require higher Mg and Fe solution concentrations than those required for formation at higher pH.

•**Objective 2: Determine the conditions required for nontronite formation from alteration of basaltic glass at low and high pH.**

- Formation of Fe²⁺-saponite under reducing conditions followed by oxidizing conditions is hypothesized to be required for nontronite formation as derived via basaltic glass alteration.

Materials and Methods

- Basalt glass synthesized to have Adirondack bulk chemistry
- 1 g glass exposed to 200°C solutions (Table 1) for 15 days in 45 ml Teflon lined reactors.
- Reducing solutions N₂ purged with 0.1 wt% hydraziniumchloride.
- Glass and solutions loaded in N₂ purged glove box to ensure reducing conditions.

•**Task 1: Determine the Fe and Mg solution concentrations required for the formation Mg²⁺-saponite and Fe²⁺-saponite in reducing and pH 8 conditions**

- Fe and Mg additions simulate dissolution of olivine and pyroxene

•**Task 2: Determine the Fe and Mg solution concentrations required for the formation of Mg²⁺-saponite and Fe²⁺-saponite at pH 3, 4, and 5.**

•Results from Task 1 will be used to determine what Fe and Mg solution concentrations are required to produce saponite at pH 3, 4, and 5.

•**Task 3: Determine the conditions for Fe³⁺-nontronite formation at low and high pH from alteration of basaltic glass.**

•Fe³⁺-nontronite form initially reducing conditions that then become oxidizing.

•Fe-(hydr)oxides, instead of nontronite will form under only continuous oxidizing conditions .

•After 15 d, 1 mM NaClO₄ will be added for two days.

•Oxidizing only experiments will mix 1 mM NaClO₄ with the basalt glass and Fe solution concentrations at the beginning.

- Solution analyses**
 - Inductively coupled plasma (ICP) solution analysis and pH
- Altered Glass Analysis.**
 - X-ray diffraction
 - Infrared Analysis
 - Mössbauer analyses
 - Scanning Electron Microscopy
 - Scanning Transmission Electron Microscopy (STEM)
 - Examine glass cross-section
 - Chemical profile
 - Sonicate glass to concentrate altered material for analyses.

•**Perceived Impact**

•The formation of Fe/Mg smectites from mildly acidic aqueous alteration of basaltic glass will provide an alternative explanation for the greater extent of smectites on Mars compared to carbonates.

•Results from this work may support a paradigm shift that that accepts phyllosilicate formation on Mars under mildly acidic conditions.

•Fe and Mg solution concentrations on an early mildly acidic Mars may be higher than currently modeled (e.g., Catling, 1999).

•Potential microbiological activity would not be eliminated under a mildly acidic Mars; however, there could be tighter constraints as to the type and species of microbiology that could exist.

References

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Background image color coded to reflect phyllosilicates (green) in the Nili Fossae region. Photo credit NASA/JPL/JHUAPL/Brown University.

Table 1. Tasks 1, 2 and 3: Experimental pH, redox and Mg (MgCl₂) and Fe (FeCl₂) concentration treatments.

Experiment	Mg	Fe	pH	redox
Task 1	mM	mM		
1	0	0	8	reduce
2	1	0	8	reduce
3	10	0	8	reduce
4	20	0	8	reduce
5	0	1	8	reduce
6	0	10	8	reduce
7	0	20	8	reduce
Task 2				
8	0	0	3	reduce
9	0	0	4	reduce
10	0	0	5	reduce
11	1	0	3	reduce
12	1	0	4	reduce
13	1	0	5	reduce
14	25	0	3	reduce
15	25	0	4	reduce
16	25	0	5	reduce
17	50	0	3	reduce
18	50	0	4	reduce
19	50	0	5	reduce
20	0	1	3	reduce
21	0	1	4	reduce
22	0	1	5	reduce
23	0	25	3	reduce
24	0	25	4	reduce
25	0	25	5	reduce
26	0	50	3	reduce
27	0	50	4	reduce
28	0	50	5	reduce
Task 3				
29	0	25	4	red → ox
30	0	50	4	red → ox
31	0	1	8	red → ox
32	0	10	8	red → ox
33	0	50	4	ox
34	0	10	8	ox