

## **The formation of Fe/Mg smectite under mildly acidic conditions on early Mars.**

B. Sutter<sup>1</sup>, D.C. Golden<sup>1</sup>, D.W. Ming<sup>3</sup>, and P.B. Niles<sup>3</sup>

<sup>1</sup> Jacobs Technology/ ESCG

<sup>2</sup> NASA Johnson Space Center.

The detection of Fe/Mg smectites and carbonate in Noachian and early Hesperian terrain of Mars has been used to suggest that neutral to mildly alkaline conditions prevailed during the early history of Mars. However, if early Mars was neutral to moderately alkaline with a denser CO<sub>2</sub> atmosphere than today, then “large” carbonate deposits should be more widely detected in Noachian terrain. The critical question is: Why have so few carbonate deposits been detected compared to Fe/Mg smectites? We suggest that Fe/Mg smectites on early Mars formed under mildly acidic conditions, which would inhibit the extensive formation of carbonate deposits. The goal of this work is to evaluate the formation of Fe/Mg smectites under mildly acidic conditions.

The stability of smectites under mildly acidic conditions is attributed to elevated Fe/Mg activities that inhibit smectite dissolution. Beidelite and saponite have been shown to form from hydrothermal alteration of basaltic glass at pH 3.5-4.0 in seawater solutions. Nontronite is also known to be stable in mildly acidic systems associated with mafic and ultramafic rock. Nontronite was shown to form in acid sulfate soils in the Bangkok Plain, Thailand due to oxidation of Fe-sulfides that transformed saponite to nontronite. Smectite is known to transform to kaolinite in naturally acid soils due to selective leaching of Mg. However, if Mg removal is limited, then based on equilibrium relationships, the dissolution of smectite should be minimized. If Fe and Mg solution activities are sufficiently high, such as might be found in a low water/rock ratio system that is poorly drained, smectite could form and remain stable under mildly acidic conditions on Mars.

The sources of mild acidity on early Mars includes elevated atmospheric CO<sub>2</sub> levels, Fe-hydrolysis reactions, and the presence of volcanic SO<sub>2</sub> aerosols. Equilibrium calculations dictate that water equilibrated with an early Mars CO<sub>2</sub> atmosphere at 1 to 4 bar yields a pH of 3.6 to 3.9. Fe hydrolysis reactions on Mars is another source of protons that would have contributed to acidity. The presence of SO<sub>2</sub> from volcanic processes could also have contributed to geochemical acidification. These sources of acidity competed with base-forming cations that resulted in mildly acidic solutions that were not favorable for carbonate formation but may have allowed for Fe/Mg smectite formation.

Noachian to early Hesperian Mars could have been mildly acidic, allowing Fe/Mg smectite formation but preventing widespread carbonate deposition. This paradigm shift from an early Mars that was neutral-alkaline to mildly acidic may possibly explain why there is a disparity between the occurrence of carbonate and Fe/Mg smectites. 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.