

ANION CHEMISTRY AND MICROORGANISMS PLAY IMPORTANT ROLES IN AUTHIGENIC CLAY FORMATION: IMPLICATIONS FOR INTERPRETING NOACHIAN MARS. C. M. Phillips-Lander¹, M. Ueshima², D. A. Fowle², and J. A. Roberts², ¹School of Geology and Geophysics, University of Oklahoma, 100 E. Boyd Street, Norman, OK 73071; charity.m.lander@ou.edu, ²Department of Geology, University of Kansas, Lawrence, KS 66047.

Introduction: Weathering during the Noachian period on Mars is expected to have occurred under hydrothermal conditions; however, the chemical composition of the hydrothermal fluids present is unclear. Silica rich rocks were observed by Spirit Rover near “Home Plate” in the Columbia Hills and are associated with chloride enrichments in the surrounding rocks [1, 2]. Orbital and rover observations of the Martian surface have confirmed the presence of phyllosilicate minerals, principally Fe/Mg-smectites, with montmorillonite and kaolinite overlying these clay minerals [3].

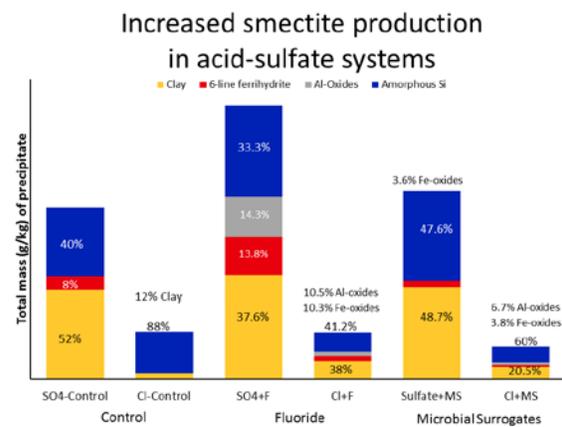
On Earth, hydrothermal systems are classified as two end-member types, acid-sulfate and neutral-chloride based on mineralogy and solution geochemistry. Neutral-chloride springs are silica-dominated and associated with circum-neutral pH (6-8) waters rich in Na, Cl, CO_3^{2-} , and minor H_2S [4, 5, 6]. In contrast, acid-sulfate spring mineralogy typically consists of mixed-layer smectites, nontronite, kaolinite, amorphous silica, Fe-oxides/-oxyhydroxysulfates and jarosite [5, 7]. This study examines the influence of anion chemistry on mineralogy in hydrothermal systems.

Methods: The initial experimental conditions were derived from field sampling of hot springs at Rincon de la Vieja, Costa Rica. Pailas de Agua I (PDAI) is an acid (pH 2.6-4) sulfate ($\text{SO}_4^{2-} = 38 \text{ mM}$), hot ($T=80\text{-}89^\circ\text{C}$) spring. PDA I spring solutions contain high concentrations of Fe (4.0-7.0 mM), Al (15 mM), and Si (8.2 mM). Experimental conditions were chosen because: 1) PDA I contains both nontronite and kaolinite clay minerals, which precipitate from model hydrothermal solutions based on PDA I’s water chemistry and 2) acid pH conditions facilitate the mobilization of Al in solution, which influenced rapid onset of authigenic clay nucleation.

Using PDA I’s geochemistry, model acid spring waters were created by adding silicon as $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, aluminum as AlOH_3 , and Fe was added as either iron sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and iron chloride pentahydrate ($\text{FeCl}_2 \cdot 5\text{H}_2\text{O}$) respectively to 1 L reactors. Solutions were adjusted to a starting pH 2.6 using hydrochloric acid. Solutions were constantly mixed using magnetic stir bars for the first two months of reaction, and then stored in a 25°C incubator for 2 years.

Experimental conditions were adjusted to account for microbial surfaces, which influence mineral nucleation in circum-neutral pH (5-8) systems [8], and F-, which influences clay formation in acid-sulfate hydrothermal systems. To mimic the behavior of microbial cell surfaces, 1 μm diameter polycarbonate microspheres with carboxyl functional groups were added at a concentration of $10^6 \text{ spheres ml}^{-1}$, which is the approximate concentration of cells in PDA I [7]. To model the influence of inorganic ligands on clay formation, 0.1 mM F-, as CaF_2 , was added to half of the reactor vessels.

Major cations were analyzed on filtered, acidified samples using inductively coupled plasma optical emission spectroscopy on a Perkin Elmer ICP-OES Optima 5300 DV. Mineral precipitates were collected and freeze-dried in the laboratory and then powdered and analyzed using a Bruker SMART APEX II X-ray Diffractometer (XRD) with a copper charge coupled detector (CCD). Glycolated clay samples were then examined using XRD to determine basal spacing and clay mineral type.



Anion Influence on Authigenic Mineralogy: Chloride experiments produced significantly less precipitates (20 mg/kg soln) relative to SO_4^{2-} (120 mg/kg soln). Moreover, Cl-trials produced primarily amorphous silica with ~10% mixed-layer smectite, even at acid pH. In contrast, SO_4^{2-} experiments consisted of nearly equal proportions of clay (52%) and 40% amorphous silica, with 8% Fe/Al-oxides. These data indi-

cate that the dominant ion in solution is the primary control on the mineralogy produced, not pH.

F⁻ addition resulted in an increase in total precipitate mass in SO₄²⁻ trials by 40%, due to increased precipitation of Fe/Al-oxides. No change in precipitate weight was observed in chloride experiments; however, F⁻ addition to Cl⁻-trials increased clay and Fe/Al-oxide formation at the expense of amorphous silica. F⁻ complexes Al in solution, facilitation clay formation in Cl⁻-trials.

Microbial Influence on Authigenic Mineralogy:

The addition of functionalized microspheres to solution resulted in a 7% increase in clay formation in SO₄²⁻ experiments at the expense of amorphous silica. In Cl⁻-trials, the addition of microspheres decreased the total precipitate weight relative to Cl⁻-controls. Microspheres increased the total percentage of clay minerals by 9%. Therefore, microbial surrogates may play an important role in clay formation in low temperature systems, regardless of pH. In low pH systems, microbial influences

Implications for Mars: These data indicate that anion chemistry influences authigenic mineral precipitation, particularly authigenic clay formation. SO₄²⁻ is a weaker ligand than Cl⁻; however, it more effectively complexes Al in solution facilitating clay formation. F⁻ addition at concentrations similar to Earth's hydrothermal systems facilitates Al-complexation and clay formation in Cl⁻ systems, and has been observed incorporated into hydrothermal clay structures [9]. Moreover, the presence of Cl⁻ or SO₄²⁻ enrichments associated with silica or clay deposits respectively may provide important clues about the type of hydrothermal systems from which Mars' clays formed. In low temperature systems, regardless of pH, microorganisms act as important nucleation sites for clay minerals. Because carboxyl functional groups on the cell surface are protonated at low pH, microbial surface effects are expected to be most significant in high ionic strength (I=0.47) solutions [7]. In these solutions, the electric double layer is compressed, overcoming electrostatic repulsion between positively charged microbial surfaces and dissolved metals. Our data show a 7-9% increase in clay formation when microbial surrogates are present. Therefore, microorganisms may have played an important role in clay formation in lower temperature systems on Mars by facilitating critical nuclei formation in acidic, low temperature solutions.

References:

[1] Squyres et al. (2008) *Science*, 320, 1063–1067.
 [2] Squyres et al. (2007) *Science*, 316, 738–742
 [3] Bishop et al. (2008) 321, 830-833. [4] Yokoyama et al., (2004) *Chem. Geo.*, 212, 329-337. [5] White and Hedenquist (1995) *SEG Newsletter*, 23, 9-13 [6] Heald

et al. (1987) [7] Phillips-Lander et al. (2014) *Geomicro. J.*, 31, 23-41. [8] Konhauser and Urrutia (1998) *Chem. Geol.*, 161, 399-413. [9] Caulet et al. (2005) *Comptes Rendus Chimie*, 8, 245-266.

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