Authigenic smectite formation in acid-sulfate systems: Implications for Martian geochemistry

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Models of clay mineral formation on Mars suggest clays form through hydrothermal processes in shallow, neutral-alkaline reservoirs [1], as nontronite formation is unfavorable at pH values >4 [2]. However, mixed-layer clays are abundant in acid-sulfate hydrothermal systems on Earth, which contradicts these models. In order to examine the nature of clay mineral formation in acid-sulfate systems, we developed experimental batch reactors based on the dry-season aqueous geochemistry of Las Pailas hot springs (pH 2.6, T=80ºC, $[SO_4^{2-}]$=38.38 mM, $[Fe^{2+}]$=22.0-38.38 mM, $[Al^{3+}]$=0.1-15.27 mM, $[F^-]$=0-0.11 mM, & $[Ca^{2+}]$= 0-0.55 mM) [3], Costa Rica. This system is notable for its clay rich hot springs, mud pots, & fumaroles. We use aqueous geochemistry, thermodynamic modeling, HR-TEM and X-ray diffraction analysis of precipitates to characterize our experiments.

Within 7 days of the onset of the experiments, authigenic mixed-layer smectites, nontronite, illite, kaolinite/halloysite, and Fe-oxides have formed in in all samples. Preliminary analysis of our results suggest that ligand stability (with Al(III), and Fe (II,III)) and exchange kinetics are a strong control on authigenic clay formation and alteration in this system. In particular, Al-complexation by sulfate enhances kaolinite and nontronite formation. Models of our experimental data indicate the aqueous sulfate activity greatly expands the stability field of nontronite into acidic pH values. The sulfate ion, therefore, mediates clay mineral formation through Al-complexation and inhibititon of rapid homogeneous nucleation of oxide phases. Progressive evaporation of hydrothermal fluids leads to the formation of jarosite and gypsum crusts.

This study shows that the mineralogy present on Mars can form geologically instantaneously (7 days) from acid-sulfate hydrothermal solutions. This broadens the range of possible geochemical conditions that may be represented by Noachian deposits on Mars.

[1] Elhmann *et al* (2013) *Space Sci. Rev.* **174**, 329-364. [2]Chevier *et al* (2007) *Nature* **448**, 60-63. [3] Phillips-Lander *et al* (2014) *Geomicro. J.* **31**, 23-41.