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New Mechanism for Smectite-catalyzed RNA polymerization on Hadean Earth and Noachian Mars

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Smectite clays (e.g., saponite, nontronite and montmorillonite), are common products of weathering of ultramafic, mafic and protocontinental rocks, including peridotites, komatiites and tonalites, were widespread on Hadean Earth and Noachian Mars and are also found at impact crater sites on both planets. In the presence of polymerization salts ($MgCl_2$ and NaCl) at pH 7, **montmorillonite catalyzes RNA polymerization with 3'-5'-phosphodiester bond regiospecificity**. The mechanism, however, remains unknown and no other catalytic clays have been identified to date. Further, montmorillonite must be activated by acid-pretreatment and base-titrated to pH 7 to realize its RNA-polymerization catalytic activity. Acid-preactivation represents weathering under high P_{CO2}, P_{H2S} and high aqueous sulfate levels on early Earth and Mars. **The classically-proposed mechanism involves interlayer cation-replacement by protons during acid-pretreatment,** which protonate the activating imidazole group RNA monomers to promote polymerization. **However**, if protons are stored only in the interlayer, then the pH-neutralization step should replace the interlayer protons with Na^+ and Mg^{2+} ions from the polymerization salts and base, **thus effectively deactivating the clay.** This brings into question the relevance of clay-catalyzed prebiotic RNA polymerization.

Here our **goals** were to: (i) reveal the detailed mechanisms of montmorillonite acid-preactivation and base neutralization; (ii) predict which other smectites may promote RNA polymerization; and (iii) correlate strength of acid treatment and smectite structure-composition to RNA polymerization efficiency. Detailed XRD, FTIR, TGA analyses of acid-treated and untreated montmorillonite and ICP-OES analyses of solutions obtained during acid-pretreatment at various acid strengths revealed chemical-structural changes in montmorillonite, which correlated with RNA polymerization efficiency determined by HPLC and MALDI-Tof MS.

We propose that ***protons partially leach and replace octahedral cations***, where they are relatively inaccessible to base-neutralization. These **octahedrally-stored protons** are released when polymerization salts are added with RNA monomers. The Mg^{2+} ions replace **octahedrally-stored** H^+s, which enter the interlayer space and protonate the activating imidazole group of the RNA monomer, thus promoting RNA polymerization. From these mechanistic insights, we predicted and showed for the first time that saponite and nontronite also catalyze RNA polymerization with variable efficiencies, thus significantly widening the potential impact of smectite-catalyzed RNA polymerization on Hadean Earth and Noachian Mars.