Effects of salinity on the adsorption of nucleotides onto phyllosilicates

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In the context of the origin of life, phyllosilicates surfaces might favor retention, concentration and reactivity of otherwise diluted prebiotic building blocks. The primitive oceanic rocks may have been abundant in Fe-Mg-rich phyllosilicates, but the salinity of the primitive ocean is still a matter of debate and of experimental uncertainties. Values ranging between 1 and 15 times the modern salinity have been proposed while there is still no consensus on the composition of the primitive ocean. Therefore we investigated the effects of salinity on the adsorption of nucleotides on phyllosilicates. We studied the adsorption of 5'-monophosphated deoxyguanosine (dGMP) as a model nucleotide onto a Fe-rich swelling clay, *i.e.* a nontronite, and an Al-rich phyllosilicate, *i.e.* a pyrophyllite, for comparison. Experiments were carried out at atmospheric pressure, 25°C and natural pH, with a series of salts NaCl, $MgCl_2$, $CaCl_2$, $MgSO_4$, NaH_2PO_4 and $LaCl_3$ in order to evaluate the specific effect of cations and anions on the adsorption of dGMP. The present study shows that nucleotides are adsorbed on both phyllosilicates through a ligand exchange mechanism. The phosphate group of the nucleotide is adsorbed on the lateral metal hydroxyls of the broken edges of the phyllosilicates. The presence of divalent cations or molecular anions, such as phosphate or sulfate, tends to inhibit the latter interaction on both mineral surfaces. However, divalent cations such as Mg^{2+} and Ca^{2+} also allow for extra cationic bridging to occur on the basal surfaces of the swelling clay. As a consequence, if local concentration is equivalent on both minerals reaching ca. 1 M for an equilibrium concentration in solution close to 1 mM, because adsorption is localized on both the lateral and basal surfaces of swelling clays, swelling clays have a higher retention capacity compared to non-swelling phyllosilicates. The present detailed study as a function of salts composition and concentration shows that adsorption is very sensitive to the presence of divalent cations, even at low concentration. The evaluation of the salility of primitive oceans is therefore critically important for a better prediction of the capacity for porous altered oceanic rocks to retain the prebiotic building blocks of life.