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INTERACTIONS OF RIBONUCLEOTIDES WITH ALUMINUM AND IRON OXIDES UNDER VARYING ENVIRONMENTAL CONDITIONS

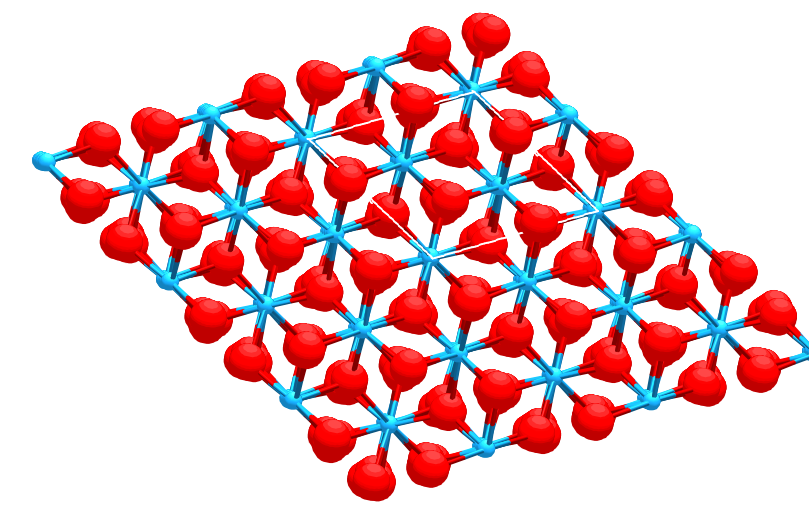
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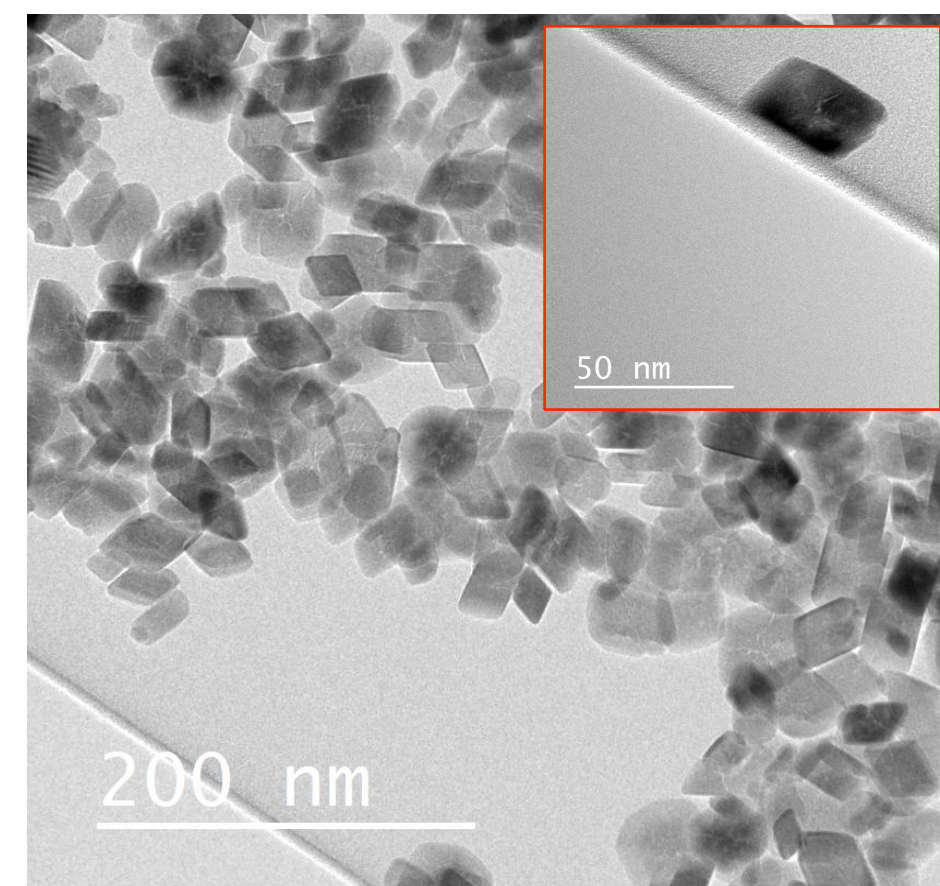
Introduction

Mineral surfaces might have concentrated building blocks of biomolecules in the context of the origin of life, facilitating their polymerization. Mineral surfaces have also been shown to protect biomolecules from degradation, facilitating their survival in soils. Previous work has highlighted the predominant role of the edges of mineral particles in the adsorption of nucleotides (Feuillie et al, 2013), implying *oxide-like adsorption sites*. The adsorption mechanism is not fully understood yet.

Here we present experimental and surface complexation modeling results on the adsorption of nucleotides with alumina and hematite, 2 oxide minerals presenting the same structure, as a function of pH, ionic strength and ligand-to-solid ratio.



Above : Crystal maker structure of α -alumina Al_2O_3 (red = O, blue = Al)
Below : TEM image of rhombohedral hematite nanoparticles used in this study.



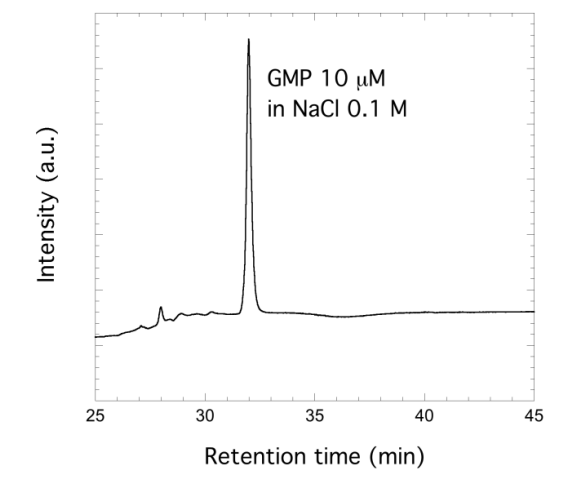
Characteristics of alumina and hematite used in this study. a: Halter & Pfeifer, 2001; b: Fukushi & Sverjensky, 2007; c: Cornell & Schwertmann, 2003; d: Sverjensky, 2005

	Corundum - Al_2O_3	Hematite - Fe_2O_3
Provenance	Well studied commercial alumina ^{a, b}	Forced hydrolysis of acid Fe^{III} salt solutions at 98°C following Schwertmann & Cornell (2000)
pH _{ZPC}	9.1 ^{a, b}	8.5 - 9.5 ^{c, d}
Particle size	~ 5 microns	~ 40 nm
Surface area	3.52 m ² /g	~ 52 m ² /g

Methods

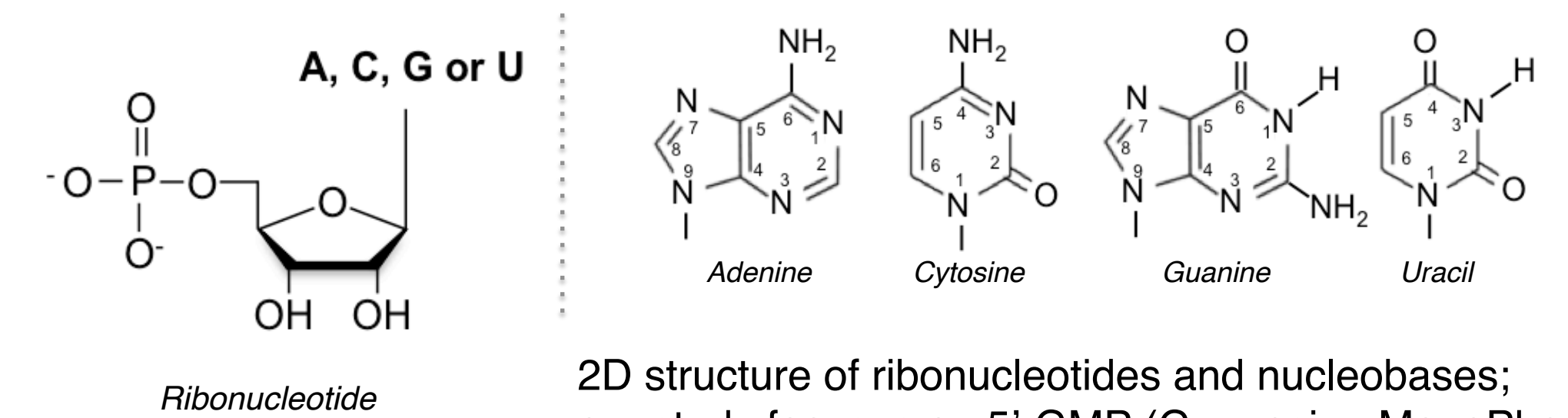
Experimental approach : batch adsorption experiments

- Adsorption at room temperature until equilibrium
- Wide range of pH (3 – 11), ionic strength (from 0 to 0.1 M of NaCl), and surface loading
- Centrifugation and filtration of the suspensions
- **Ion Chromatography** analysis of the supernatant (ICS-5000 – Dionex; AminoPac PA10 column)



Theoretical approach : surface complexation calculations using the Extended Triple Layer Model (ETLM)

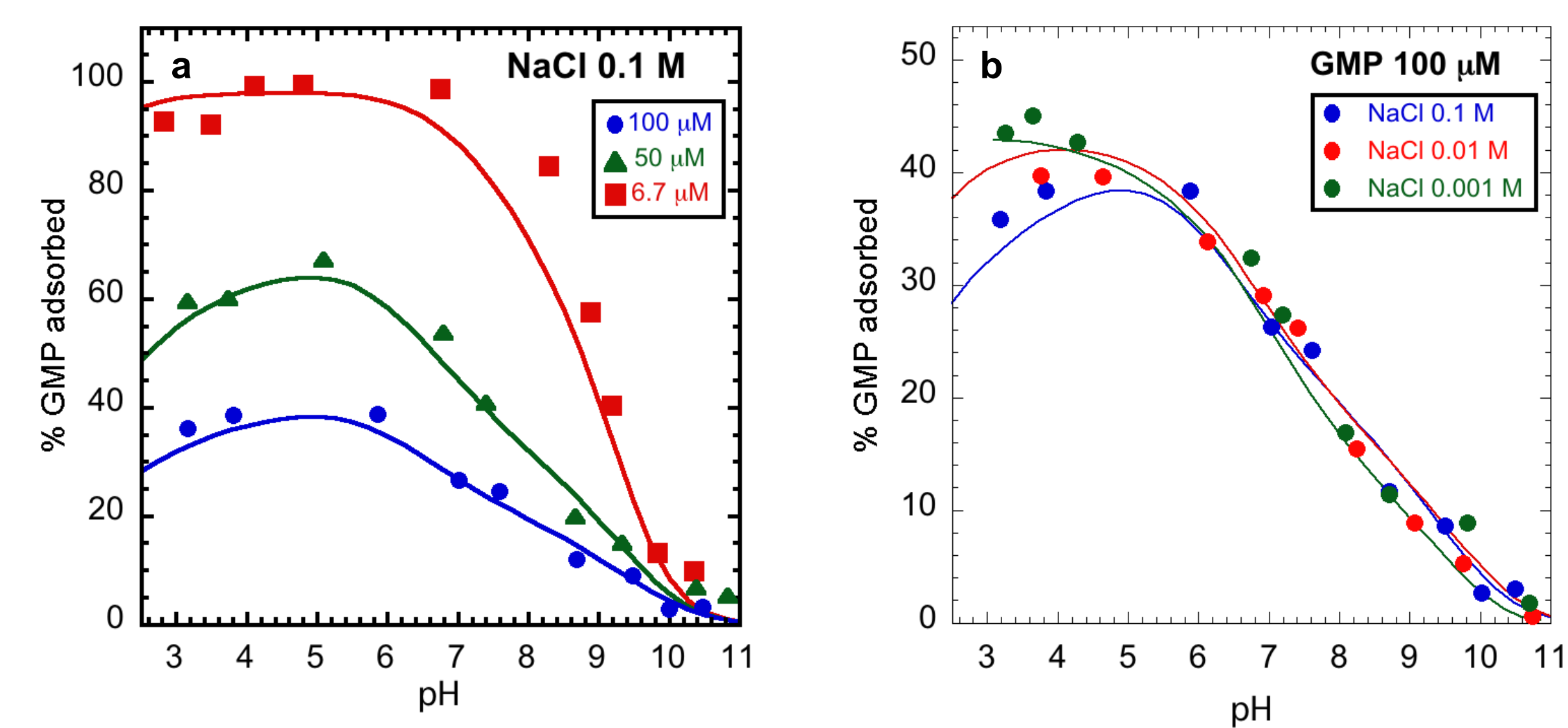
- 1 site model
- Takes into account the electrical work linked to the desorption of chemisorbed water
- Establish the speciation of surface species, the stoichiometry and the thermodynamic equilibrium constants for the adsorption of nucleotides on oxide minerals



2D structure of ribonucleotides and nucleobases; our study focuses on 5'-GMP (Guanosine MonoPhosphate)

Adsorption of GMP on Al_2O_3 (Feuillie et al, 2015)

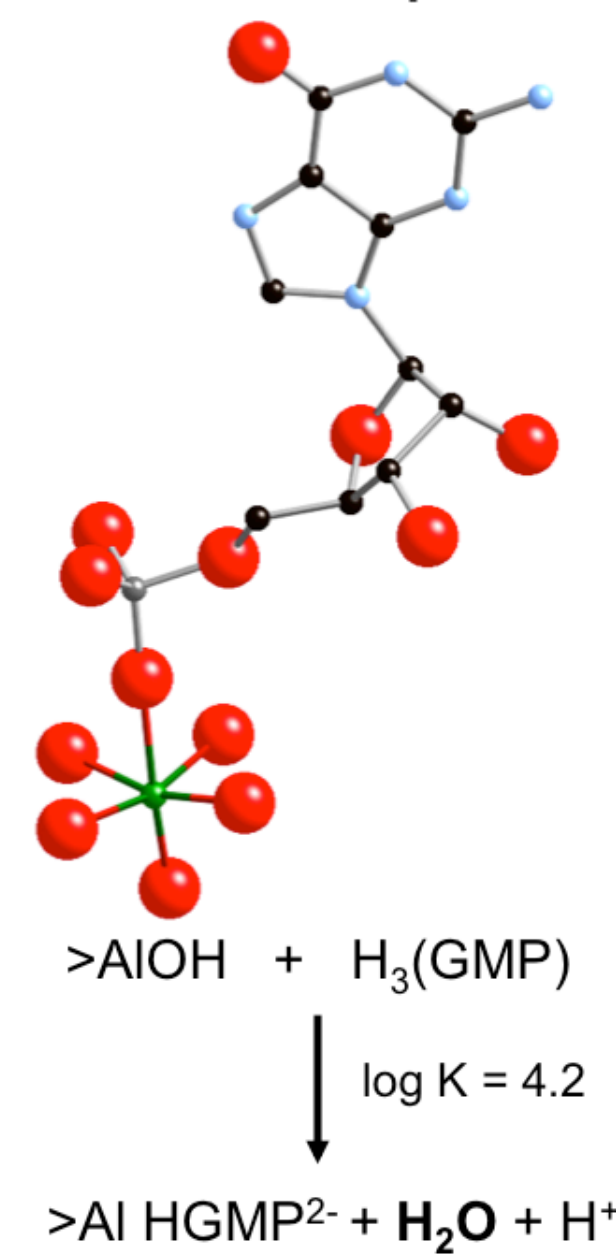
5 g/L ; equilibrium reached after 24 h of adsorption



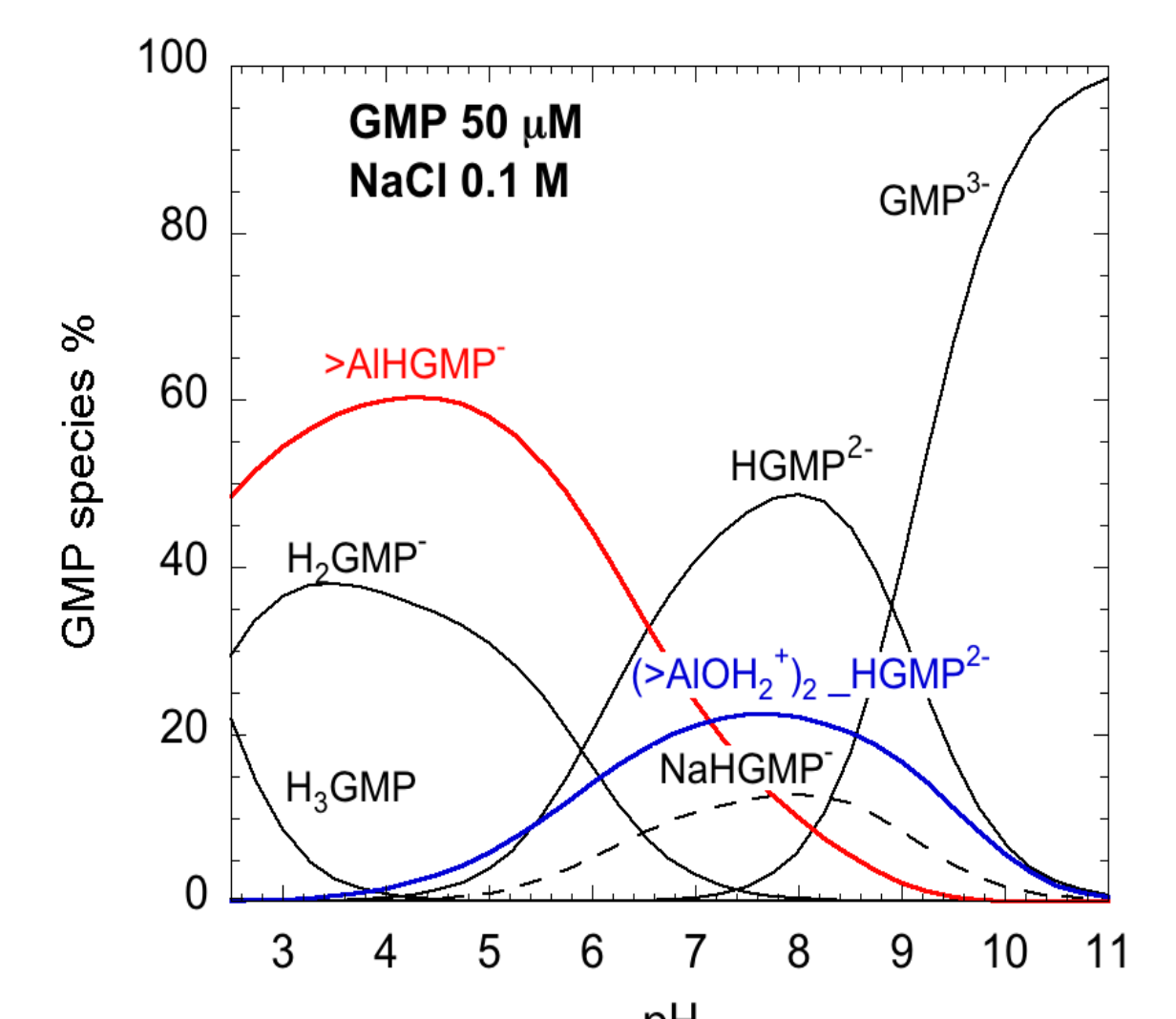
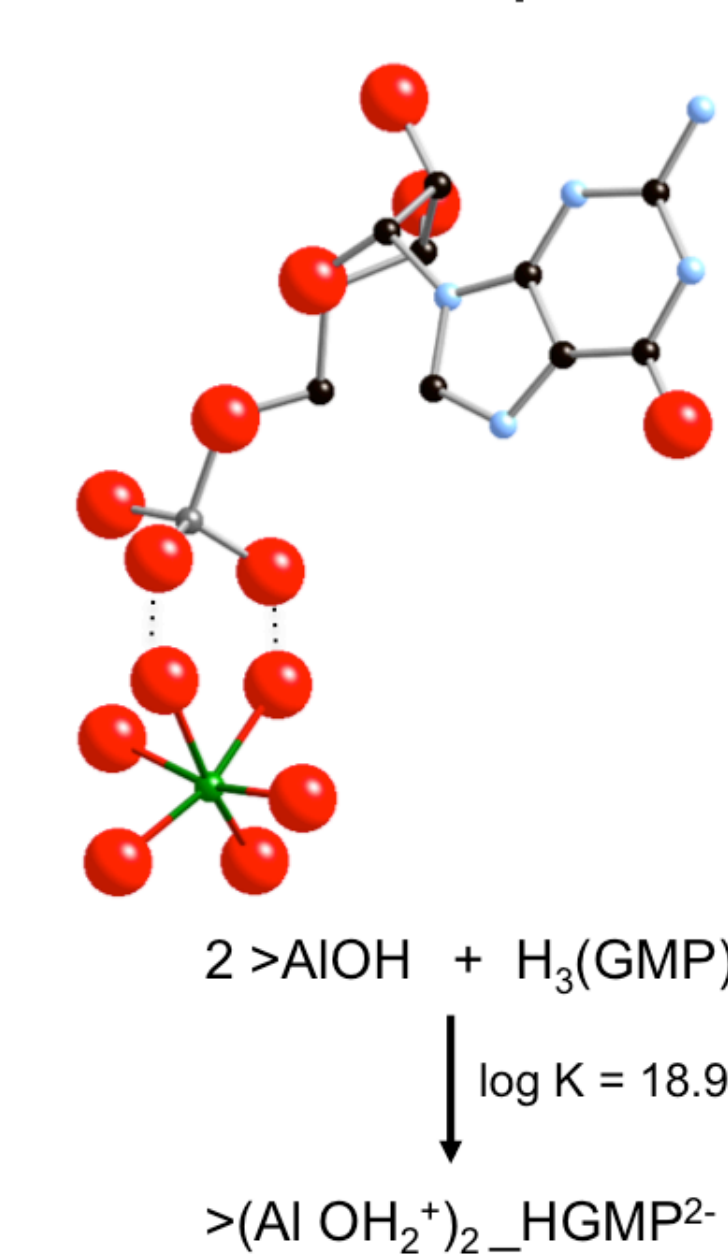
(a) pH profiles of the adsorption of GMP at a constant ionic strength; NaCl 0.1 M. (b) Ionic strength effect on the adsorption of GMP on alumina, for a concentration of GMP of 100 μM . Alumina: 5 g/L. Experimental error is <0.2 μM of GMP. Symbols are experimental data and solid lines are modeling results.

High adsorption at low pH; maximum adsorption at pH 5; > 2 $\mu\text{mol} / \text{m}^2$
No ionic strength effect above pH 5
Below pH 5, when ionic strength increases the adsorption decreases → similar to phosphate adsorption (He et al, 1997)

Monodentate inner - sphere complex



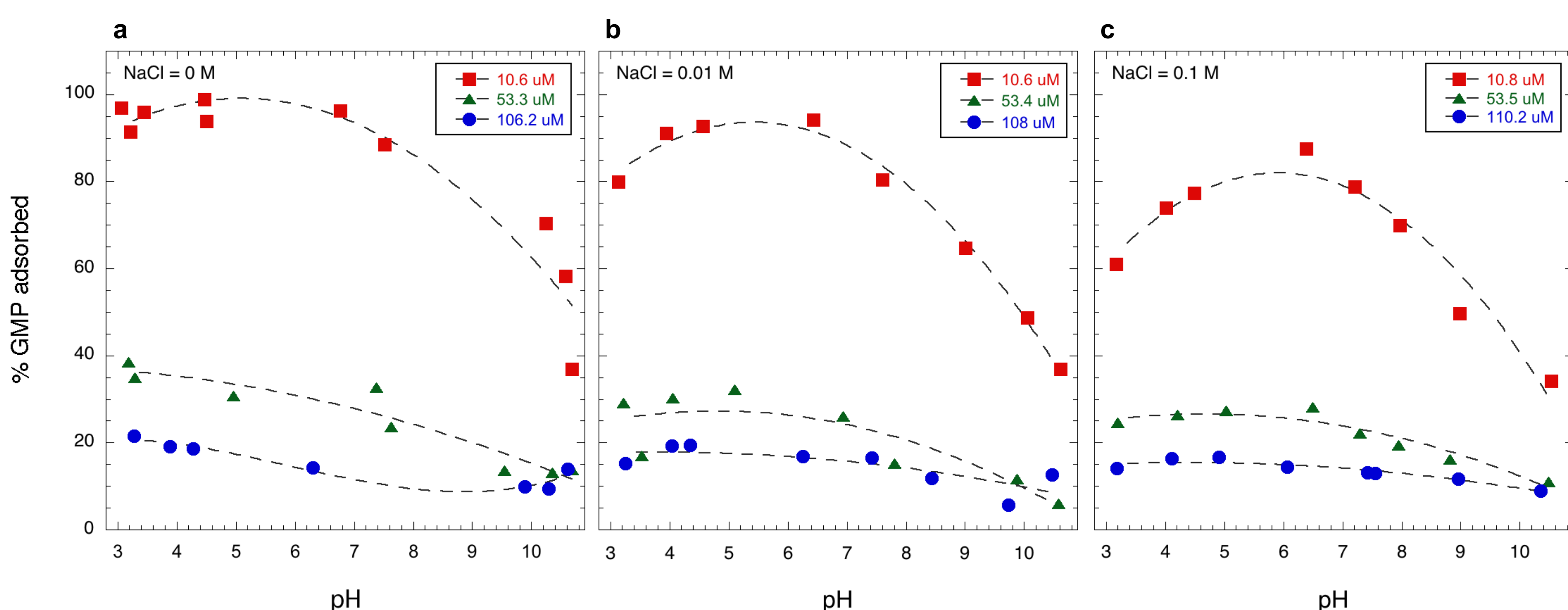
Bidentate outer - sphere complex



Speciation of aqueous and surface species obtained from the ETLM

Adsorption of GMP on Fe_2O_3

0.2 g/L ; equilibrium reached in under one hour of adsorption



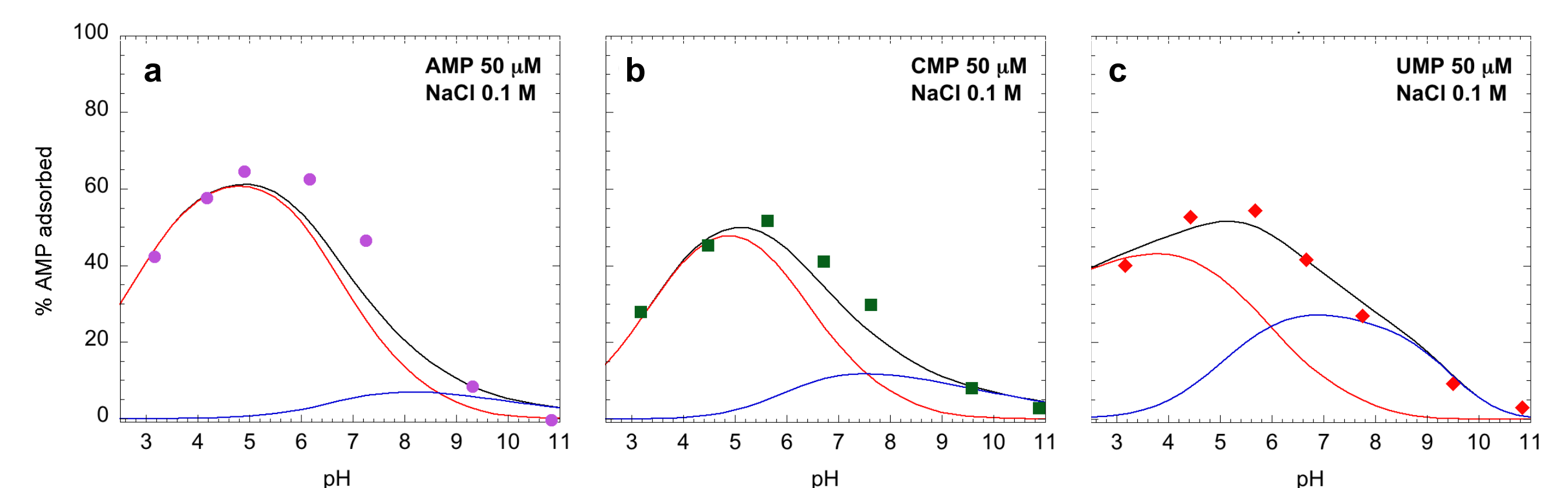
pH profiles of the adsorption of GMP on hematite nanoparticles obtained at an ionic strength of (a) NaCl 0 M, (b) NaCl 0.01 M, and (c) NaCl 0.1 M. Experimental error is ~ 5%. Symbols are experimental data; dashed lines are guides for the eyes and do not represent modeling data.

High adsorption, similar to alumina : above 2 $\mu\text{mol} / \text{m}^2$
High adsorption at low pH; maximum adsorption at pH 5.5 – 6
Similar ionic strength effect at low pH
Contrary to alumina, hematite shows adsorption even at high pH

Surface complexation calculations coming soon...

Other nucleotides on Al_2O_3 (Feuillie et al, 2015)

5 g/L ; equilibrium reached after 24 h of adsorption



pH profiles of the adsorption of AMP (a), CMP (b) and UMP (c); nucleotide concentration 50 μM ; NaCl 0.1 M. Symbols are experimental data and black solid lines are modeling results. The monodentate inner-sphere is figured in red, the bidentate outer-sphere complex in blue.

Summary

- High adsorption of GMP on both Alumina and Hematite, **above 2 $\mu\text{mol}/\text{m}^2$**
- Same behaviour at low pH for both minerals, but higher adsorption at high pH for hematite
- **One mechanism** for all nucleotides adsorption **on alumina** : 1 monodentate inner-sphere at low pH, 1 bidentate outer-sphere complex at high pH, involving phosphate groups
- More strongly bound at low pH : Availability of nucleotides for polymerization in the context of the origin of life and in modern soils ?