Proton and Cu^{2+} reactivity of Xanthan, a model bacterial exopolysaccharide

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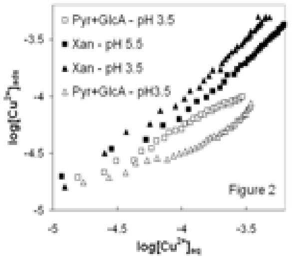
Biofilms components such as exopolysaccharides are involved in metal binding in soils. We consequently explored the reactivity of Xanthan, a non-gelling exopolysaccharide of known structure produced by *Xanthomonas campestris* strains. Its acid-base reactivity compares to that of its constituting acids, the monocarboxylic glucuronic and pyruvic acids whereas its Cu sorption capacity is higher. Moreover, Xanthan adsorbs more metal at pH 3.5 than at pH 5.5 (Fig.1 and Fig.2). This might be due to conformational changes and aggregation processes occurring at low pH [1]. These data suggest that the ternary structure of biopolymers may be involved in metal binding processes. Molecular modeling using molecular dynamics on Xanthan+Cu systems at different pH are underway to validate this hypothesis.



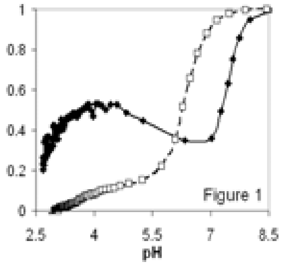


Figure 1: (Left) Copper adsorption during titration experiment on Xanthan+[Cu]i=10ppm (black lozenges) and equivalent mixture of Pyruvic and Glucuronic acids + [Cu]i=10ppm (white squares). Above pH 6, the adsorption of copper is due to the precipitation of $Cu(OH)_{2(s)}$. In the range of pH 2.5 to 6, Xanthan adsorbs always more copper than the equivalent mixtures of constituting acids. Xanthan adsorbs more Cu at pH 3.5 than it does at pH 5.5. NB : the presence of Xanthan retards the precipitation of copper hydroxide.

Figure 2: (Right) Isotherm experiment on Xanthan+Cu and Pyruvic+Glucuronic equivalent mixture + Cu at constant pH 3.5 and 5.5. Xanthan adsorbs always more copper than the equivalent mixtures of constituting acids. Xanthan adsorbs more Cu at pH 3.5 than it does at pH 5.5.

[1] Paradossi *et al.* (2002) *Biomacromolecules* **3**, 498-504.

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^{40}Ar diffusion in muscovite

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Due to its ubiquitous presence in low grade metamorphic rocks, low solubility for Ar_{xs}, and high retentivity for $^{40}Ar^*$, muscovite is among the most utilised minerals in $^{40}Ar/^{39}Ar$ thermochronology. However, despite its widespread use, no published experimental study of the diffusion of Ar in muscovite – crucial to calculation of closure temperature (T_c) – has yet appeared. Instead, the thermochronological community has tended to adopt a nominal closure temperature value of 350°C. We report $^{40}Ar/^{39}Ar$ analyses of muscovite MUS 1, treated at high temperature (730-600°C) and water pressure (10-20 kbars) in a piston cylinder apparatus, that yield a linear array indicative of $^{40}Ar^*$ transport by volume diffusion. The *in vacuo* $^{40}Ar/^{39}Ar$ degassing behaviour of the run products is characterised by a sigmoidal form characteristic of outgassing from multiple diffusion domains (MDD). SEM textural characterisation of the run products shows that, despite careful sieving of the run products, the size population is not uniform. A numerical model constructed to test this MDD hypothesis yields excellent fits between synthetic and actual degassing spectra but significantly impacts calculated diffusion parameters. Deconvolution of the contribution of multiple diffusion domains to the experimentally determined factional loss yield estimates of D that are an order of magnitude lower than that assuming bulk loss from a single domain size. Diffusion data generated in this manner yield a much higher activation energy than previously assumed and correspond to a T_c of >400°C for a sample with a 100 μm radius cooling at 10°C/Ma at 5 kbar.