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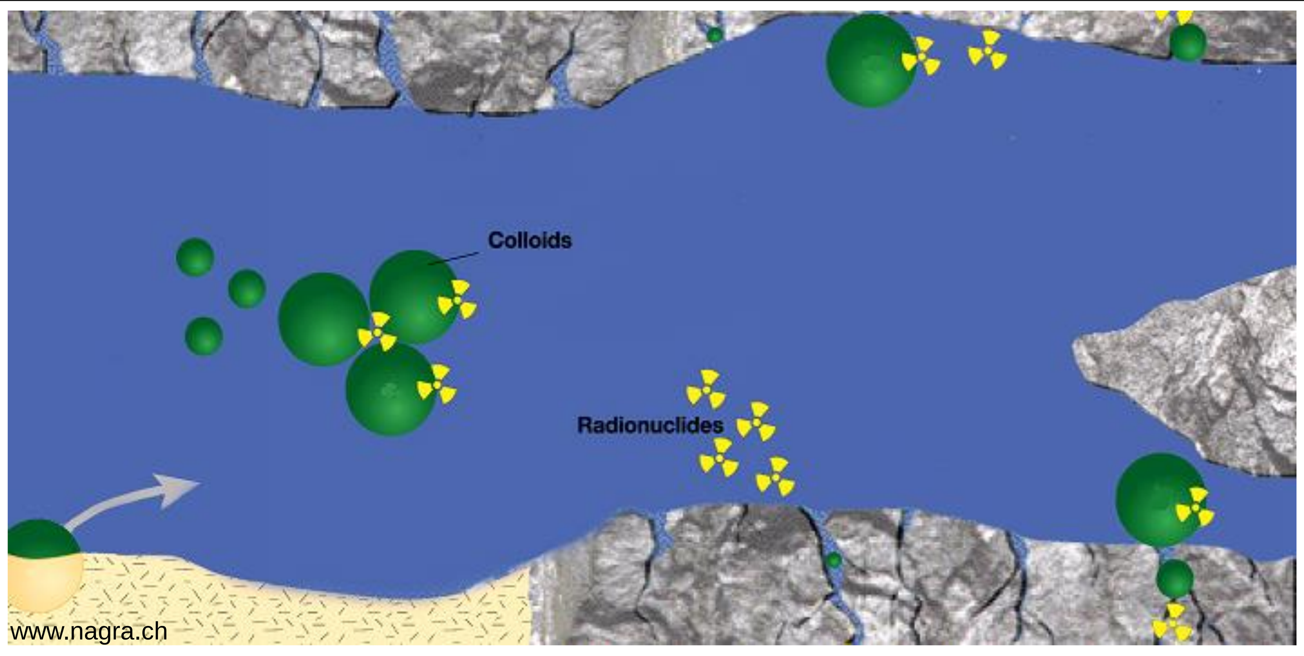
Interaction of carboxylate-modified latex colloids with muscovite surfaces

Introduction

The interaction of colloids, as radionuclide carriers, with natural mineral surfaces is only insufficiently understood. Laboratory experiments showed, that carboxylated polystyrene colloids can be retained in granitic fractures, although both surfaces are charged negatively on a macroscopic scale [1]. In this study, carboxylate-modified fluorescent polystyrene nanoparticles were used as a model for negatively charged colloids. Fluorescence microscopy has been employed for studying the sorption behaviour of the fluorescent colloids on freshly cleaved muscovite. By using Eu(III) as homologue for trivalent actinide ions, the sorption behaviour at different pH values and constant ionic strength was studied. In order to quantify and identify the forces responsible for the different modes of interaction of colloids with muscovite the AFM-colloid probe method was used.



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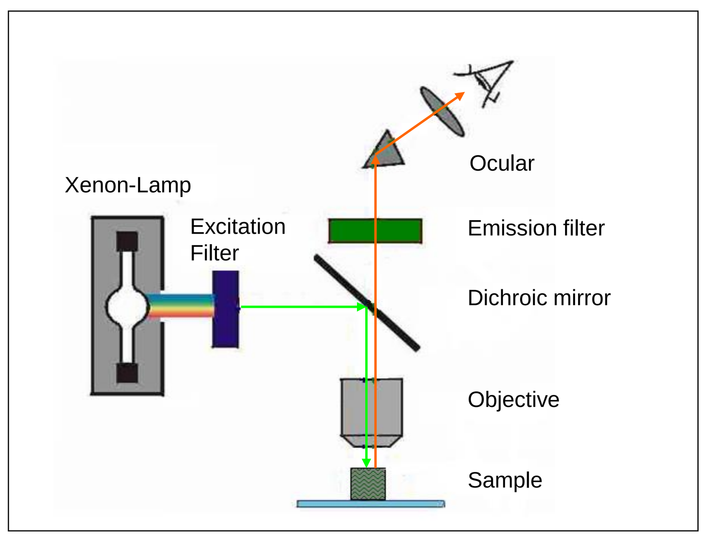
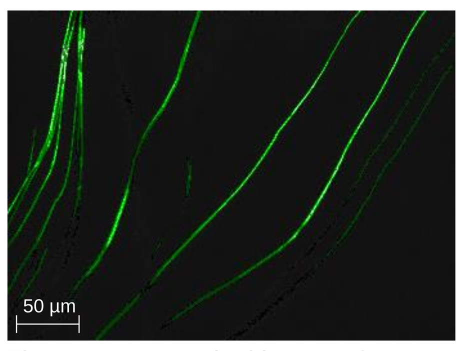
Fluorescence microscopy

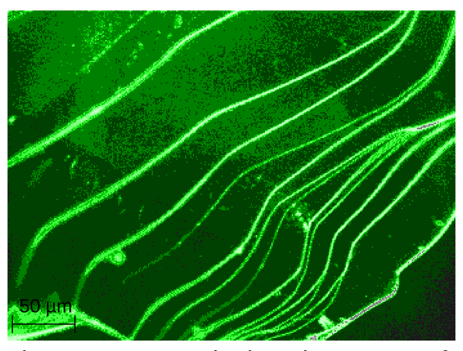


λ_{ex} = 552 nm
λ_{em} = 580 nm

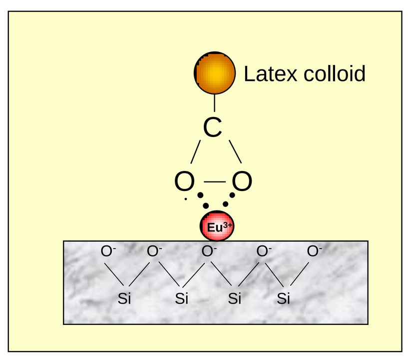
Results



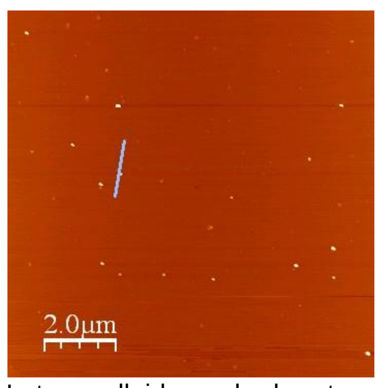
Fluorescence-optical image of muscovite; pH = 4, I = 0,01 M NaCl. Colloid sorption is only detectable on the crystal steps.



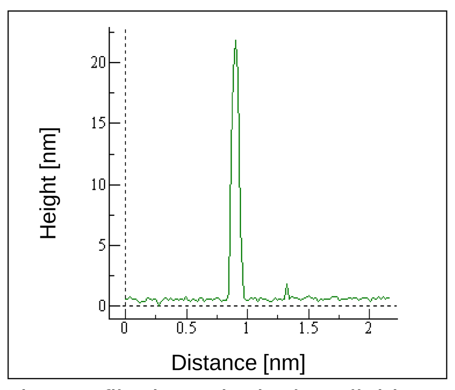
Fluorescence-optical image of Muscovite; pH = 4, I = 0,01 M NaCl, $[Eu^{3+}] = 10^{-5}$ M. Colloid sorption is detected on the whole mineral surface.



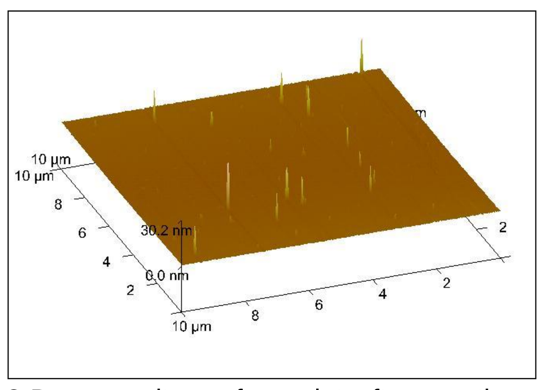
Polyvalent cation bridges between carboxylated latex particle and mica basal planes.



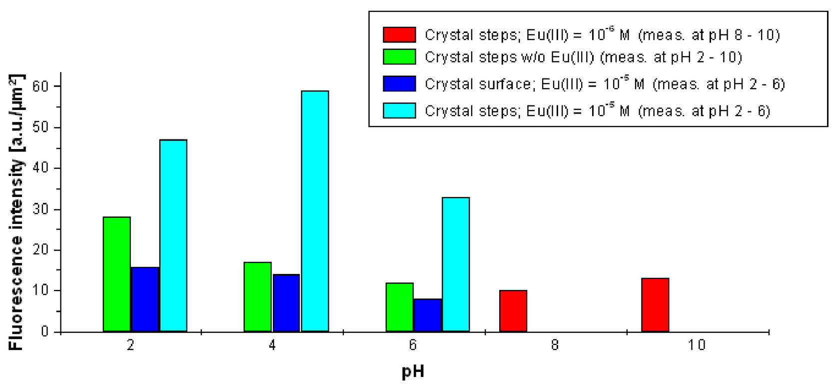
Latex colloids sorbed onto freshly cleaved mica at pH 6 and $[Eu^{3+}] = 10^{-6}$ M.



Line profile through single colloid.

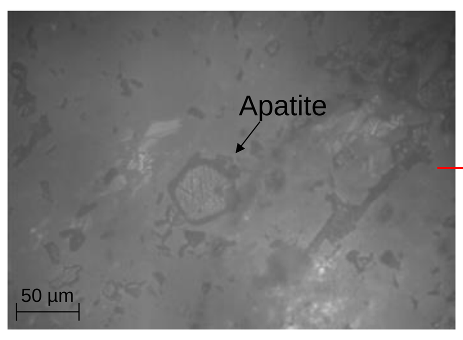


3-D muscovite surface plot after sorption experiment.

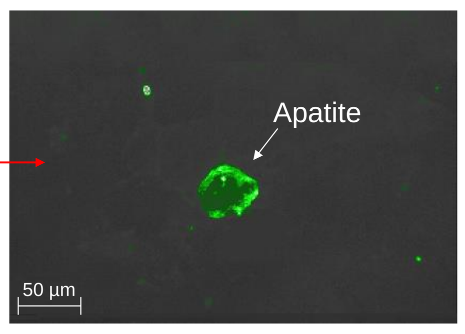


- Mica basal planes: permanent negatively charged
- Silanol groups: Si-OH ⇆ $Si-O^-$; pH_{pzc} = 2
- Aluminol groups: Al- OH_2^+ ⇆Al-OH; pH_{pzc} = 9 - 10
- Calculated edge potential based on [2] is 8 - 8.5

- In absence of Eu(III) decreasing sorption with increasing pH because of deprotonation of COOH groups on colloid surface and deprotonation of minerals
- Comparatively higher sorption on crystal steps and basal planes in presence of Eu(III)
- In presence of Eu(III) colloid sorption takes place also on crystal steps at pH 8 and 10
- no sorption detectable on basal planes in absence of Eu(III)



Light-optical image of granodiorite surface

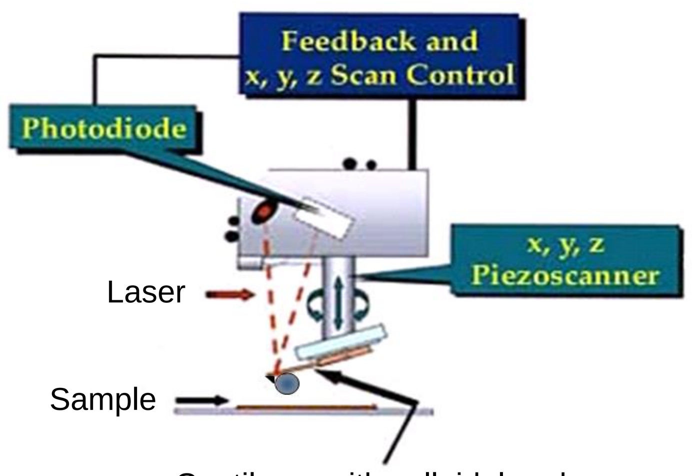


Fluorescence-optical image of granodiorite surface

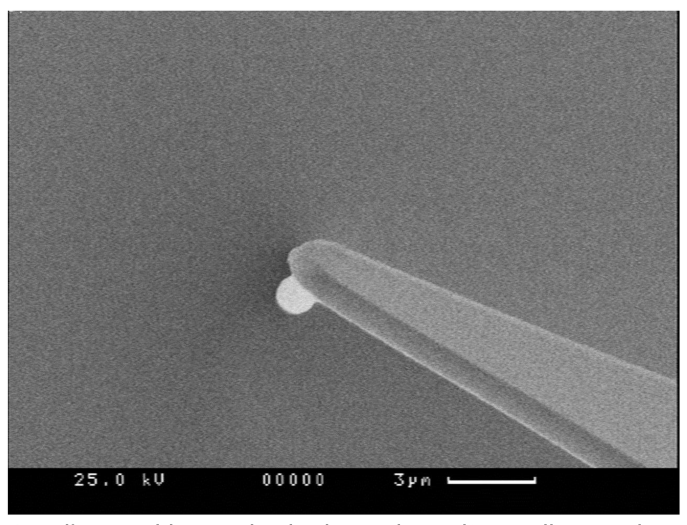
Similar sorption experiments with grimsel granodiorite showed selective and pH-dependent sorption on certain minerals, e.g. Apatite, Illite and Titanite.

Even at pH 8 – 10 (in general repulsive conditions, in absence of Eu (III)) sorption was detected on granodiorite surface presumably because of surface roughness.

AFM-colloidal probe technique

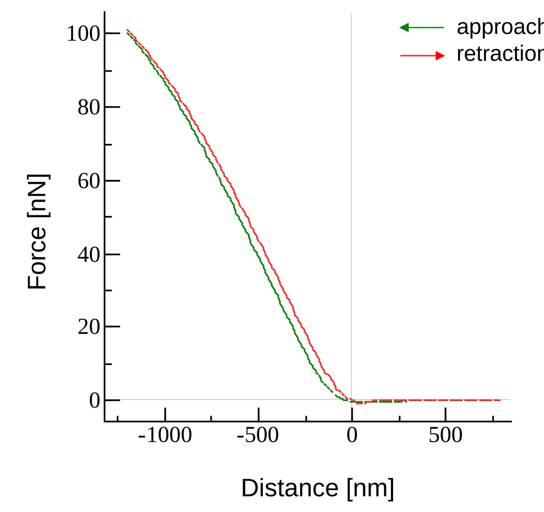


Cantilever with colloidal probe

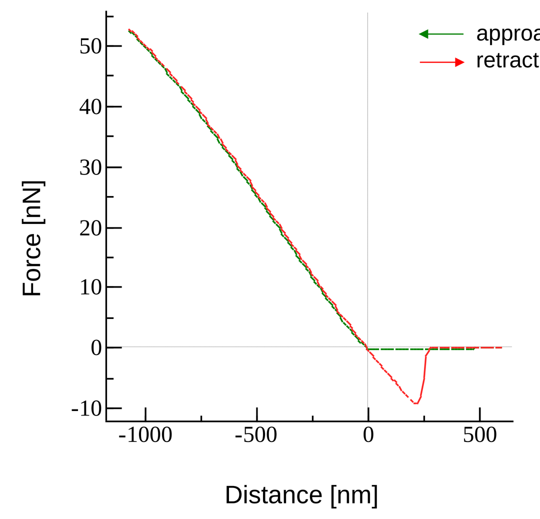


Cantilever with attached microsphere (1 µm diameter).

Results

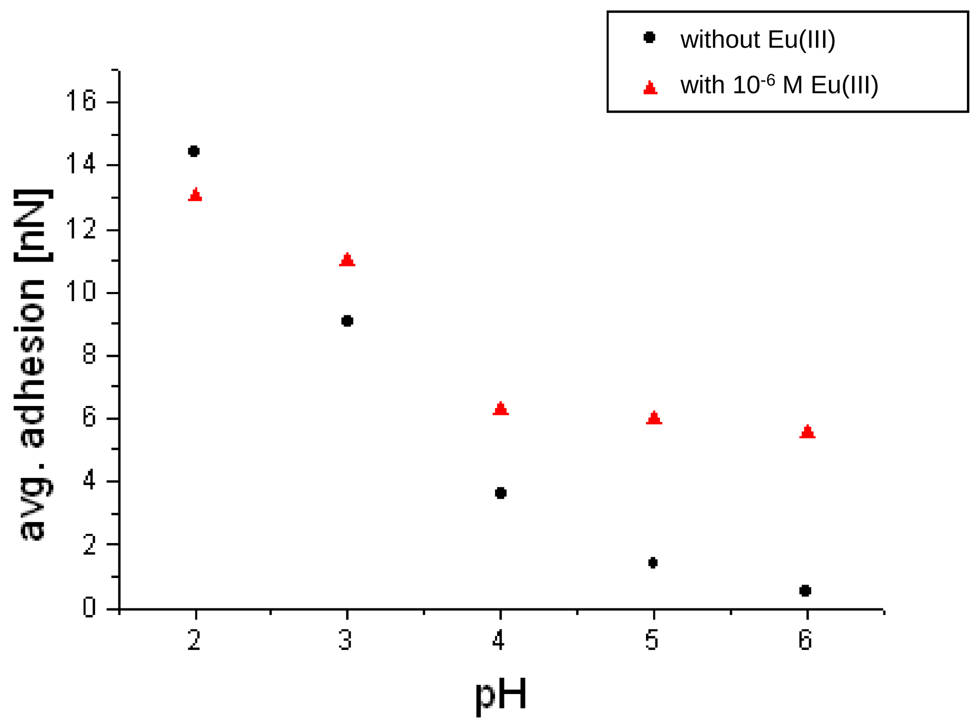


Force-distance curve between a latex microsphere and muscovite basal plane at pH 6, I = 0,01 M NaCl. Only repulsive interaction is measured.



Force-distance curve between a latex microsphere and muscovite at pH 6, I = 0,01 M NaCl, $[Eu^{3+}]=10^{-6}$ M. Presumably because of cation bridging considerably higher adhesion forces.

Adhesion forces vs. pH



- decreasing adhesion forces with increasing pH because of deprotonation of COOH groups on colloid surface
- Comparatively higher pull-off forces were measured in presence of Eu(III) at pH > 4
- Because of protonation of carboxylate-groups influence of Eu(III) decreases with decreasing pH

Conclusions

- Eu(III) causes sorption of latex colloids on negatively charged muscovite basal planes presumably by cation bridging [3]
- In the absence of Eu(III) pull-off forces increase with decreasing pH because of protonation of latex colloids
- Significantly higher pull-off forces were measured in the presence of Eu(III) at pH 4 - 6 compared to measurement in its absence

[1] Schäfer, Th., Geckeis, H., Bouby, M., Fanghänel, Th., *Radiochim. Acta 92* (2004), 731-737
[2] Schäfer, Th., Geckeis, H., Bouby, M., Mihai, S., Delos, A., Alonso, U., Missana, T., Prediction of bentonite colloid stability in natural and stimulated granite groundwater, 1st Annual Workshop Proceedings, France, Dec. 2005
[3] Greenland, D. J., Interaction between humic and fulvic acids and clays, *Soil Sci.* 111 (1971), 34-41

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mit der Universität Karlsruhe verbunden in KIT Karlsruhe Institute of Technology