

Belbar

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Background

- The build up of colloidal bentonite (nano)particles at the bentonite/groundwater interface is a well-established phenomenon.
- Actually it is the whole focus of the BelBar project.



Background

- Since the seminal work of Missana et al (2003) we know that bentonite colloids may build both under advective and diffusive conditions.
- The pure diffusive condition generates a gel as a precursor of colloidal generation.
- Under advective conditions the colloidal generation is enhanced by physical erosion



Observations by Missana et al (2003)

T. Missana et al / Journal of Contaminant Hydrology 61 (2003) 17-31

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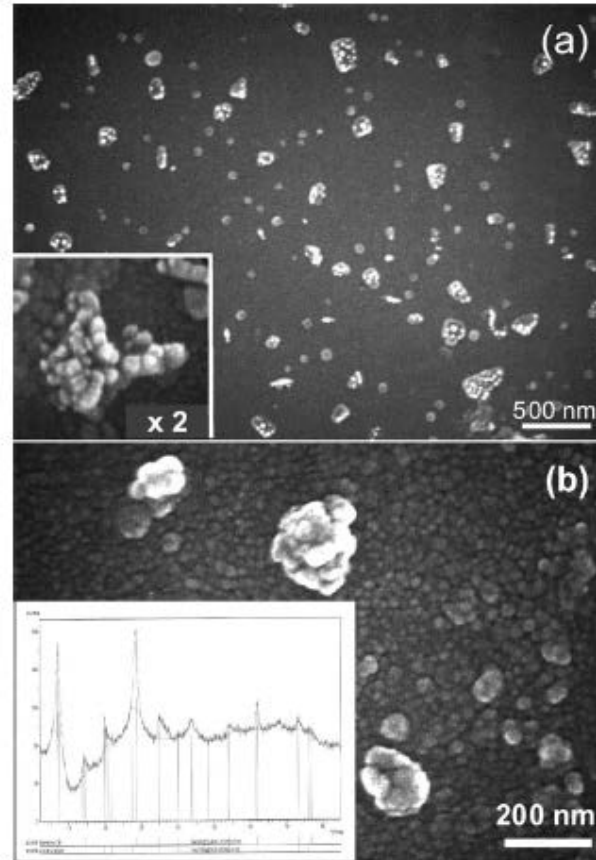


Fig. 2. (a) SEM image of bentonite colloids generated at the granite/bentonite interface in dynamic experiments. In the inset, a detail of the structure of bentonite colloids can be appreciated. (b) SEM image of laboratory-made bentonite colloids. In the inset, the XRD spectra of colloids extracted from bentonite (previously Na-humionised) are shown.



Background

- Already Missana et al (2003) set the path for what is the purpose of our presentation by proposing:
- *...the gel formation and the intrinsic tactoid structure of the clay play an important role in the submicron particle generation even in compacted clay and in a confined system*



Background

- Bentonite swelling leads to the formation of a gel-like front moving with the montmorillonite concentration gradient
- Because of the high hydration of montmorillonite in the gel phase the attractive forces between the negatively charged sheets and the hydrated interlayer cations becomes weaker and particles detach and diffuse away from the montmorillonite/groundwater interface.



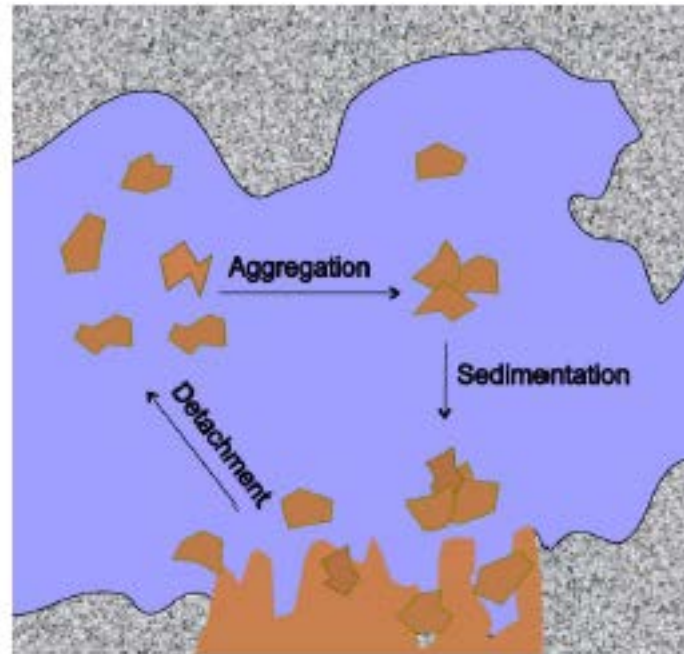
Background

- From the phenomenological point of view then, all parameters that influence swelling, will influence colloidal particle generation.
 - Ca-montmorillonite swells less than Na-montmorillonite and consequently particle generation is lower.
 - Increasing ionic strength, compaction density and pH decrease swelling and particle generation.



Background

- The colloidal life-cycle according to Sandra García (2010)



Background

- The colloidal life-cycle reaches steady-state under quasi-static flow conditions (Garcia, 2010)

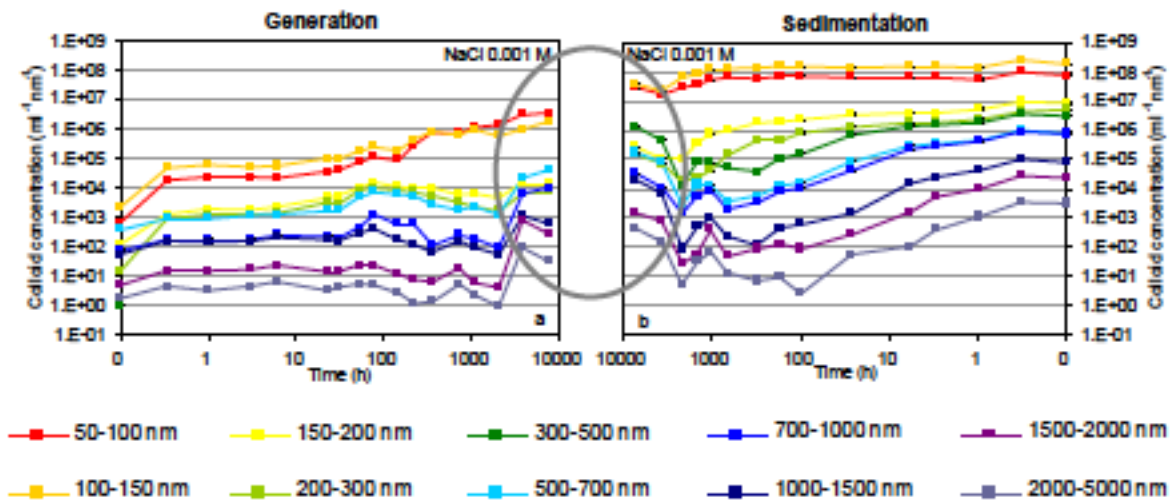


Figure 9: Normalised Na-montmorillonite colloid concentrations for generation (a) and sedimentation (b) experiments as a function of time at NaCl concentration 0.001 M. Samples taken in the middle of the batch.

Background

- Visual conceptualisation of clay layering and effect of compaction (Miller and Wang, 2012)

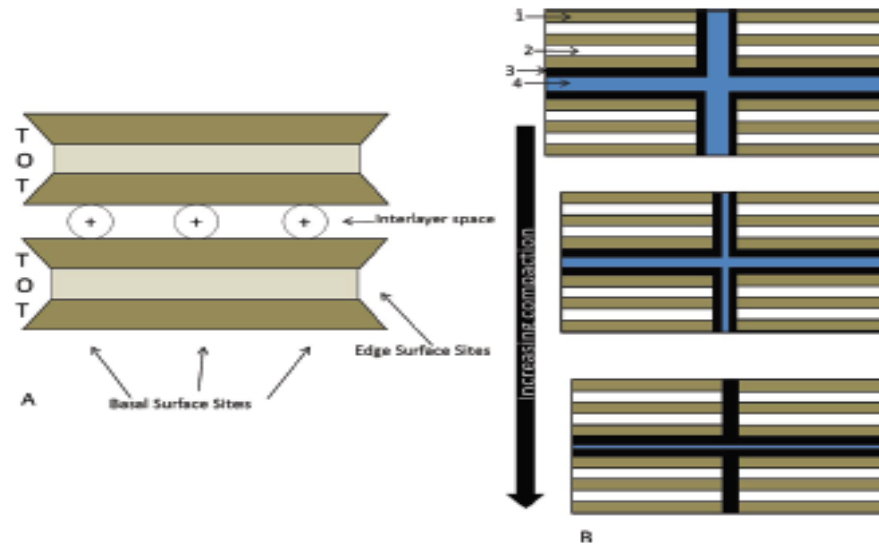
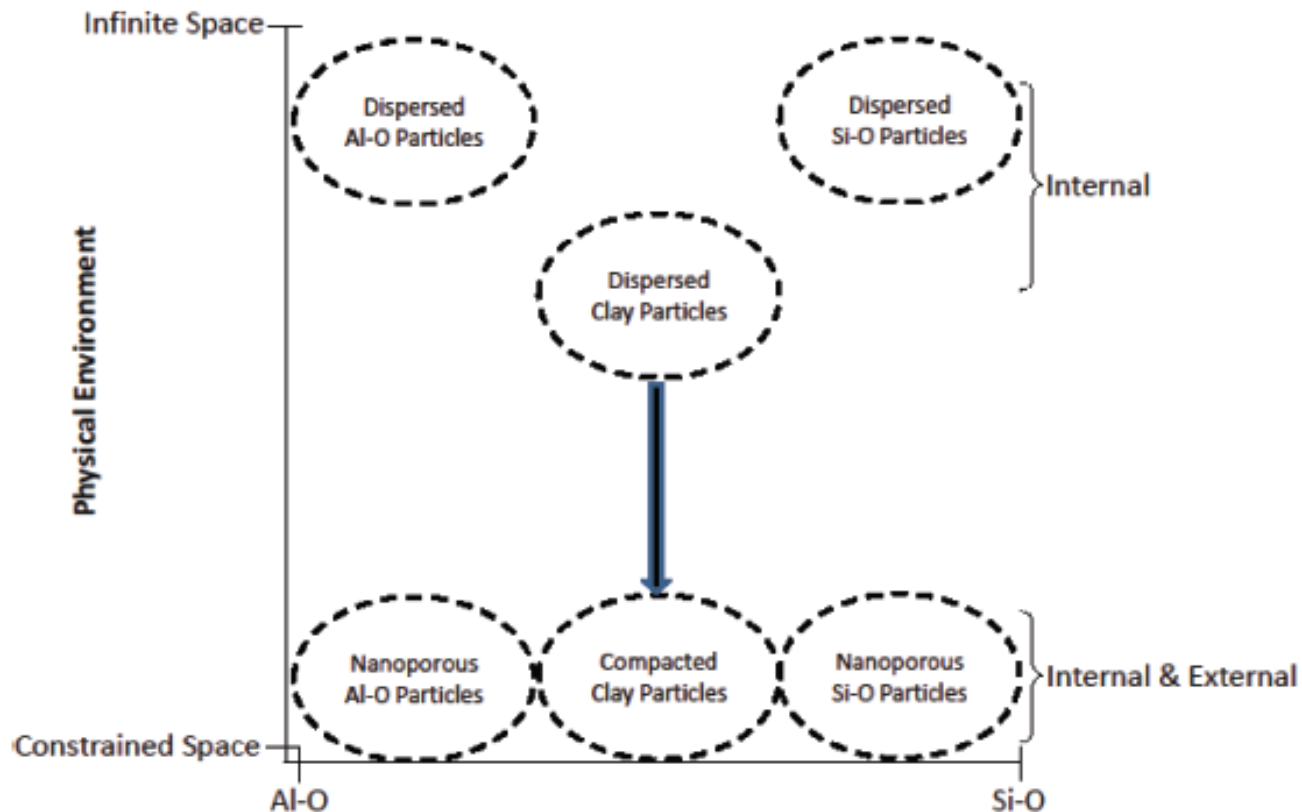


Figure 1. (A) Visual conceptualization of clay layering. T sheets are tetrahedral Si–O sheets, O sheets are octahedral Al–O (or Mg–O) sheets. This picture shows a 2:1 clay; a 1:1 clay would only have 1 T sheet and 1 O sheet comprising a TO layer. As pictured there are cations in the interlayer space denoted by the circles with + symbols. In certain clays the interlayer is only filled with water. Also shown are the physical locations of the basal and edge surfaces. (B) Visual conceptualization of clay stacks under various degrees of compaction (adapted from ref 1). (1) TOT clay layer, (2) interlayer water, (3) diffuse double layer water, (4) free water. Crystallographic images of clay stacking available in ref 2.

Background

- How do chemical and physical conditions affect the chemical behaviour of clays? (Miller and Wang, 2012)



Questions?

- Is this the whole picture for bentonite colloidal generation under diffusive regimes?
- Is water the only reagent that will have an enhancing effect on colloidal generation?
- Is montmorillonite stable in water?



Montmorillonite stability

- Na and Ca montmorillonite alters in contact with water even at low T.

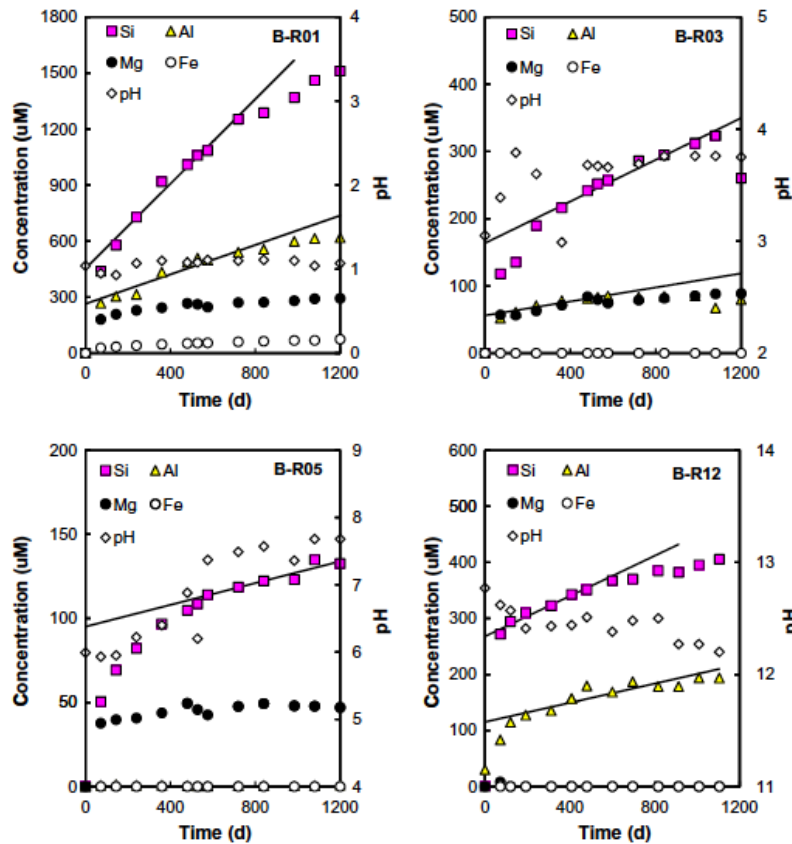
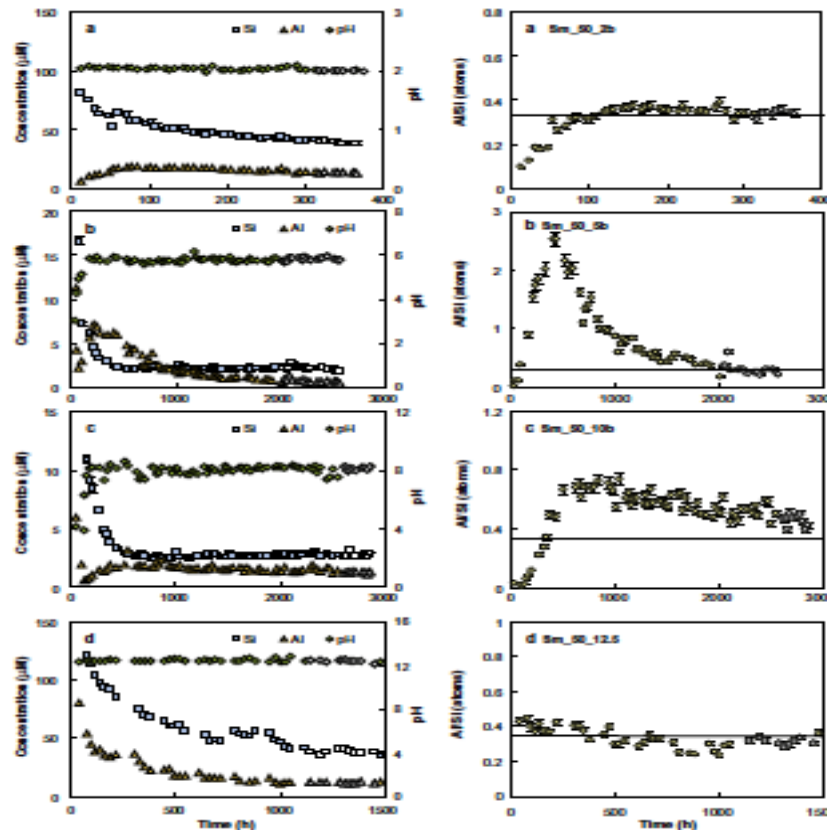


Fig. 4. Evolution of the pH, and concentrations of Si, Al, Mg and Fe in the dissolution experiments conducted in batch reactors.

Montmorillonite stability

- Alteration is evident from Rozalén et al (2009) experiments at various T.



Dissolution experiments of MX-80 bentonite at pH=8 (Suzuki et al, 2011)

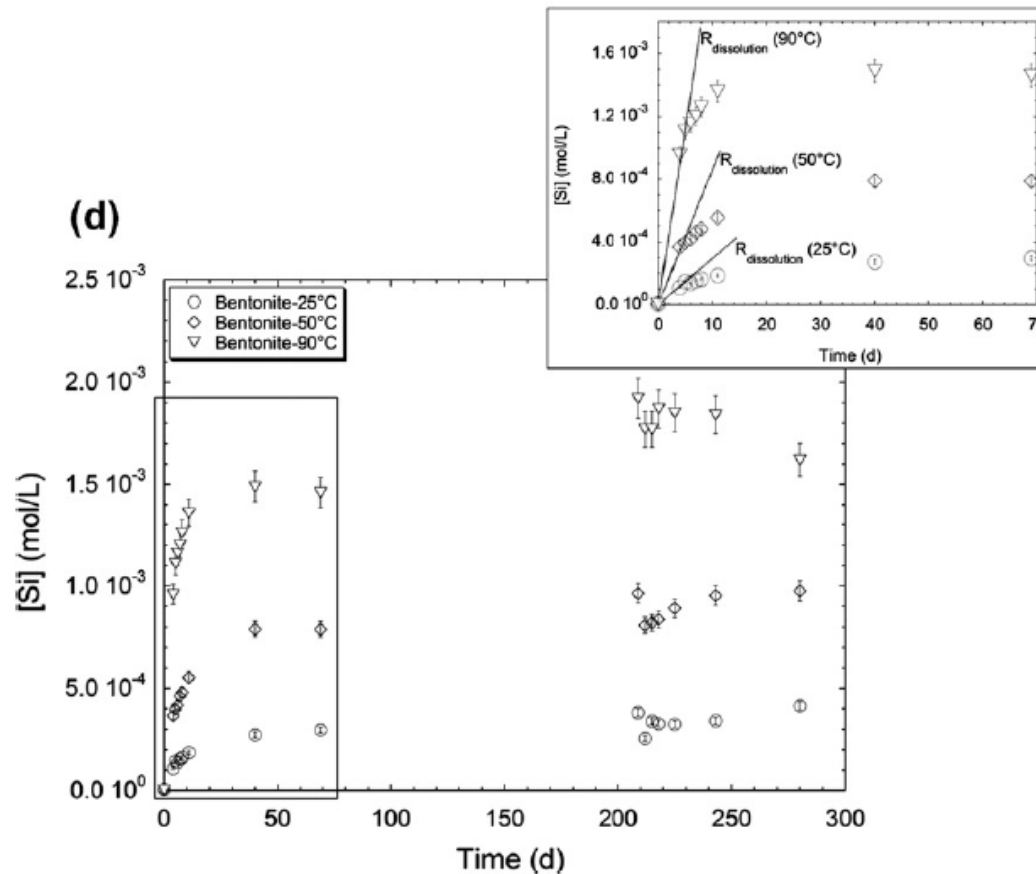


Fig. 1 (continued)

Montmorillonite alteration

- Recently a number of modelling efforts have taken into consideration the fact that montmorillonite is not stable in contact with water and that its (geo)chemical behaviour goes beyond ion-exchanger properties.



Montmorillonite alteration

- i.e. Marty et al (2008)

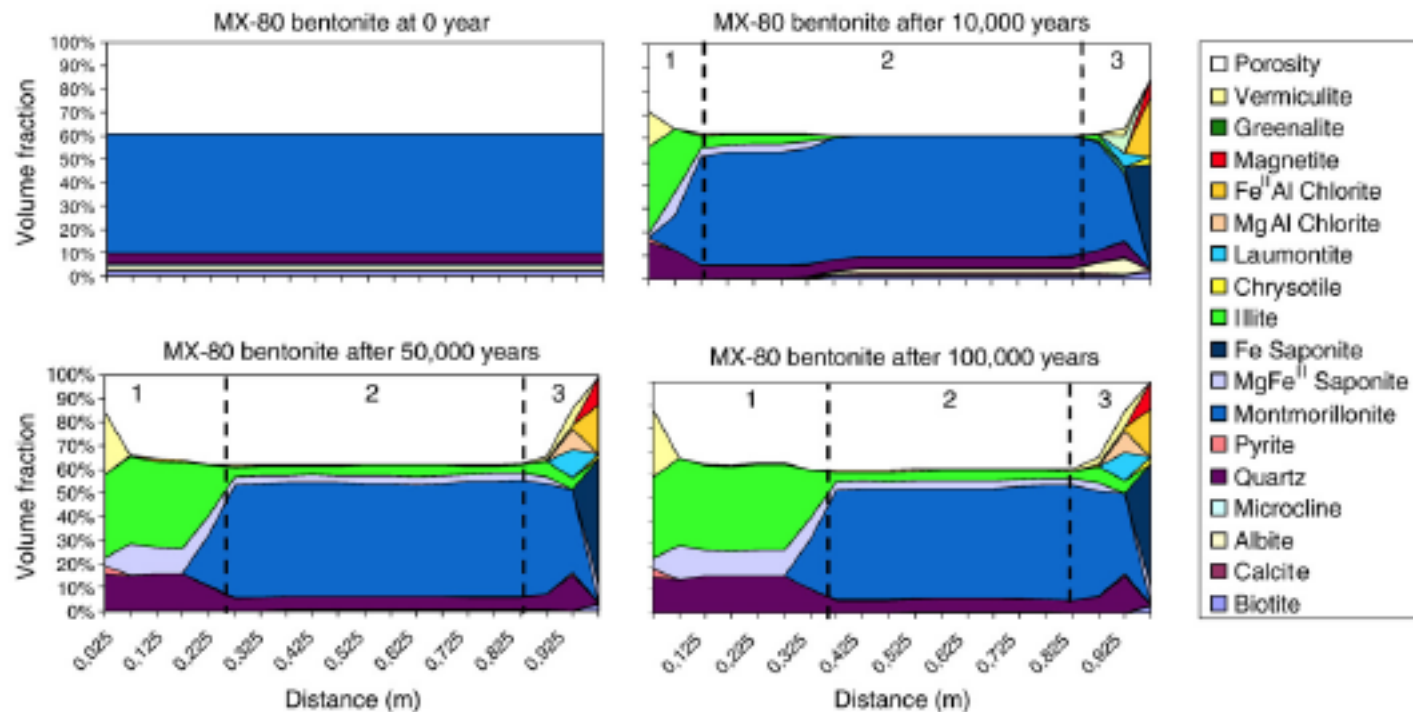


Fig. 2. Mineralogical evolution at 100 °C of the MX-80 bentonite (EBS) in contact with the Callovo-Oxfordian formation (COX) and with the modelling cell of the steel overpack corrosion.

Montmorillonite alteration

- More recently Savage et al, 2011

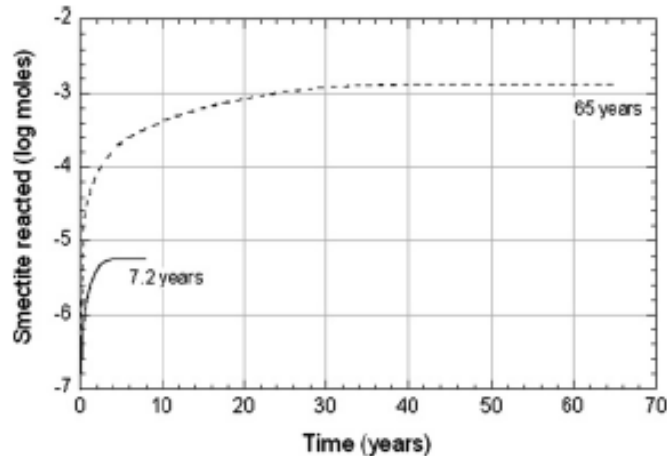


Fig. 1. Calculated amounts of smectite dissolved in squeezing experiments with *L1* dilute pore water (solid line) and *L2* hyperalkaline pore water (dashed line) for Model B over time periods required to achieve equilibrium (indicated by symbols) at 25 °C, 1 bar. Model B: dissolution of MX-80 smectite for time until equilibrium at 25 °C, 1 bar, ignoring all other mineral dissolution-precipitation reactions.

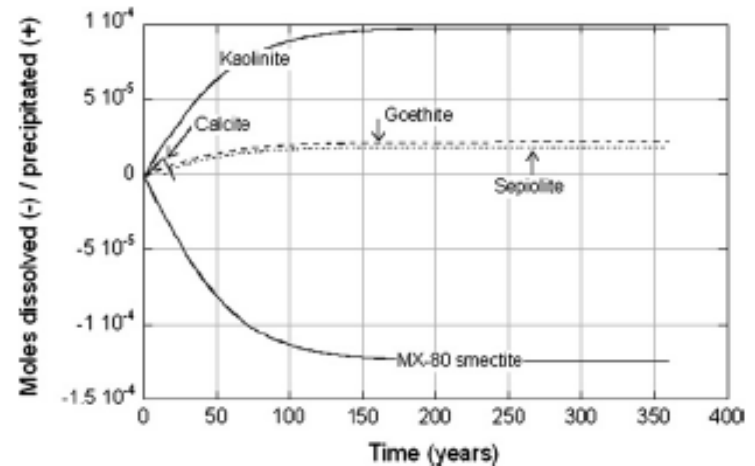


Fig. 3. Variations in mineral abundances in squeezing experiments as dilute (*L1*) pore water equilibrates with MX-80 smectite. Equilibration time = 360 years, Model C: dissolution of MX-80 smectite for time until equilibrium at 25 °C, 1 bar, including equilibrium precipitation of secondary minerals.

Where do we go from here?

- The questions we would like to address are:
 - Which role does montmorillonite dissolution play in colloidal generation?
 - How does montmorillonite alteration affect colloidal generation?
 - Can we link the previously developed geochemical models for bentonite behaviour to colloidal generation in order to predict the chemical conditions for bentonite stability under glacial/post-glacial conditions?



Colloid formation

Fully physical processes

Significant groundwater flow at interface

→ Flow-driven Erosion

Bentonite hydration

→ Colloid formation due to swelling in open space

Low ionic strength
(low Ca concentration)

→ Loss of bentonite density

Smectite stability
(kinetic dissolution)

Incongruent dissolution

- Transformation into non-swelling clays
- Fe and Al hydroxides colloids

Fully chemical processes



Groundwater composition effects

Ca-Montmorillonite → Na-Montmorillonite → Montmorillonite colloid

1

2

1. Already considered in geochemical models: $\text{CaX}_2 \rightarrow \text{NaX}$
2. Not yet considered:
 - How can this process be considered?
 - Do we know the exact dependency of water chemical composition?
 - What is the exact process?
 - Can be described from a chemical perspective?

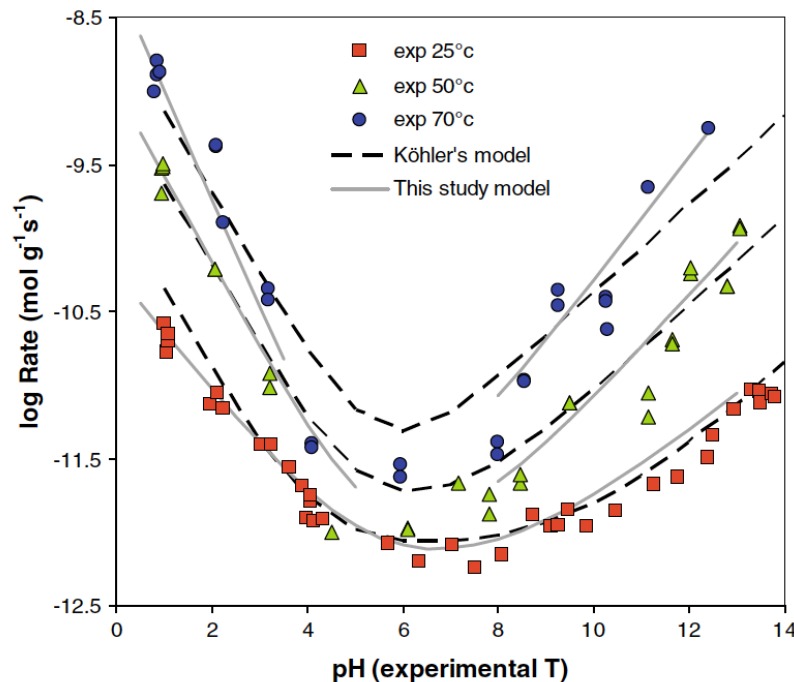


Chemical stability of smectite

1. Kinetic dissolution of smectite (montmorillonite)

- There are several experiments, whose results can be easily implemented into geochemical models

$$R(\text{mol m}^{-2} \text{s}^{-1}) = 10^{-12.30} a_{H^+}^{0.40} + 10^{-14.37} + 10^{-13.05} a_{OH^-}^{0.27}$$



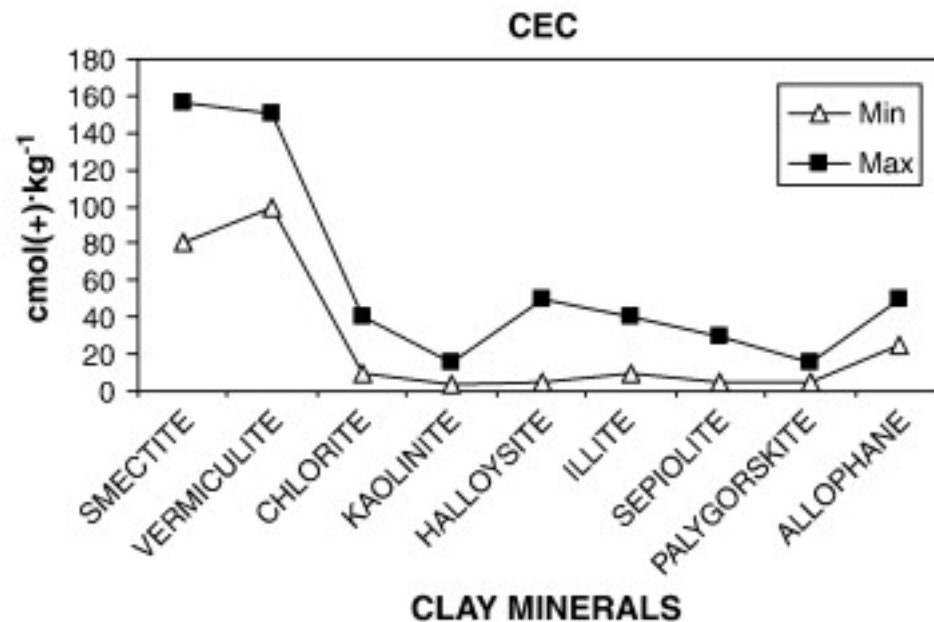
from Rozalen et al. (2008, 2009)



Chemical stability of smectite

2. Incongruent dissolution of smectite

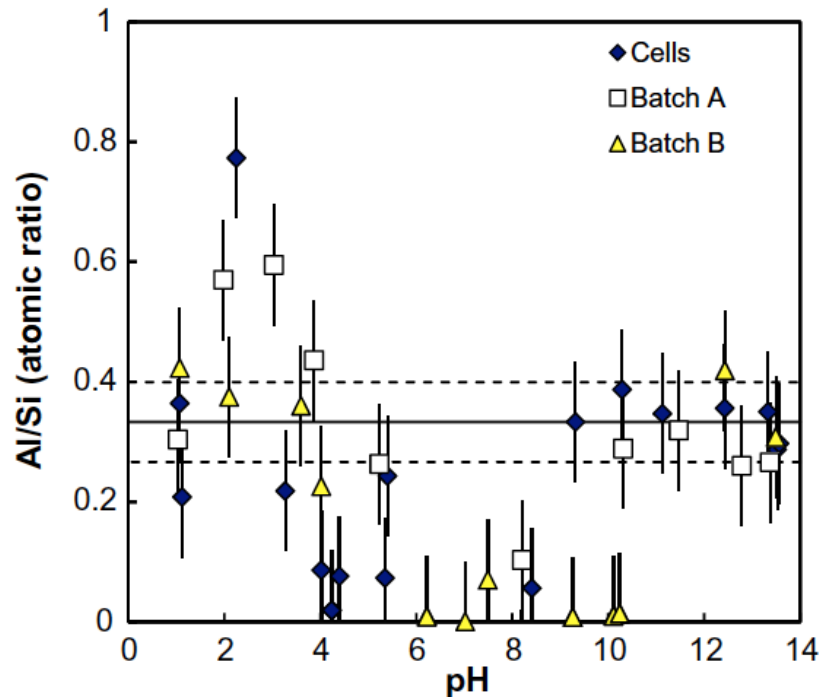
- Transformation into other clay minerals (i.e. saponite), with different CEC and swelling capacity
- Transformation into non-swelling clays (i.e. kaolinite)



Chemical stability of smectite

2. Incongruent dissolution of smectite

- Precipitation of $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$
 - Are these phases precipitating or do they form colloids?



from Rozalen et al. (2008)

Where is the frontier between colloids and dissolved polynuclear complexes?

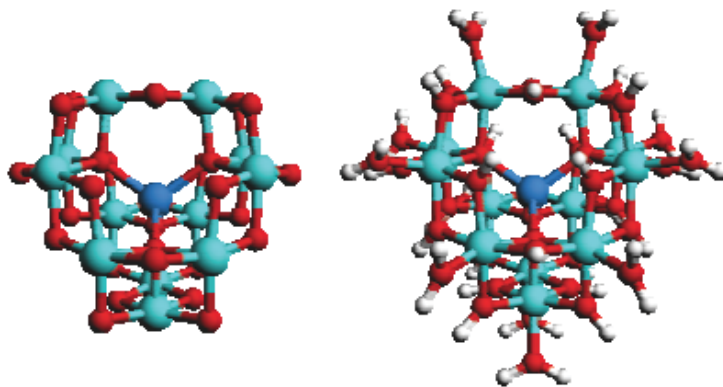


Fig. 5. The Keggin ϵ -isomer of $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$. The aluminum of the central $\text{Al}(\text{O}^+)_4$ unit is in dark blue. [5] [59] The overall structure in the right and the core of the Keggin isomer on the left.

Outlook

- There are a number of questions that should be posed to our present understanding of montmorillonite stability under diffusive regime.
- Likewise, our current representation of the geochemical behaviour of the buffer should incorporate montmorillonite alteration and colloid formation and stability in an integral approach.
- Let's do it!

