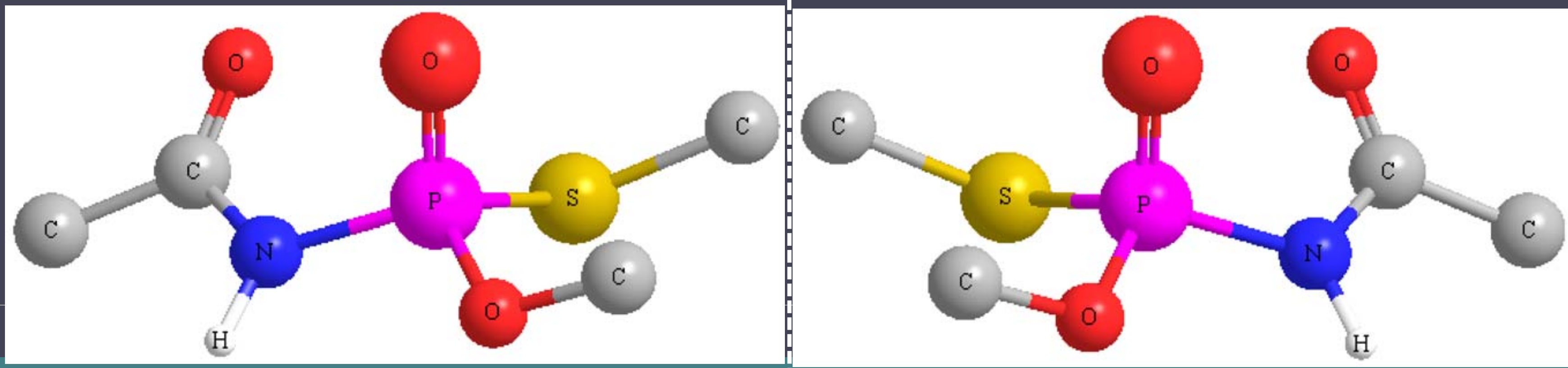
Chiral selectivity at mineral surfaces



A case study with the organo-phosphorus pesticide acephate

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Acknowledgments

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Professor R. Raval

Experimental: Anu Thomson
Syed Abid
Maria Tamara

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Introduction to Environmental Chirality

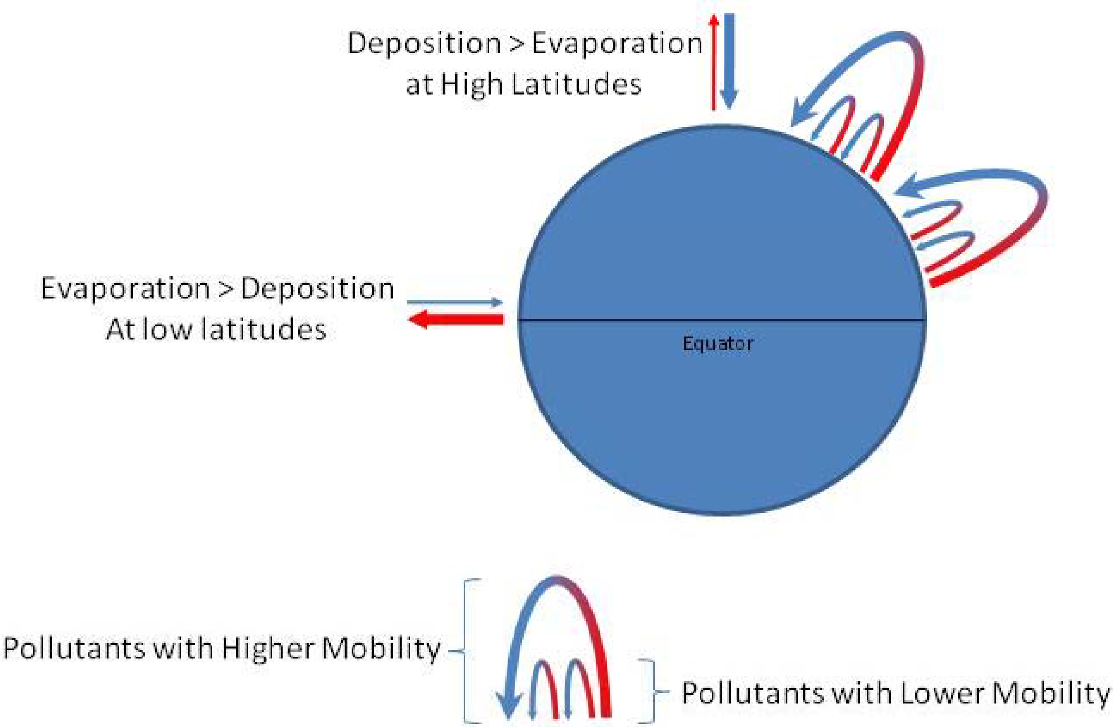
- Chiral molecules have enormous environmental significance (e.g. amino acids)
- Some pollutants are chiral
- Chiral pollutants are generally manufactured as racemic mixtures
- However environmental signatures are often non-racemic

Enantiomer selectivity

- Enantiomer-selective processes are important because
  - Origins of life theories
  - Relevance to environmental significance of chiral molecules e.g. toxicity, residence time estimates
  - There is considerable industrial demand e.g. by pharmaceutical companies

Long-range pollutant transport

- Pollutants reach remote (e.g. polar) regions through the "Grasshopper Effect"
- This involves semi-volatile organic compounds (SVOCs) travelling polewards due to repeated deposition and volatilization cycles ('hops') (Gouin et al. 2004)



Examples…

- Polar regions show non-racemic ratios of chemicals that are only produced in racemic mixtures.
- EF = (+)/[(+) + (–)]
- ER = (+)/(–)
- Therefore the EF of a racemic mixture = 0.5

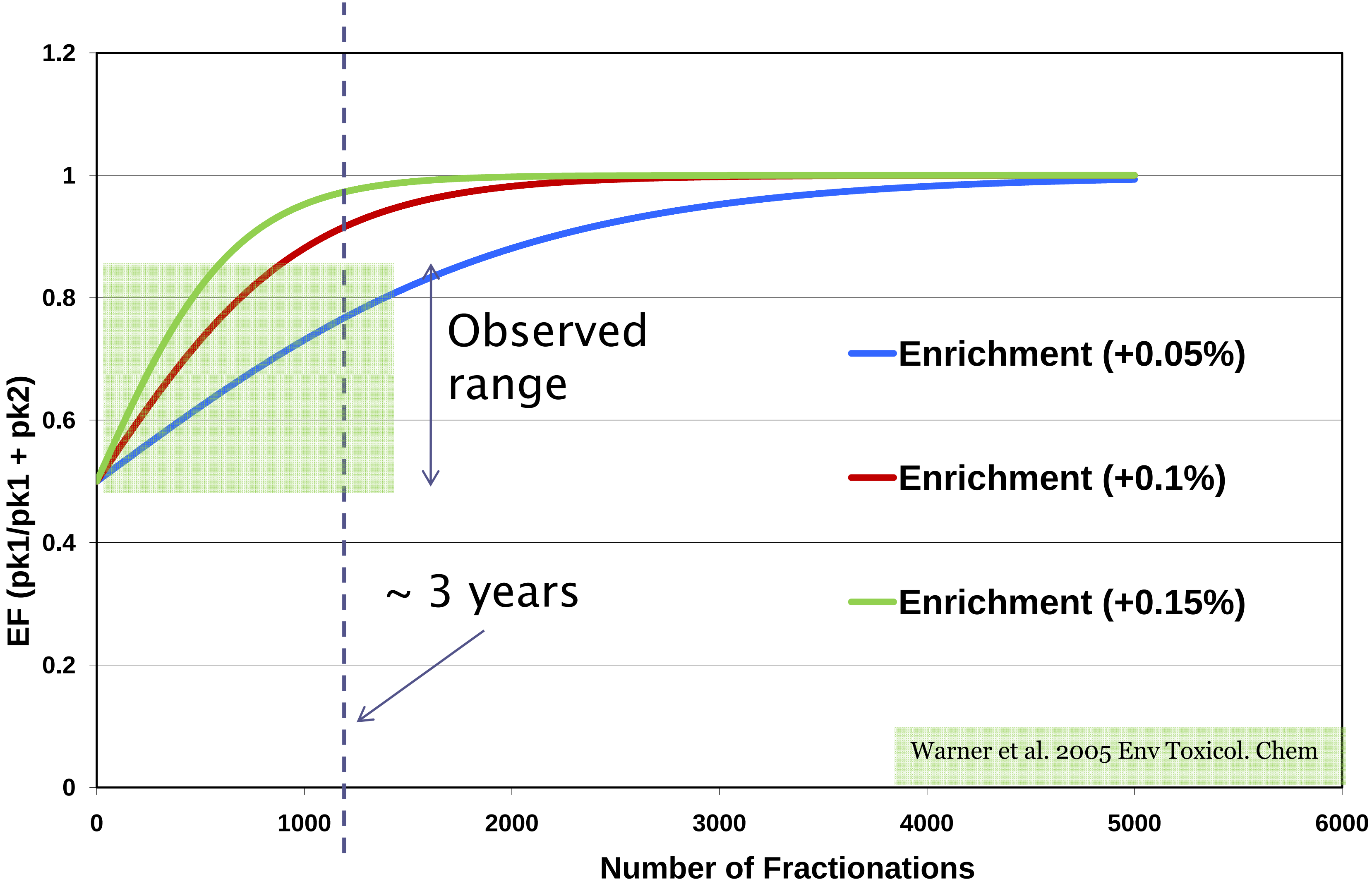
System	Compound	ER	Ref
High lattitude, Greenland Sea	Dissolved α-HCH	~ 0.75	(Jantunen & Bidleman 1998)
Resolute Bay, Canada	PCB (3-MeSO2-CB149)	~ 0.32	(Wiberg et al. 1998)

- Why?

Primary hypothesis

- Can small repeated (e.g. day/night), enantiomer-selective adsorptions on mineral surfaces lead to the observed deviations from the racemic state
- And if so, how?
- The current view is that this is a result of biological selectivity
- But – recent work has shown evidence of abiotic selectivity (Wedyan & Preston 2005)

Fractionation model

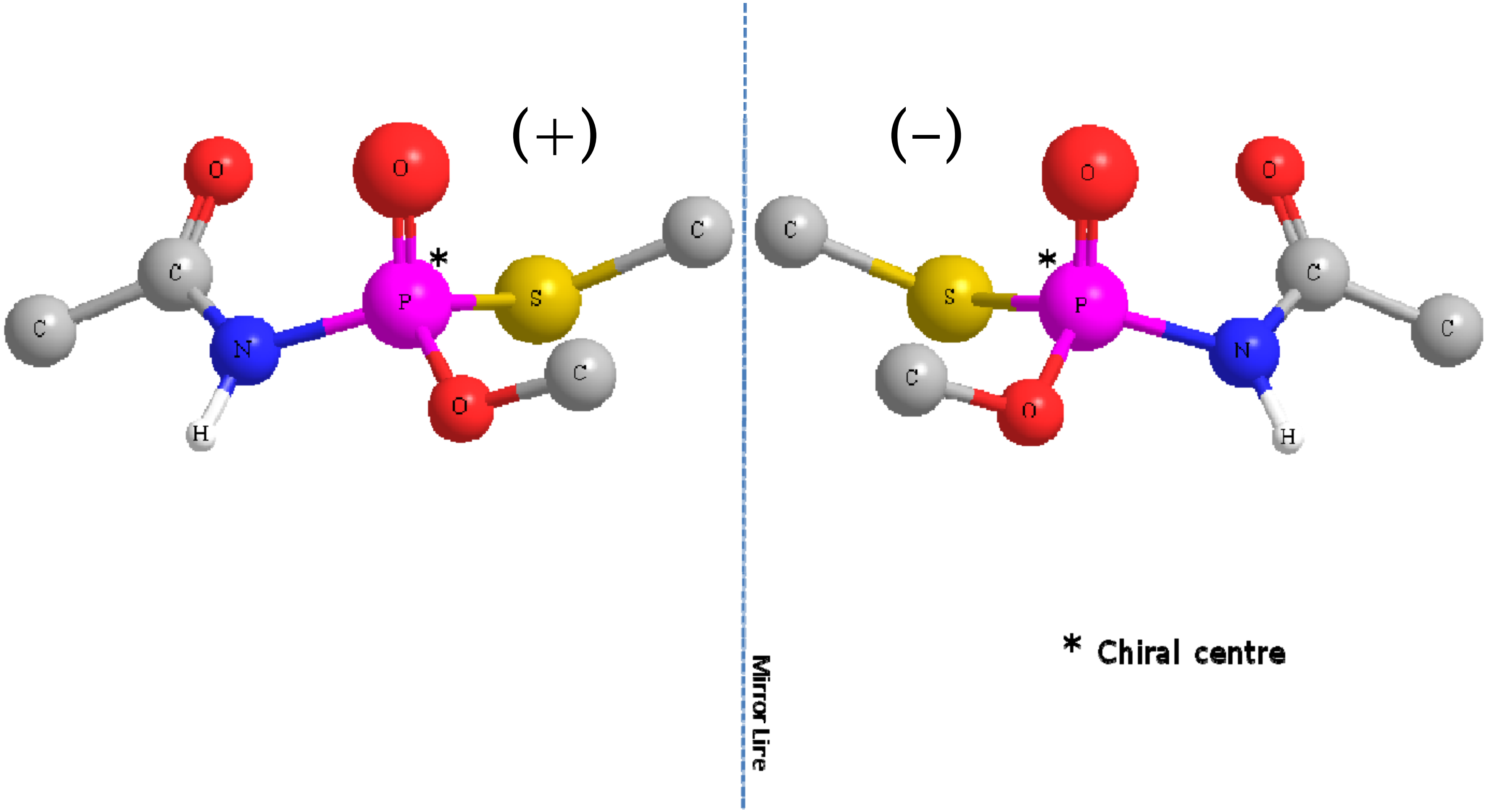


Outline of current work

- Ongoing development of GC method for separation of chiral organophosphorus pesticide acephate as a case study
- Adsorption of acephate onto mineral surfaces
- Identify chirally selective adsorption on mineral surfaces
- Investigate the factors and mechanisms responsible for this selectivity

Experimental

acephate



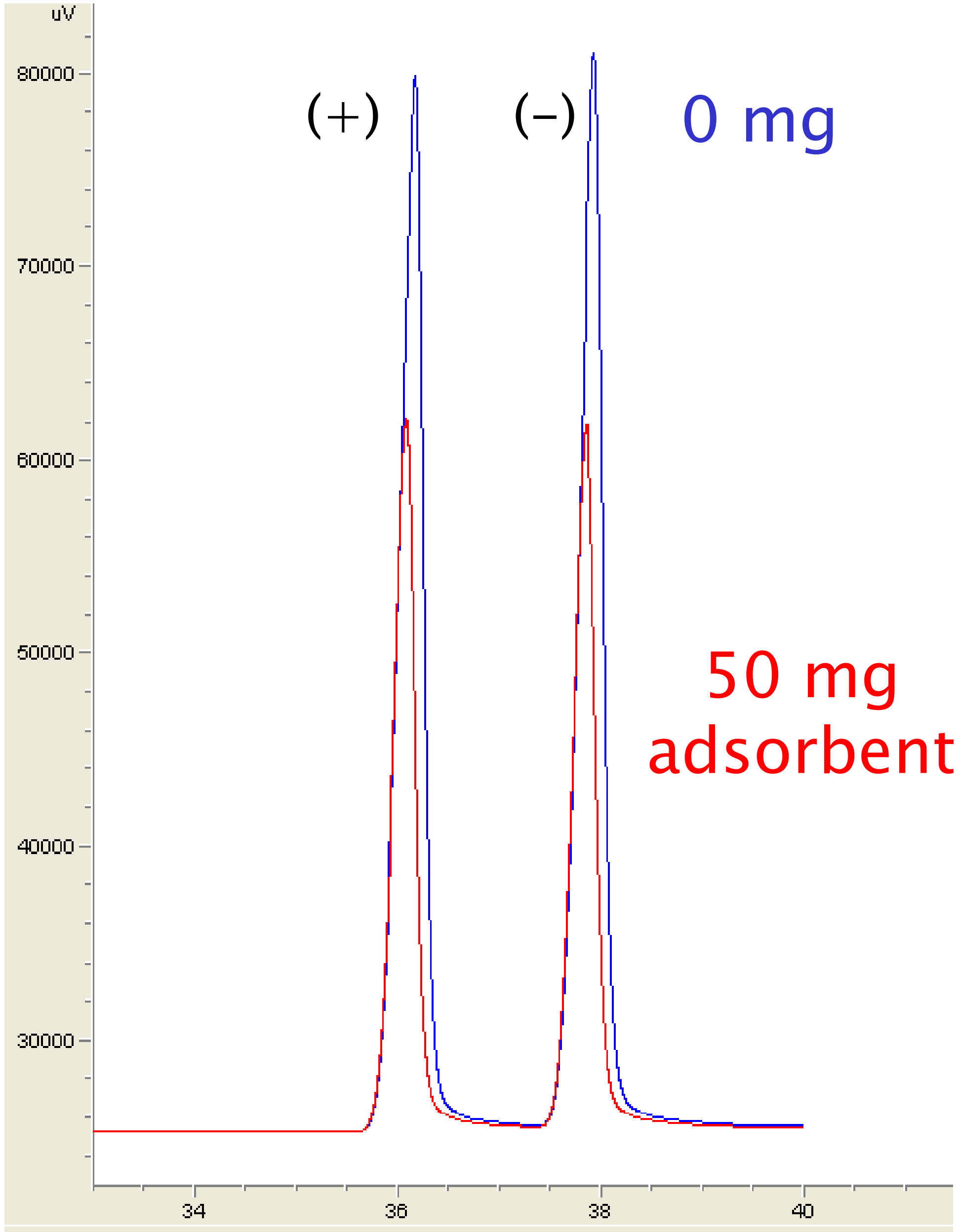
Adsorption experiments

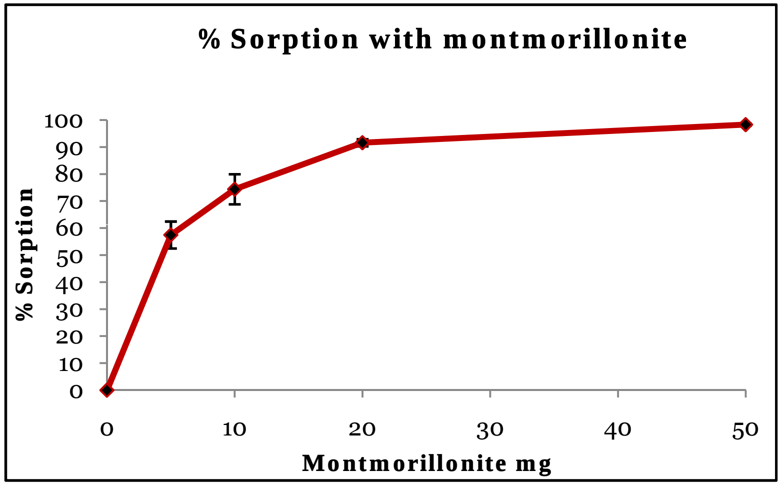
- Involving acephate and a variety of minerals
  - Quartz
  - Montmorillonite
  - Kaolinite
  - Alumina
- 750μmL of acephate (100mg/L)
- 0 and 50 mg of mineral
- 96 h agitation
- Removal of supernatant

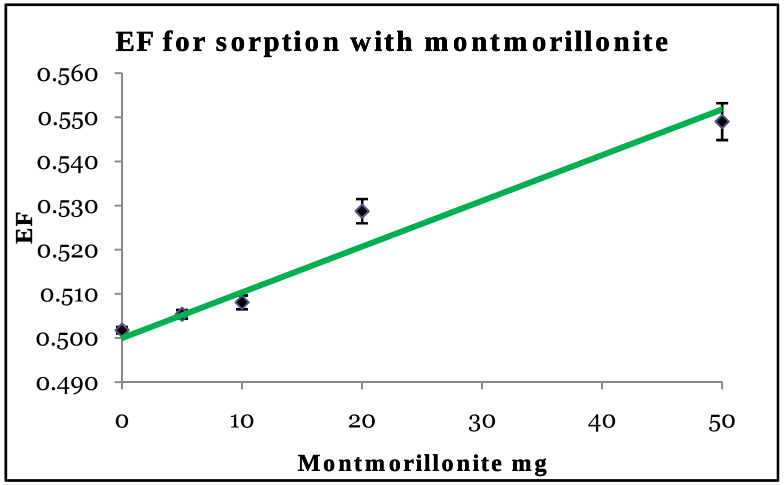
- Sorption and enantiomer selectivity will be apparent from GC analysis...

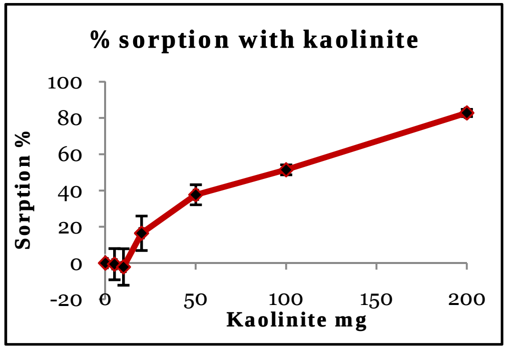
Results

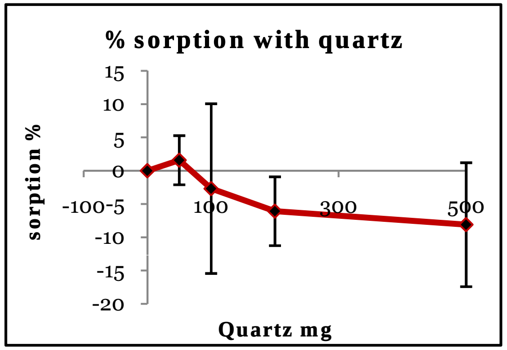
- Good resolution
- Good sensitivity
- Evidence of significant sorption
- Need peak areas to determine selectivity

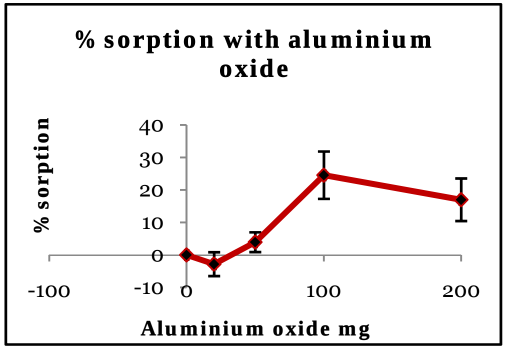


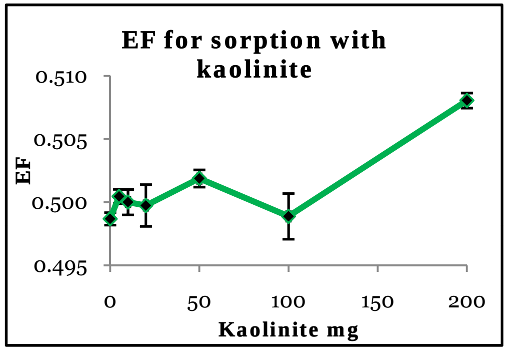

% Sorption with montmorillonite
% Sorption
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
Montmorillonite mg

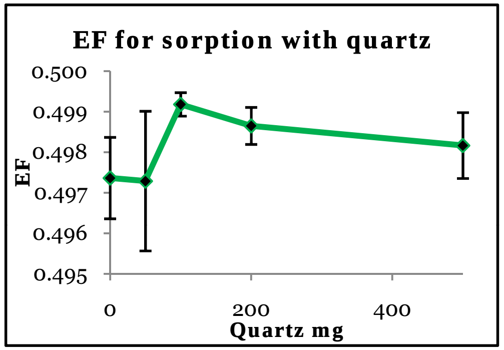

EF for sorption with montmorillonite
EF
0.560
0.550
0.540
0.530
0.520
0.510
0.500
0.490
0
10
20
30
40
50
Montmorillonite mg

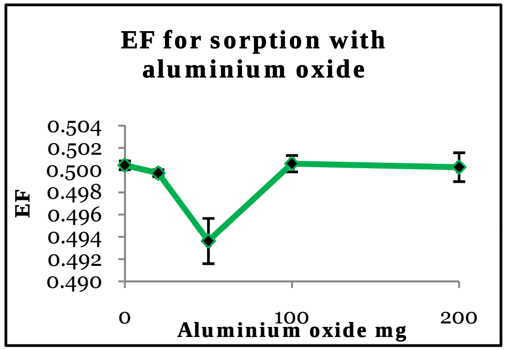

% sorption with kaolinite
Sorption %
100
80
60
40
20
0
-20
0
50
100
150
200
Kaolinite mg


% sorption with quartz
sorption %
15
10
5
0
-100
-5
-10
-15
-20
100
300
500
Quartz mg

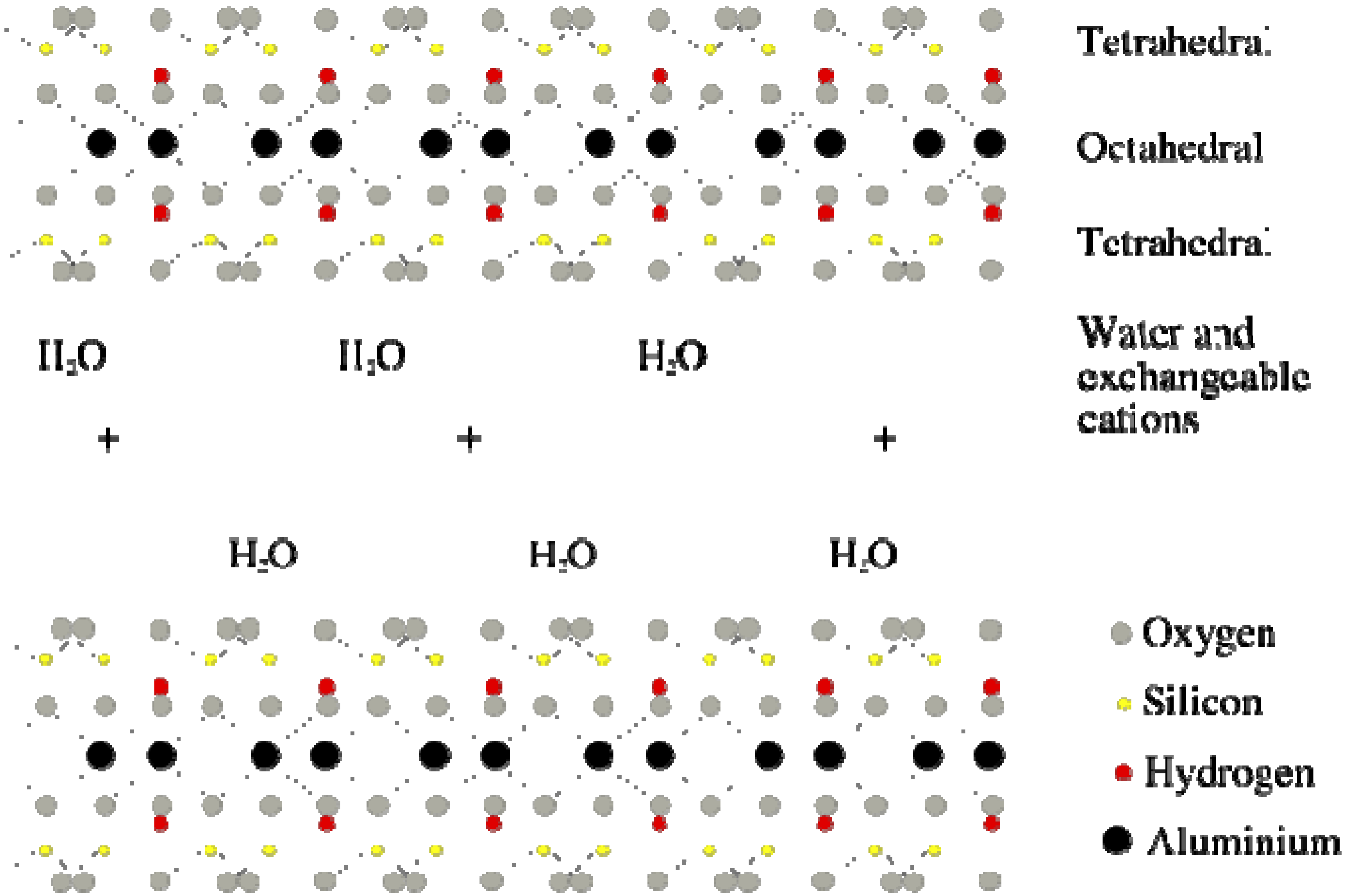

% sorption with aluminium oxide
% sorption
40
30
20
10
0
-10
-100
0
100
200
Aluminium oxide mg


EF for sorption with kaolinite
EF
0.510
0.505
0.500
0.495
0
50
100
150
200
Kaolinite mg


EF for sorption with quartz
EF
0.500
0.499
0.498
0.497
0.496
0.495
0
200
400
Quartz mg


EF for sorption with aluminium oxide
EF
0.504
0.502
0.500
0.498
0.496
0.494
0.492
0.490
0
100
200
Aluminium oxide mg

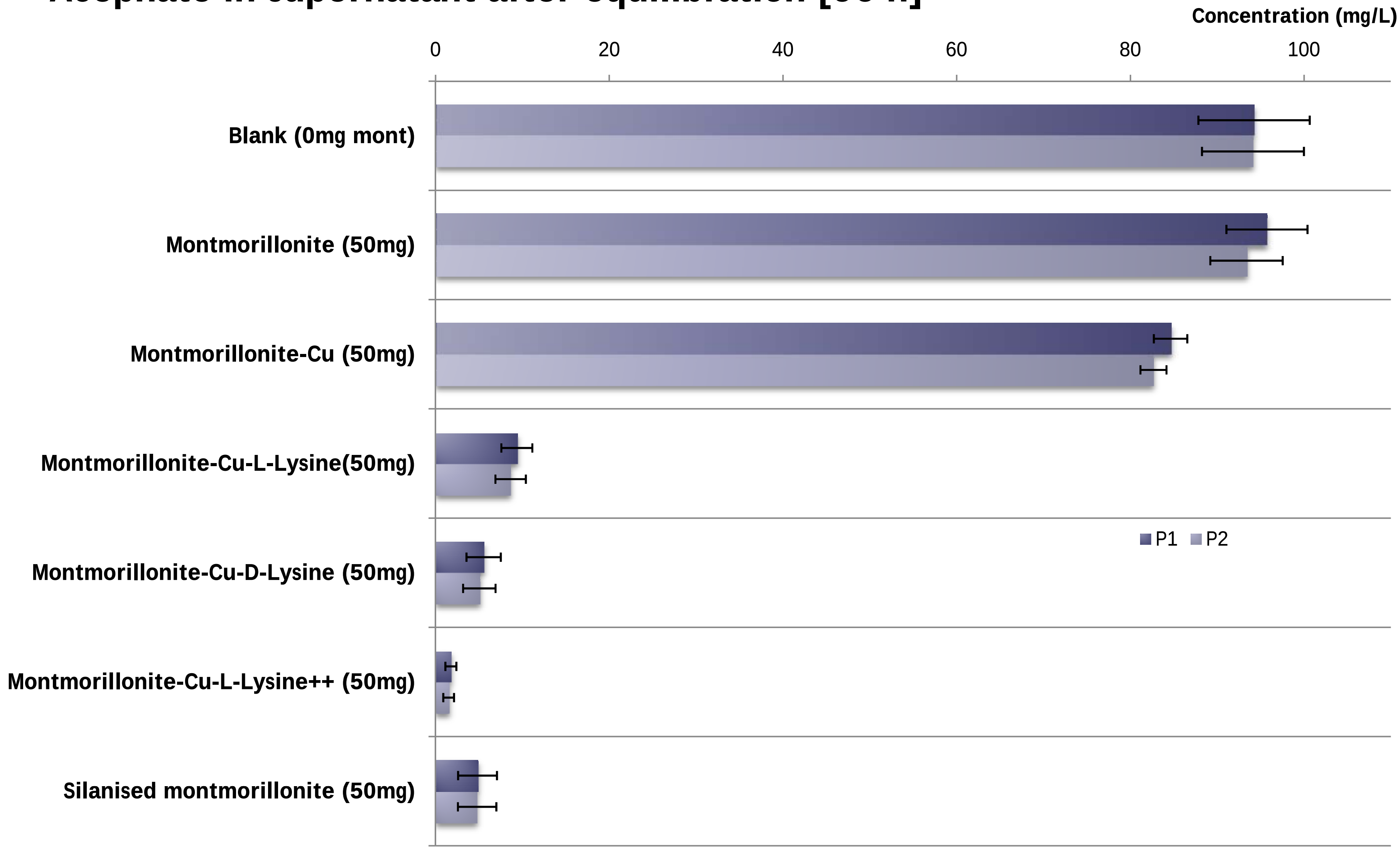
Montmorillonite Structure



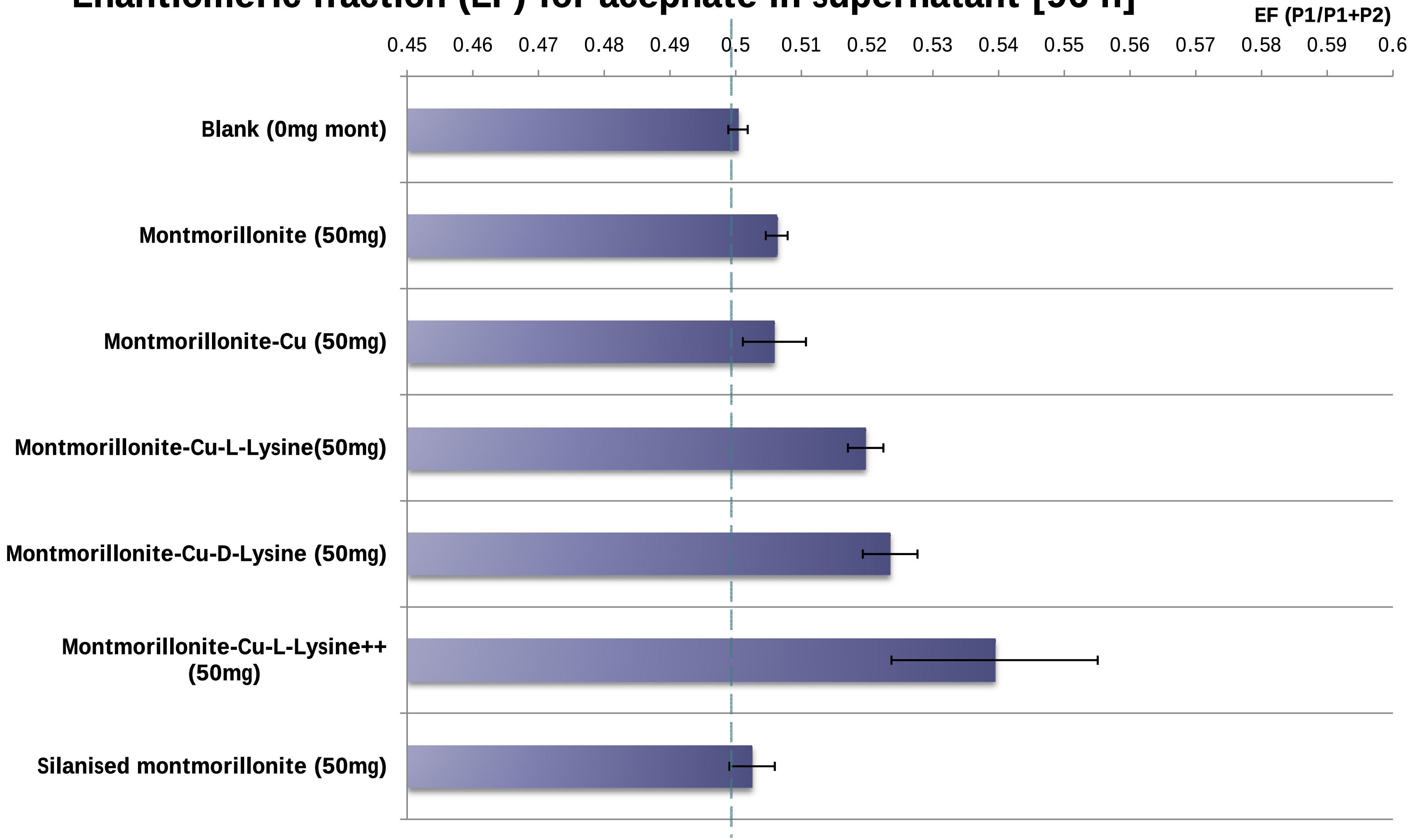
Modified montmorillonite

M	montmorillonite
MC	montmorillonite – Cu
MCL	montmorillonite – Cu – L – Lysine
MCDL	montmorillonite – Cu – D – Lysine
MCL+	montmorillonite – Cu – L – Lysine (increased proportions of Cu – lys – mont)
MD	derivatized montmorillonite

Acephate in supernatant after equilibration [96 h]



Enantiomeric fraction (EF) for acephate in supernatant [96 h]



- Observations

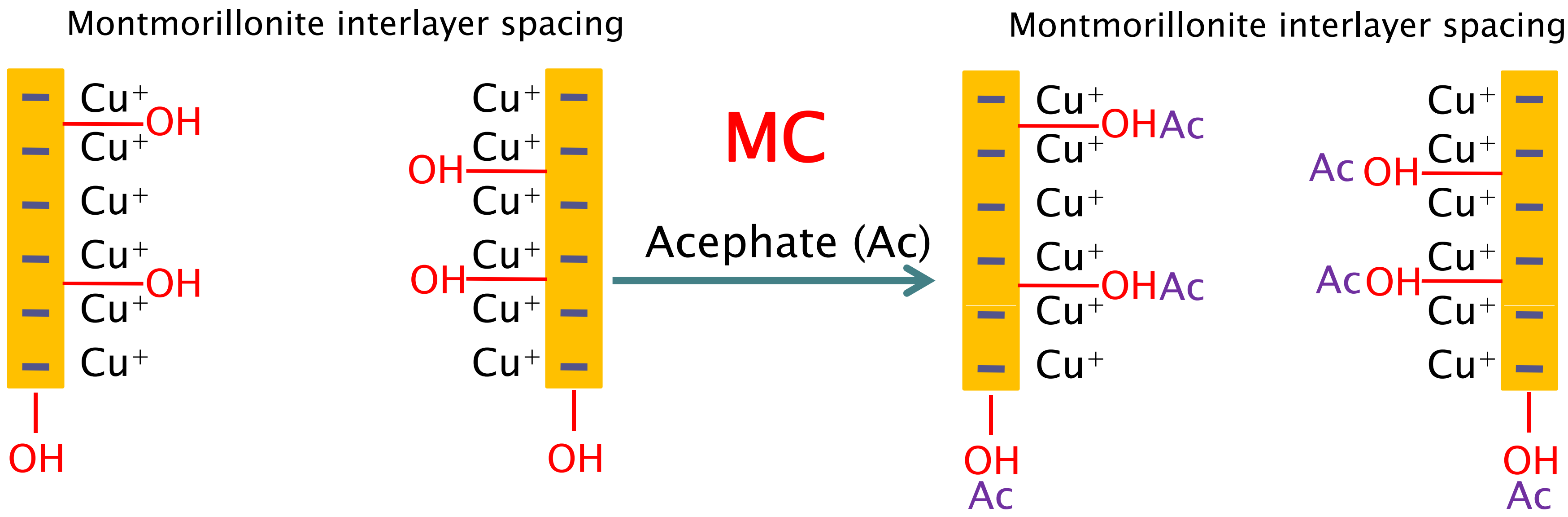
    - Some selective adsorption of acephate enantiomers on montmorillonite surface with low overall adsorption

    - Stronger selectivity on lysine-modified montmorillonite surface with high adsorption

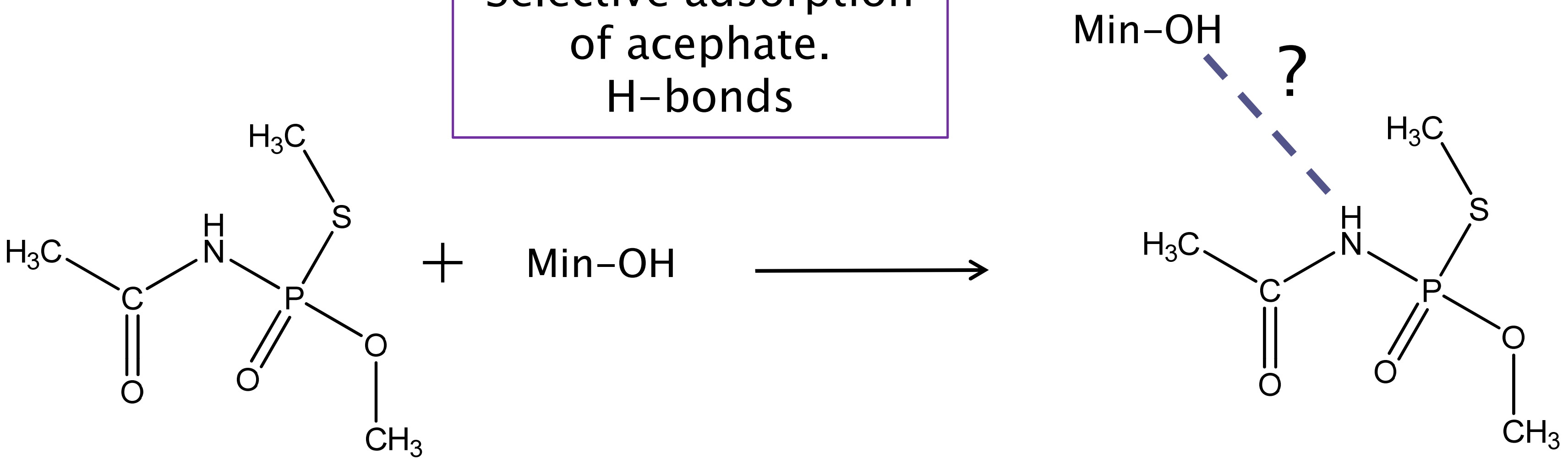
    - No selectivity on silanised montmorillonite but high adsorption

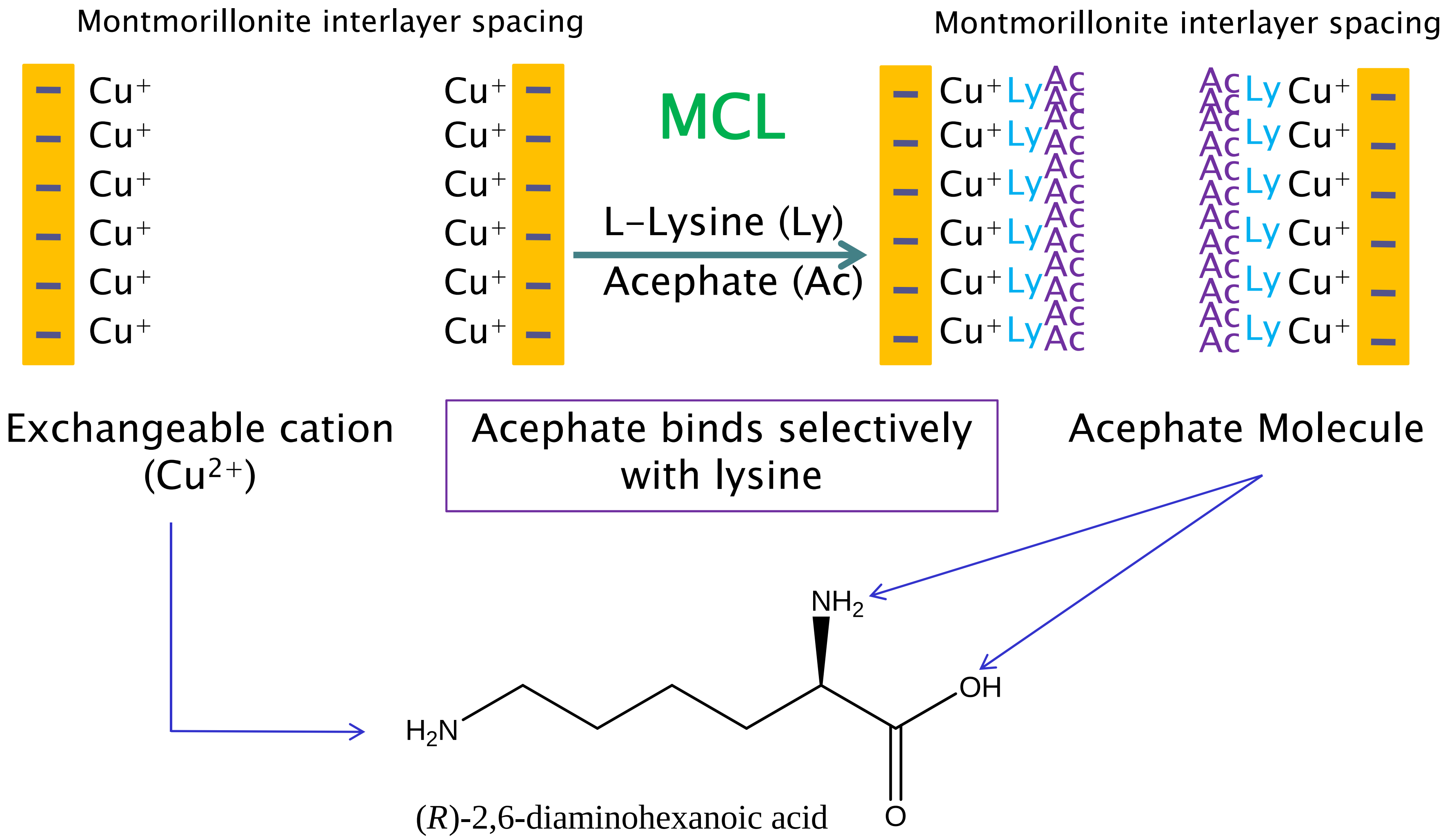
- What mechanisms might be responsible?

Hypotheses for adsorption mechanisms at montmorillonite surfaces

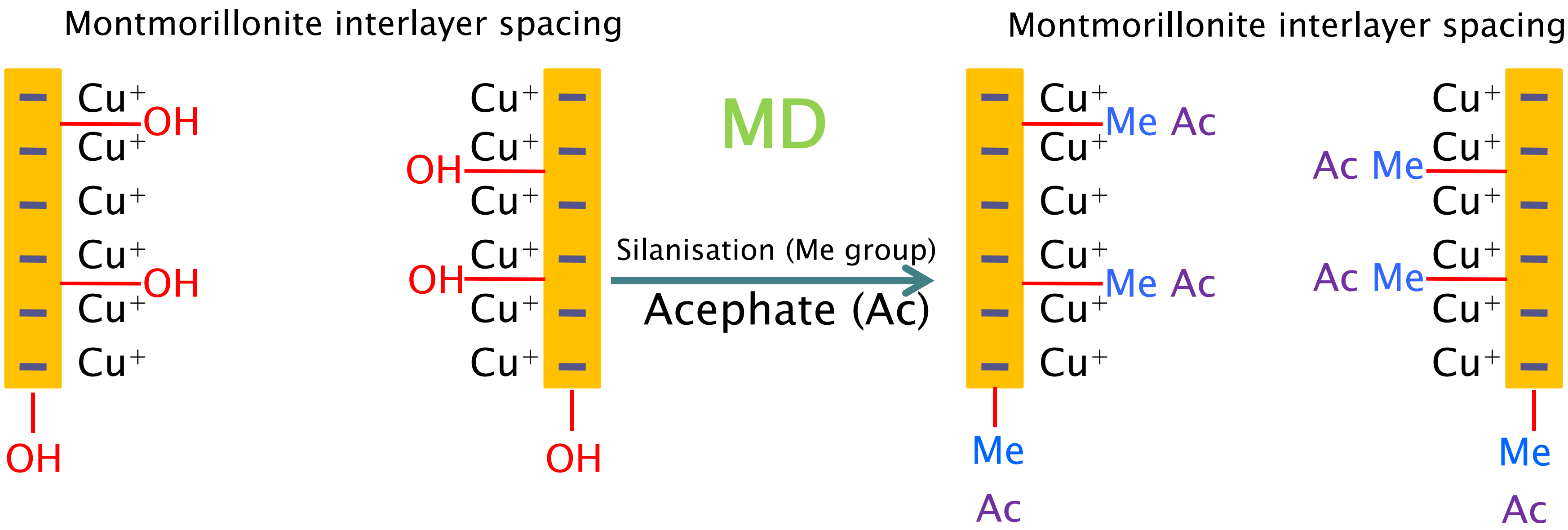


Selective adsorption of acephate.
H-bonds

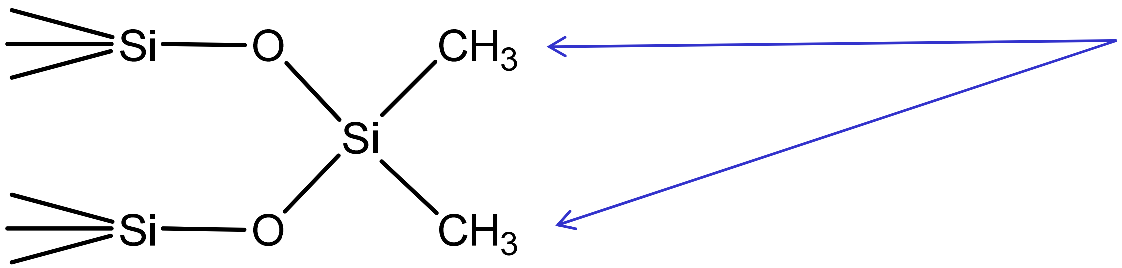




Adapter plug mechanism?



Acephate binds with methyl group but not selectively



Acephate Molecule

Conclusions

- Selective adsorption of acephate on unmodified montmorillonite surface is small
- Strong selective adsorption on lysine-modified montmorillonite surface
- Strong but non-selective adsorption on silanised montmorillonite surface

Further work

- Confirm initial binding mechanism
  - Will lysine bind with interchangeable cations other than copper? Enantioselectivity ~ Z^6 so try e.g. Hg^{2+}
- Compare lysine to other amino acids e.g. glycine (achiral) and alanine (chiral)
  - To understand the importance of the amino acid chirality in the selection process