eMinerals and the Condor Pool

John Brodholt
UCL

Presenting the work of:

Marc Blanchard

Arnaud Marmier

Zhimei Du

Maria Alfredsson

Clovis Chapman

eScience: Environment from the molecular level

University of Cambridge (Earth Sciences & Chemistry)
UCL (Chemistry, Computer Science & Earth Science)
University of Bath (Chemistry)
The Royal Institution
University of Reading (Computer Science)
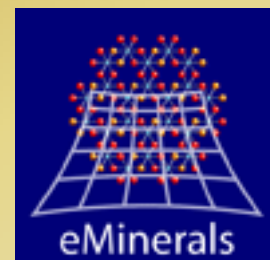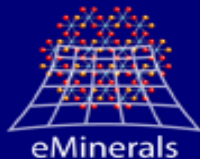Birkbeck (Dept. of Crystallography)
Daresbury eScience Centre

Funded by NERC (eScience)
2002-2005 £1.66 M
2005-2008 £1.33 M

Largest NERC eScience project.

eMinerals

Research undertaken by:

Bath group:
A. Marmier, D.J. Cooke, S.C. Parker

Birkbeck group:
Z. Du and N.H. de Leeuw

Cambridge group:
K. Trachenko, E. Artacho, J.M Pruneda,
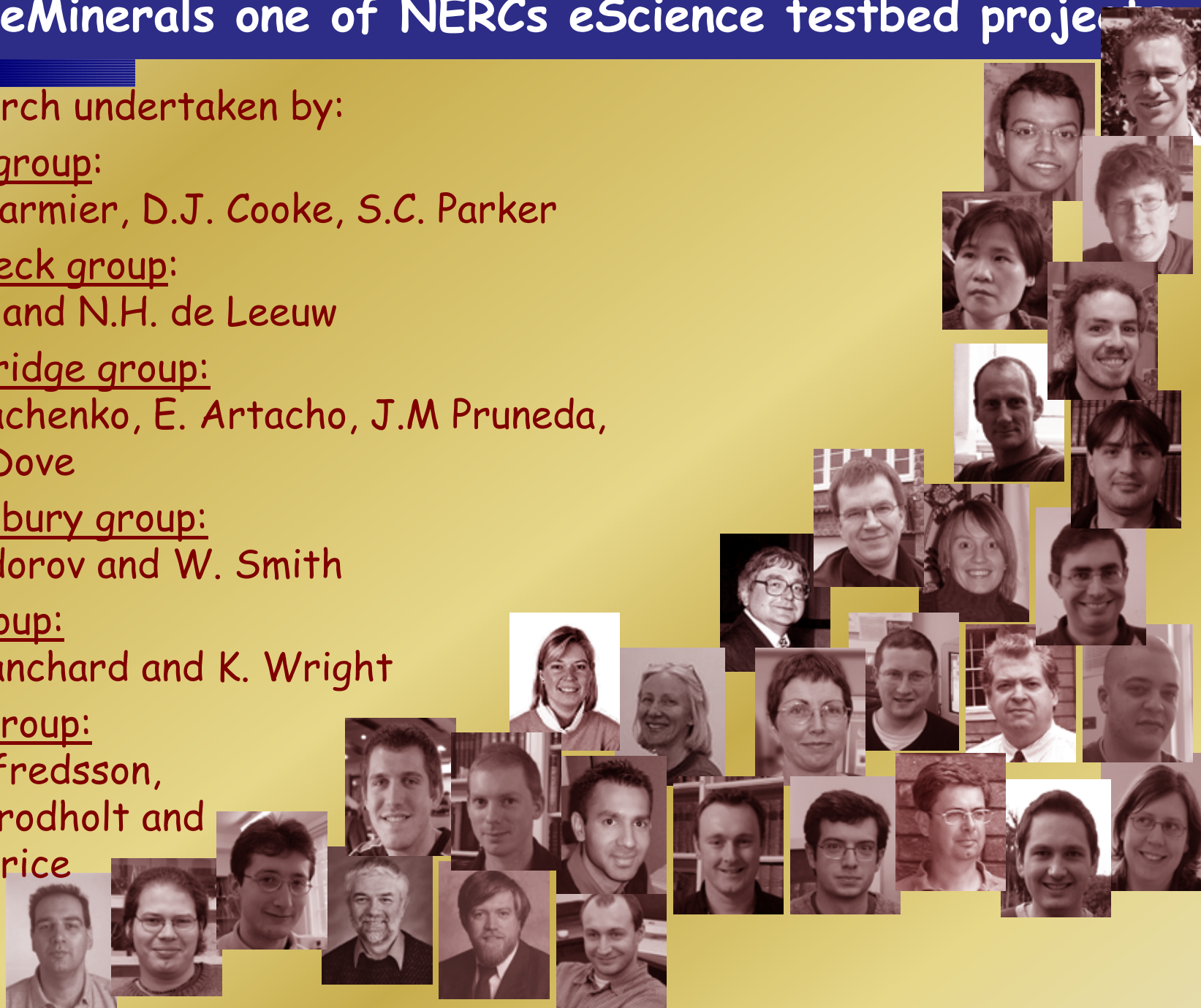M.T. Dove

Daresbury group:
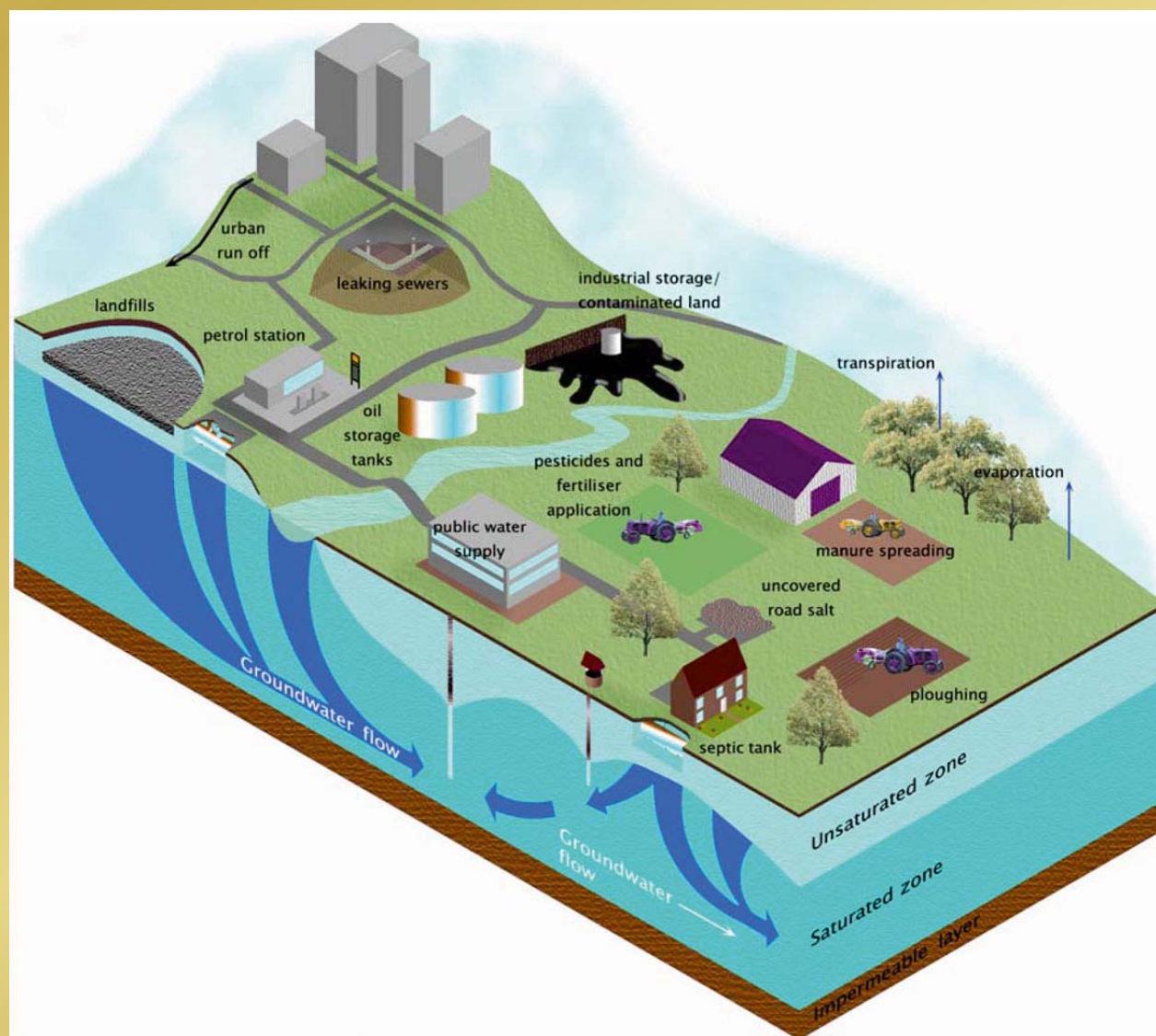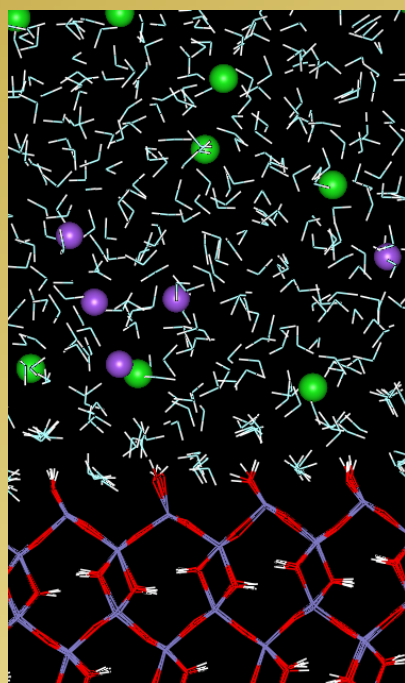I. Todorov and W. Smith

RI group:
M. Blanchard and K. Wright
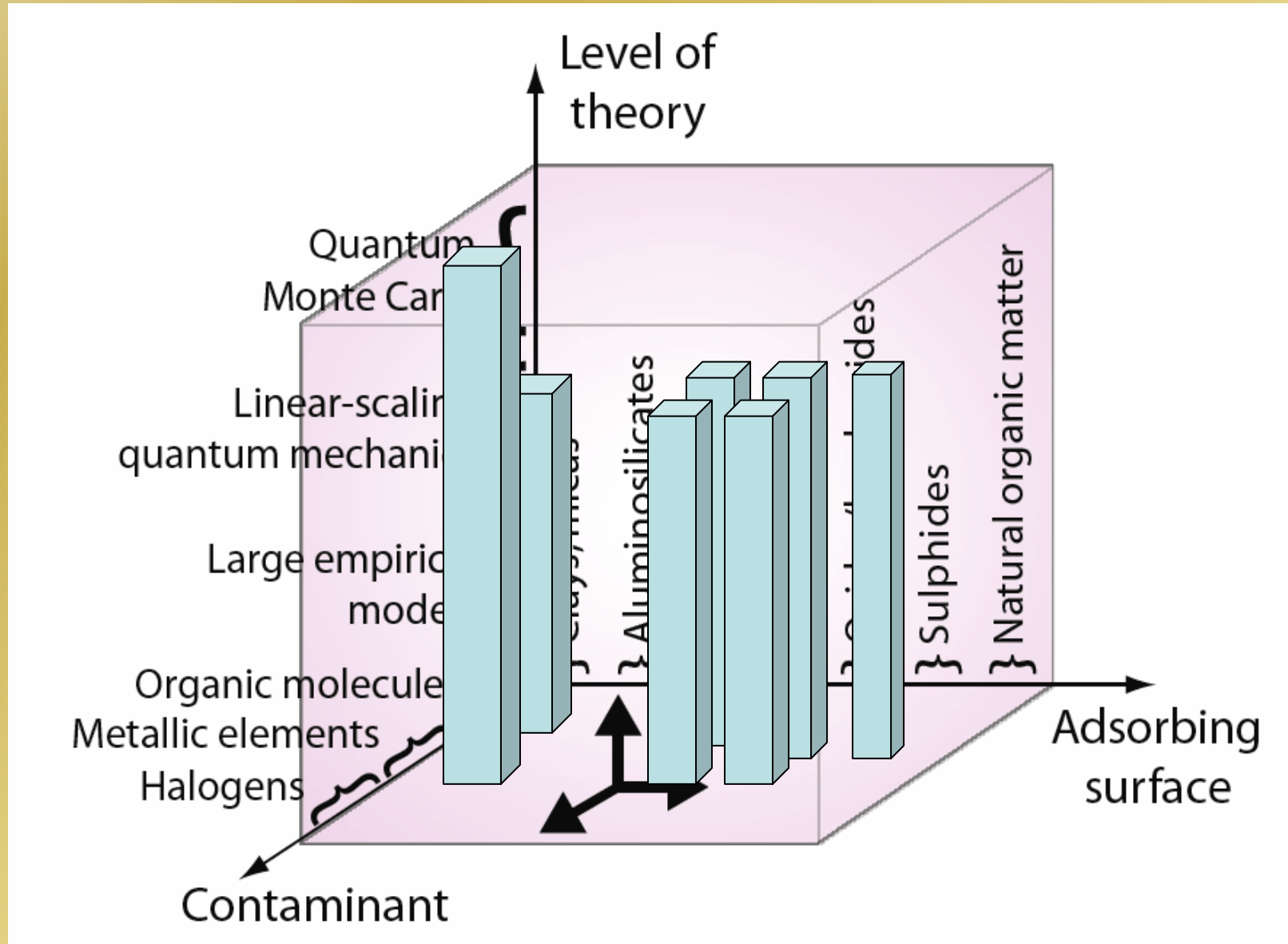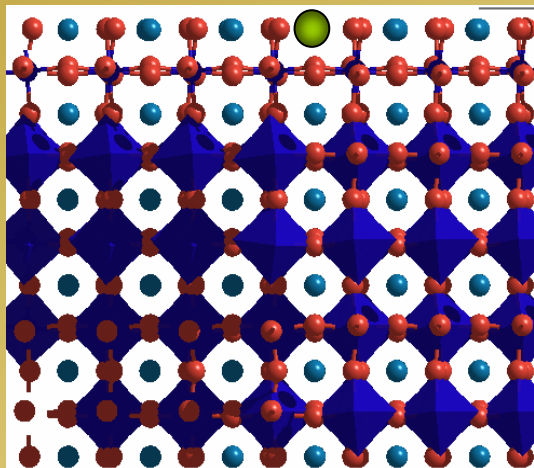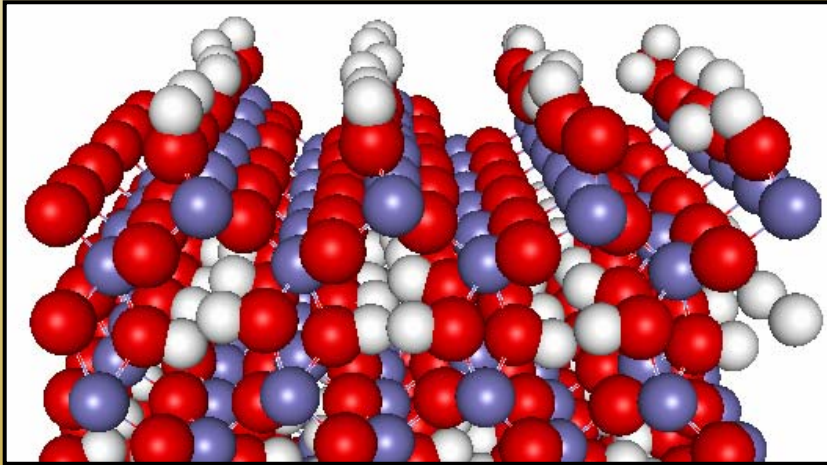
UCL group:
M. Alfredsson,
J.P. Brodholt and
G.D. Price

…. to understand the environment from the molecular level.
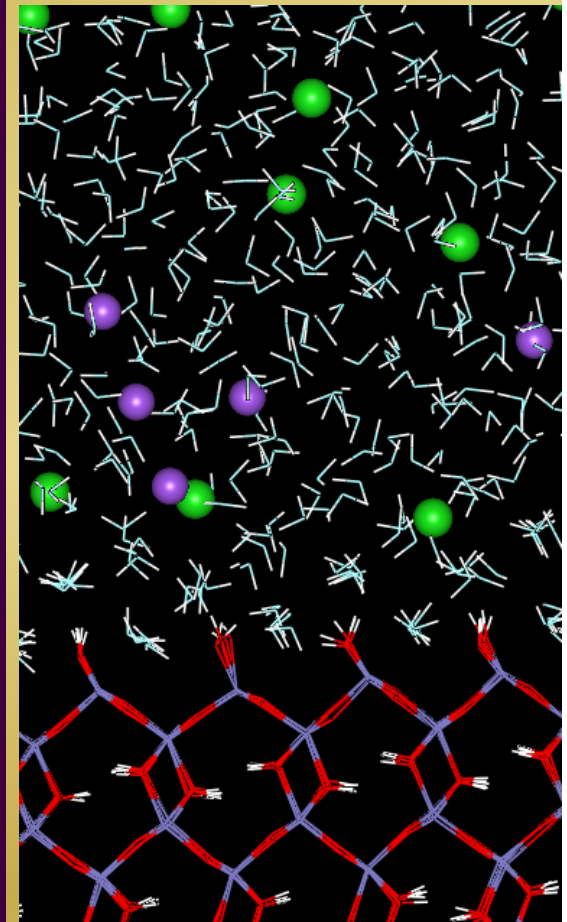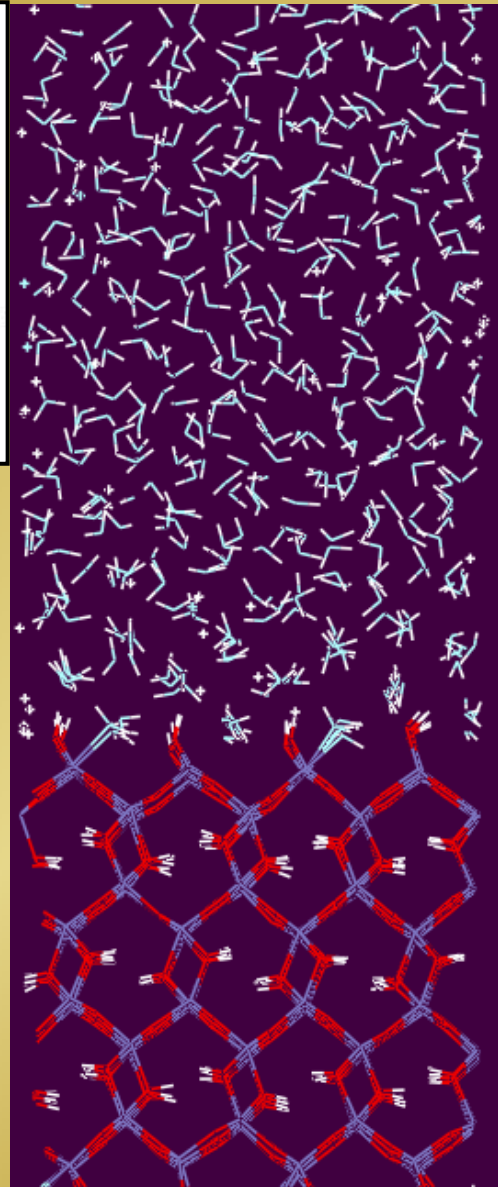
R = retardation factor.

Phase Space Diagram from the Proposal
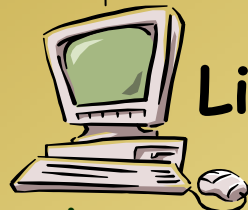
Some need big
computers (i.e. HPCX),
some can be run on the
Condor pool.

The UCL Condor Pool

submission machines

Linux

central manager

UCL Pool > 1000 CPUS
Platforms: Windows XP and 2000
Capacity: 256Mb-1Gb RAM;
Intel 3 (1Ghz) –
Intel 4 (3.2Ghz)

Different projects can have their own submission machine

Note: need Windows executable (.exe file)

The UCL Condor Pool

➢ Generally best for jobs requiring 3 or 4 hours of CPU

➢ Perfect for projects requiring hundreds/thousands or more jobs

➢ The average use of the resource is less than 5%
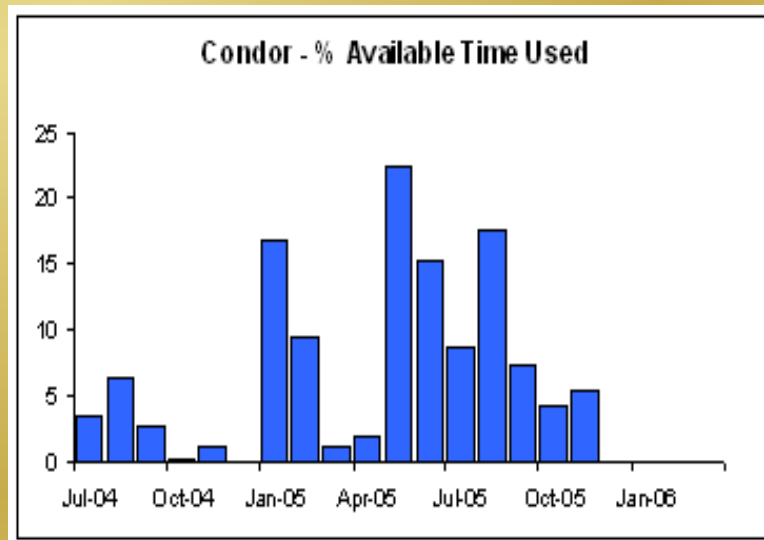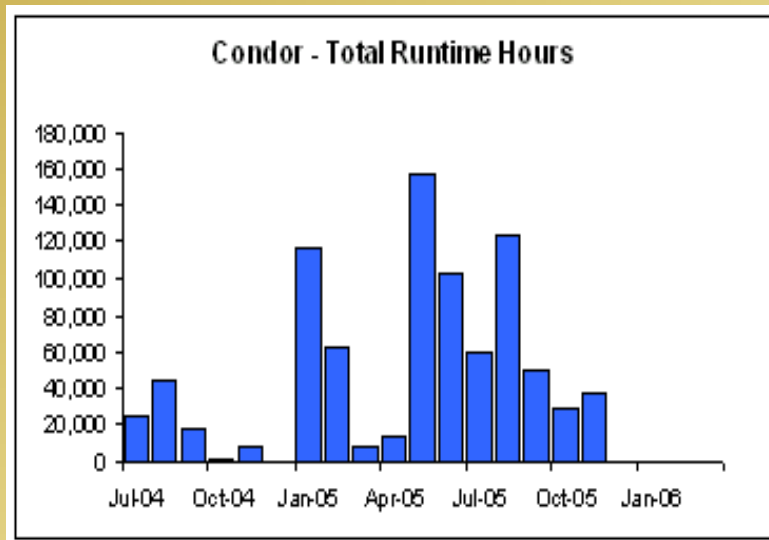
Codes currently compiled and used in the eMinerals project:

Inter-atomic potential codes (Lattice statics, Molecular dynamics, and Monte-Carlo calculations)
- DL_POLY
- METADISE
- GULP
- Marvin

Quantum-Mechanical codes:
- ABINIT
- CRYSTAL

Mineral Surfaces

Calculations:
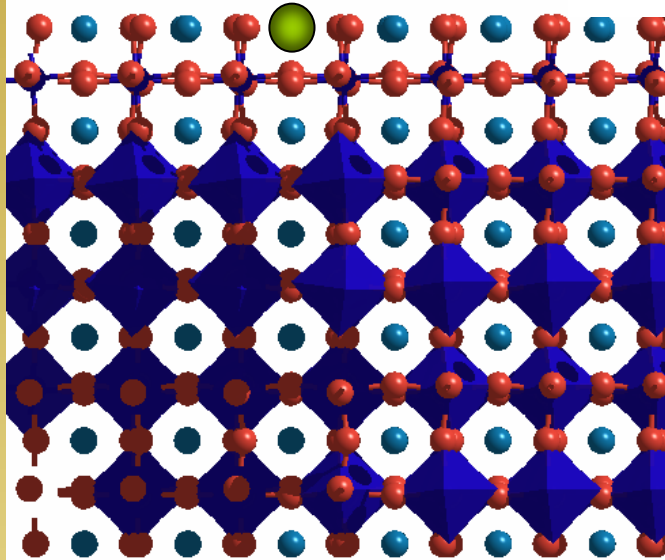- investigate 10-20 surfaces
- 2 to 5 surface terminations
- 4 to 16 impurity positions
- > 4 concentrations

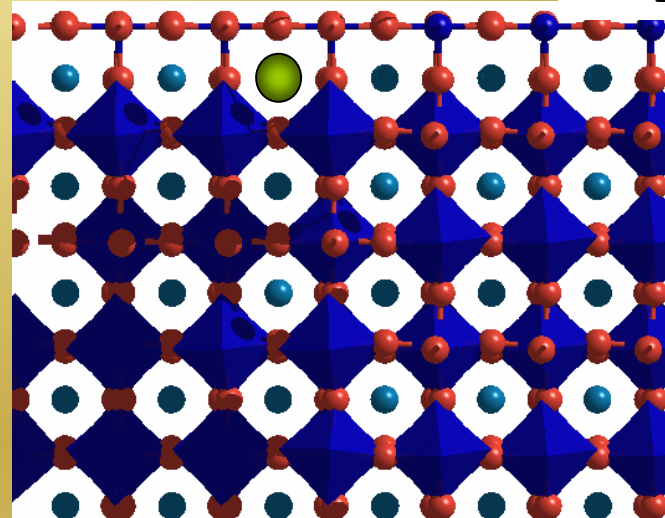**Total number** of calculations per impurity: 120-2440

M. Alfredsson, J.P. Brodholt and G.D. Price et al, Submitted to Nature Materials

CaO-termimated

TiO$_2$-termimated

{001} surfaces of CaTiO$_3$
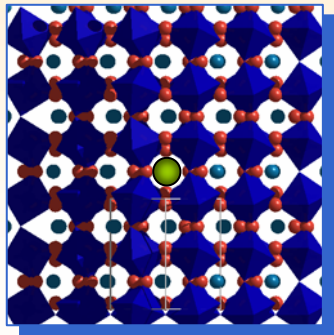
Surface Energy for doped surfaces

X_M:bulk + M_M:surface $\rightarrow$ M_M:bulk + X_M:surface,

M_M=un-doped material and
X_M=doped material

(Ca,M)TiO$_3$:*bulk* + CaTiO$_3$:*surface* $\rightarrow$ CaTiO$_3$:*bulk* + (Ca,M)TiO$_3$:*surface*

$$E_S(n) = E^0_S + (n/S) \cdot E_{seg}$$

E^0_S = un-doped E_{surf}
E_{seg} = Segregation energy
n = dopants on surface
S = Surface Area
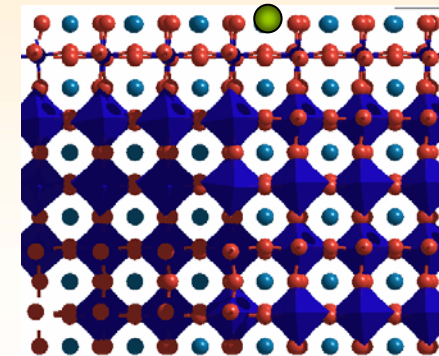
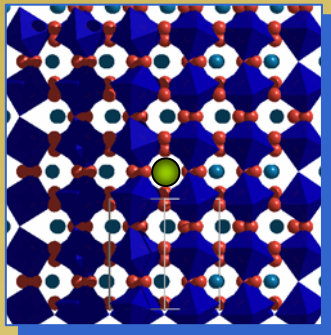**Determine Equilibrium Situation $\Rightarrow$ Beyond Langmuir Isotherm**

Surface Energy for doped surfaces

$$E_S(n) = E^0_S + (n/S) \cdot E_{seg}$$

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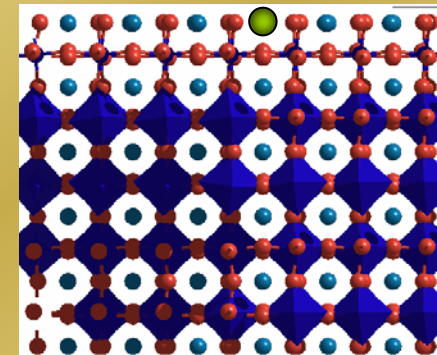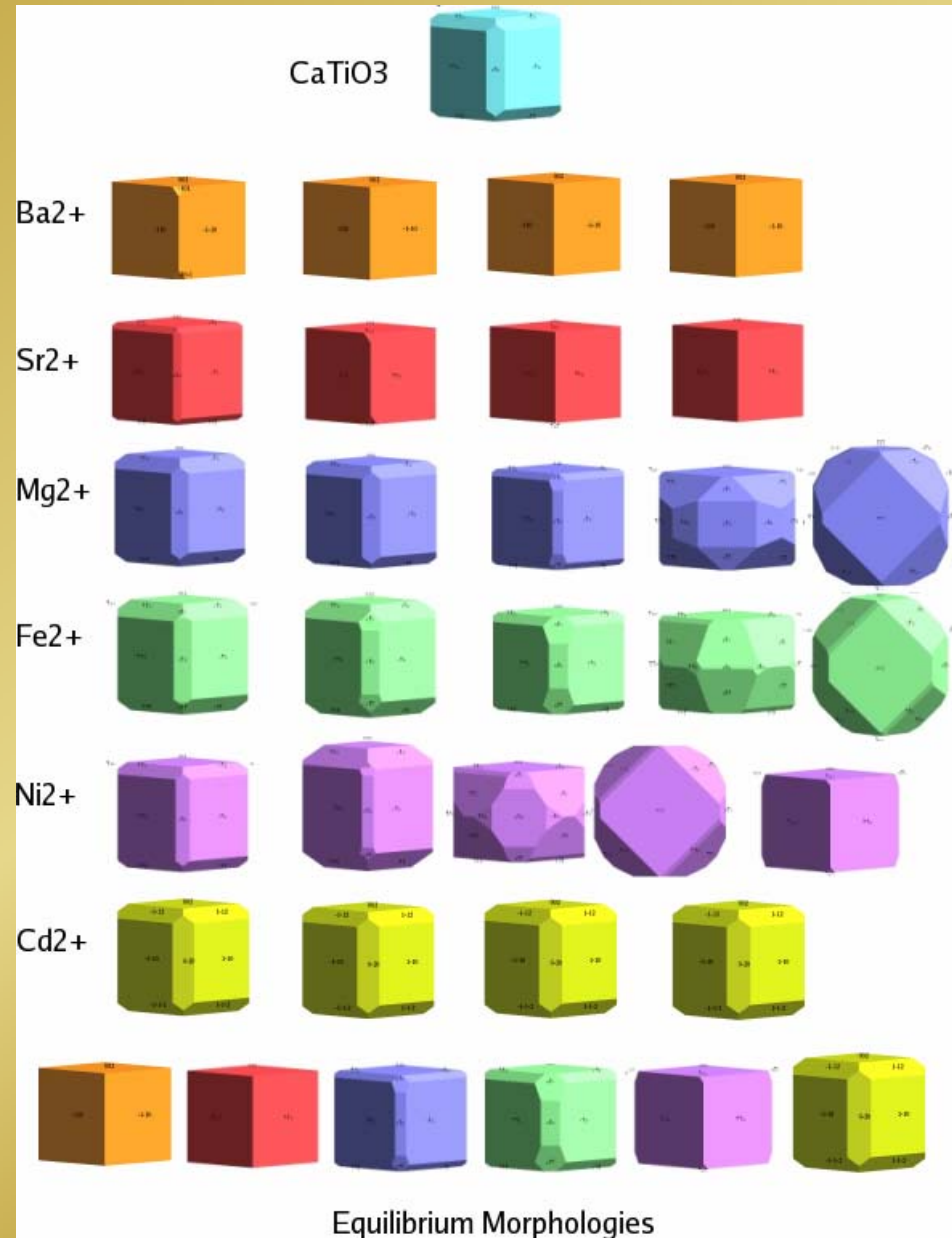**Determine Equilibrium Situation $\Rightarrow$ Beyond Langmuir Isotherm**

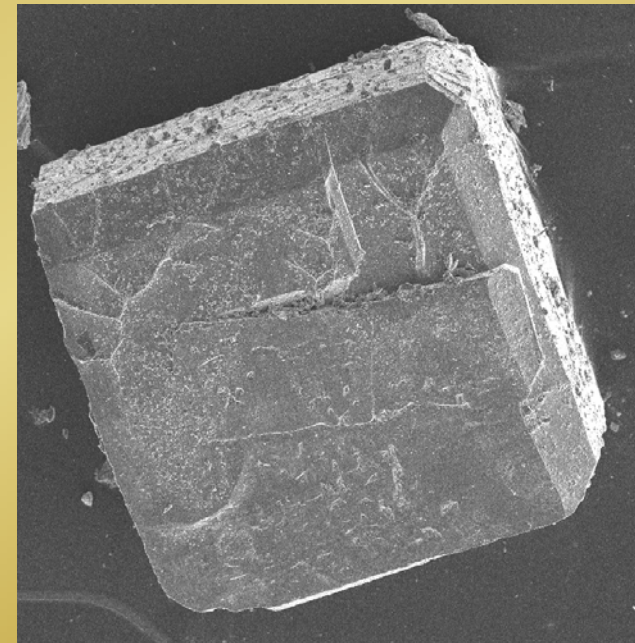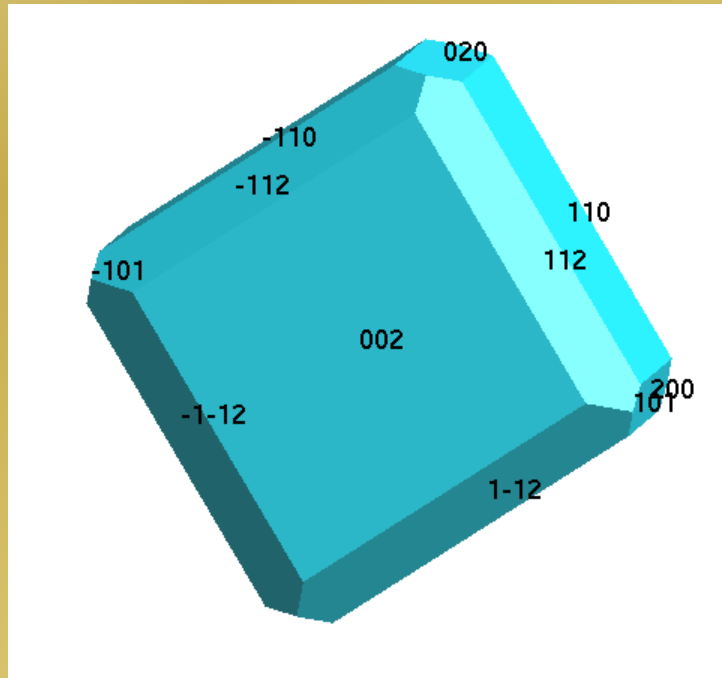Use these surface energies to predict crystal forms as a function of type dopant AND concentration:

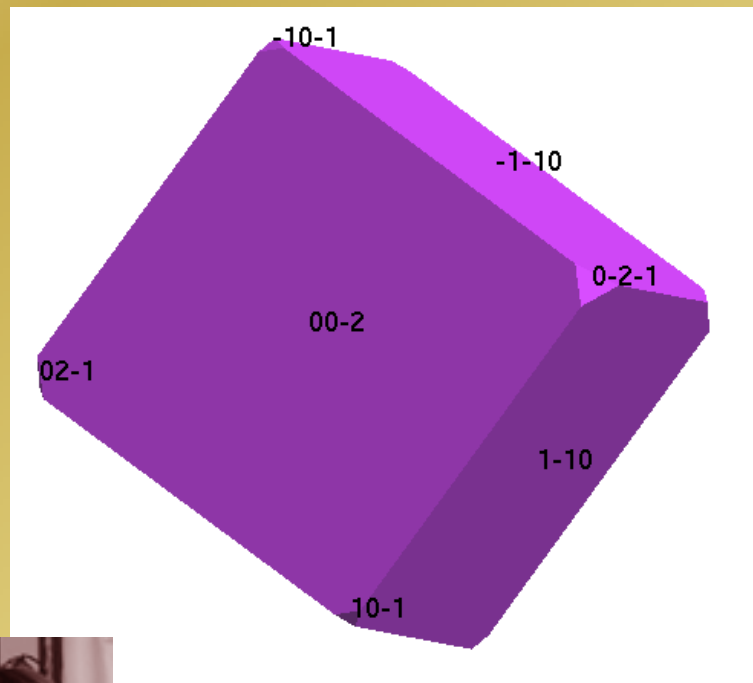Equilibrium Morphologies

Crystal Morphologies of CaTiO₃

Predicted Morphology of CaTiO₃

SEM-picture of pure CaTiO₃

Crystal Morphologies of Ni-doped CaTiO$_3$

Predicted Morphology of Ni-doped CaTiO$_3$

SEM-picture of Ni-doped CaTiO$_3$
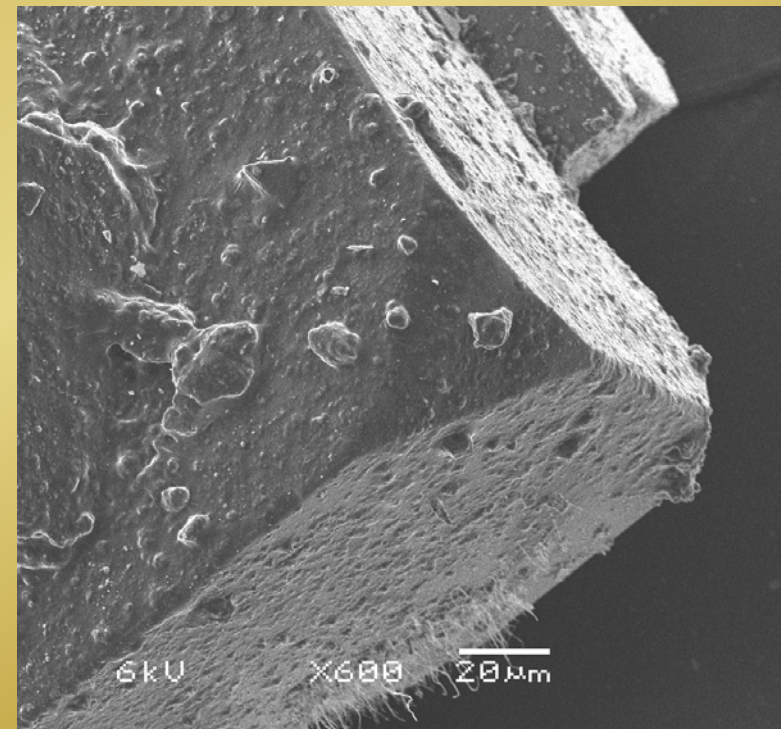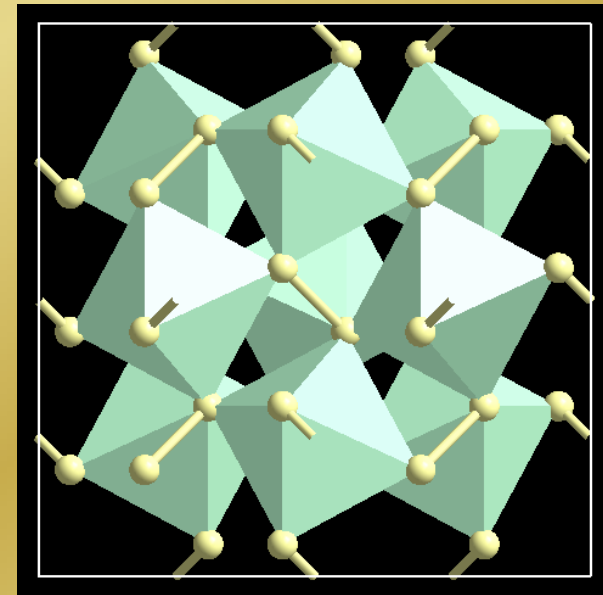

(submitted to Nature Materials)

Iron Sulphides

Iron-bearing sulphide minerals play an important role in the control of acid mine drainage and transport of heavy metals like arsenic.

Pyrite, FeS$_2$

❧ Most abundant of all metal sulphides

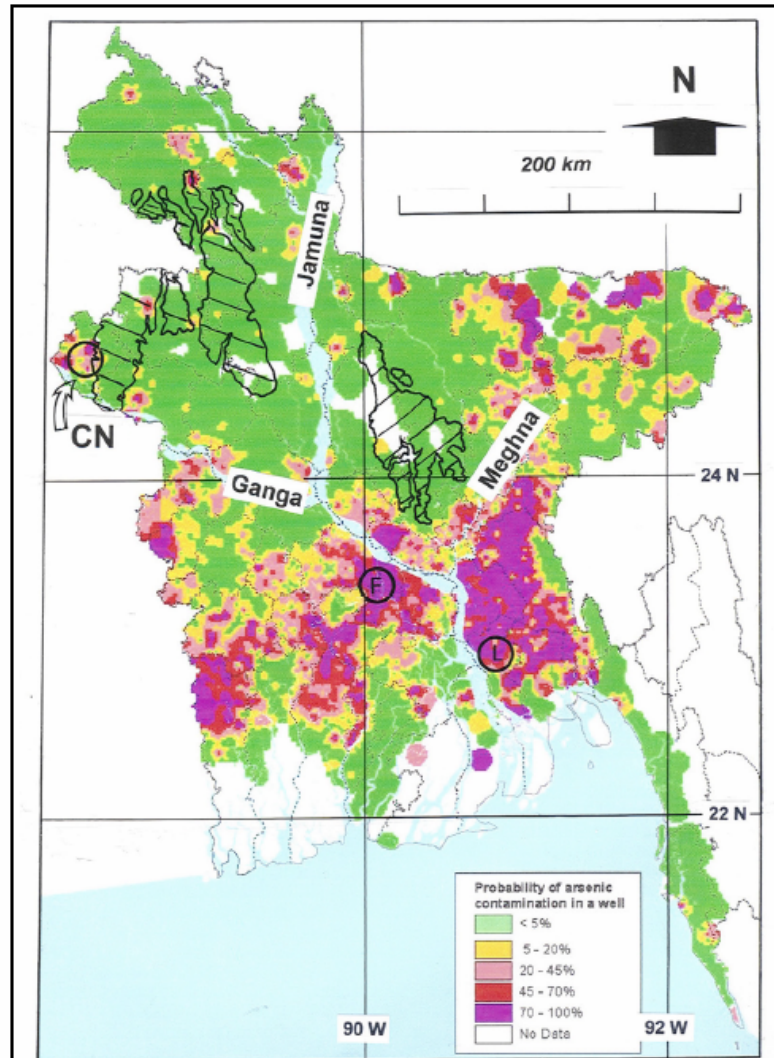❧ Can incorporate large amounts of As (up to ~ 10 wt %)

Fig. 1. Map of Bangladesh with circled areas showing study areas of DPHE [1999, 2000]. CN = Chapai Nawabganj, F = Faridpur, L = Lakshmipur. Colouring shows the percentage of wells that exceed an arsenic concentration of 0.05 mg l^{-1}, as estimated from Union averages of 18 471 data and based on the centre of each Union. Calculated using a fixed radius of 7.5 km, a 1.5 km grid, and 3125 Union centres. Unions are administrative areas. Cross hatched areas are old and elevated terraces in which groundwater is free of arsenic pollution. Cross-hatched areas are elevated Madhupur and Barind Tracts.

Number of papers in Web of Science with keywords "Arsenic" and "Groundwater"
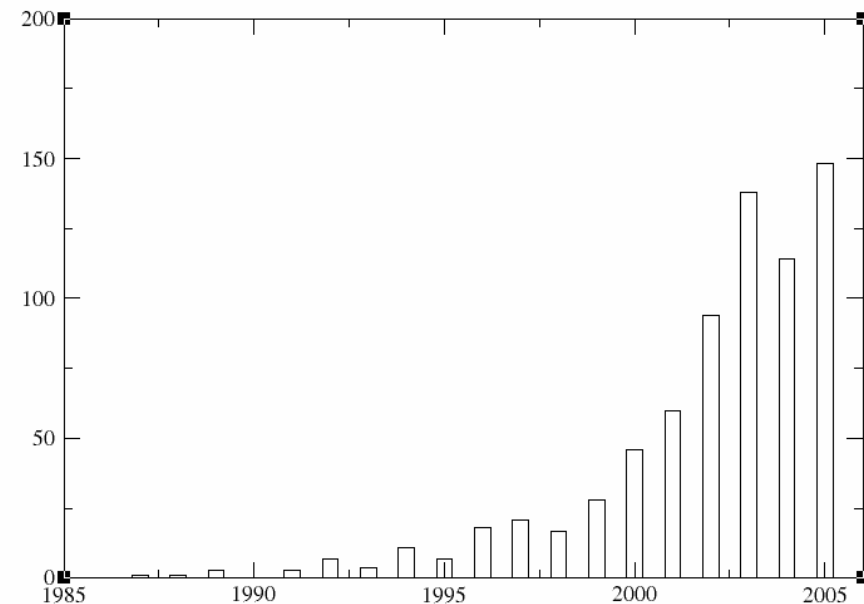
Arsenic incorporation into FeS$_2$ pyrite
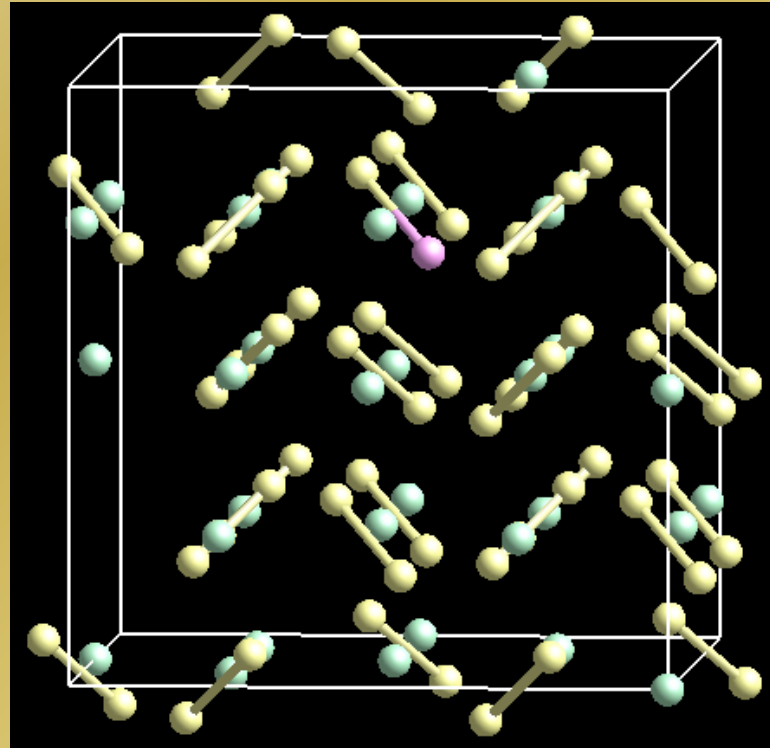
At low concentration, arsenic should be in the same configuration as in arsenopyrite (FeAsS), i.e. forming As-S.

Perspectives:
- Surface segregation of arsenic
- Stability of the different surfaces of arsenic-bearing pyrite

Also: Mackinawite, FeS

✎ First iron sulphide to form in most ambient aqueous environment

✎ Possible host for metals in the interlayer.

$c \sim 5$ Å

✎ Highly reactive phase

✎ Linked to the origin of life on Earth.

✎ Structure = layers hold by Van der Waals forces $\Rightarrow$ difficult to model by DFT
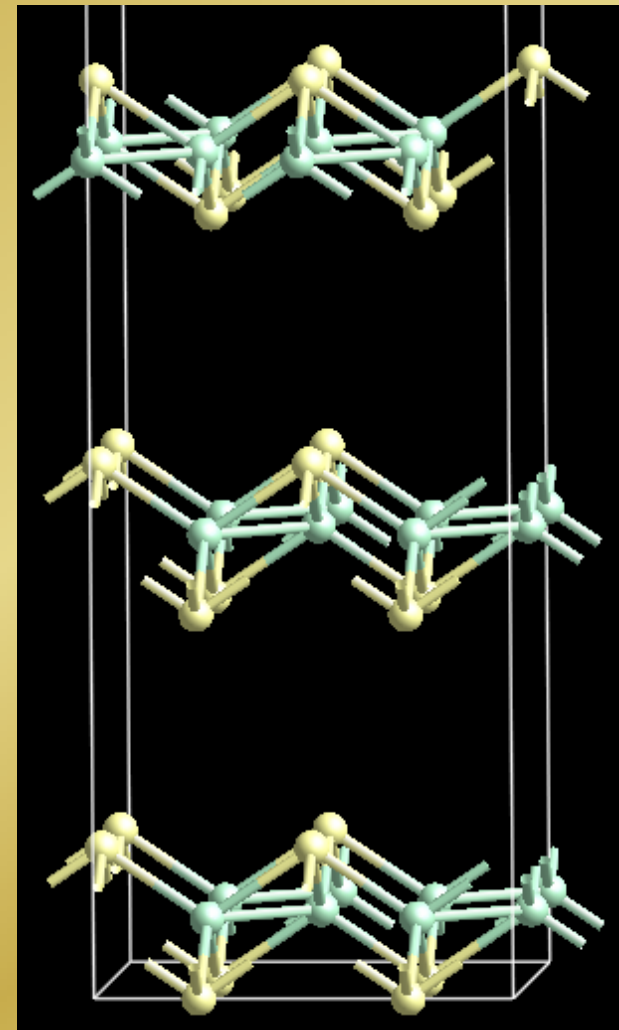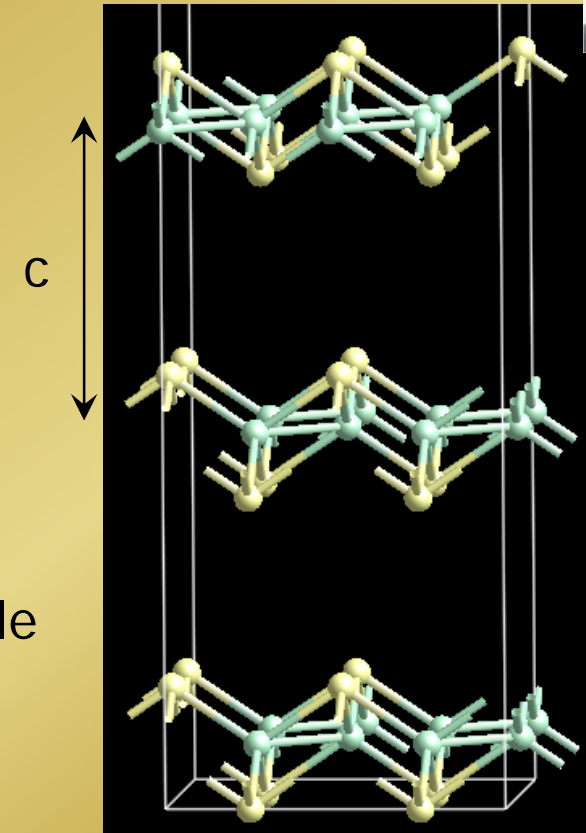
Mackinawite inclusions

1.0 cm

© Jeff Weissman

Comparison of the results given by different simulation codes available within the eMinerals project (SIESTA, CASTEP, VASP, CRYSTAL)

	Obs.	GGA	LDA	B3LYP
a = b	3.67	3.6-3.7	3.5-3.6	3.62
c	5.03	6.0-6.9	4.8-4.9	5.03

c

Globally GGA overestimates the c parameter while LDA slightly underestimates it.
B3LYP gives the best result.

This study, using several codes, was facilitated a lot by the collaborative tools developed in the project.
Information, input/output files and executables have been shared using the SRB, E-mails…
Calculations have been performed within the eMinerals minigrid (Lakes, Condor pools…)

Mineral/Solvent Interfaces
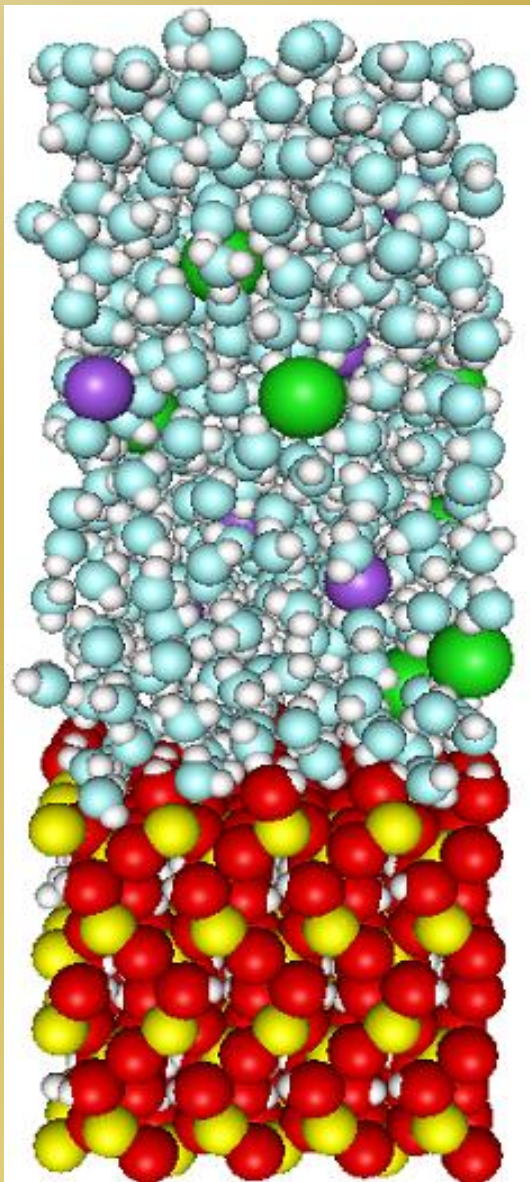
To fully understand transport and immobilisation processes of contaminants we need an accurate description of the mineral/solvent interfaces.

Molecular Dynamics simulations using DL_POLY. On the Condor-pool we cannot run jobs exceeding 24hrs BUT we can distribute many independent calculations over the machines available with the Condor pool.
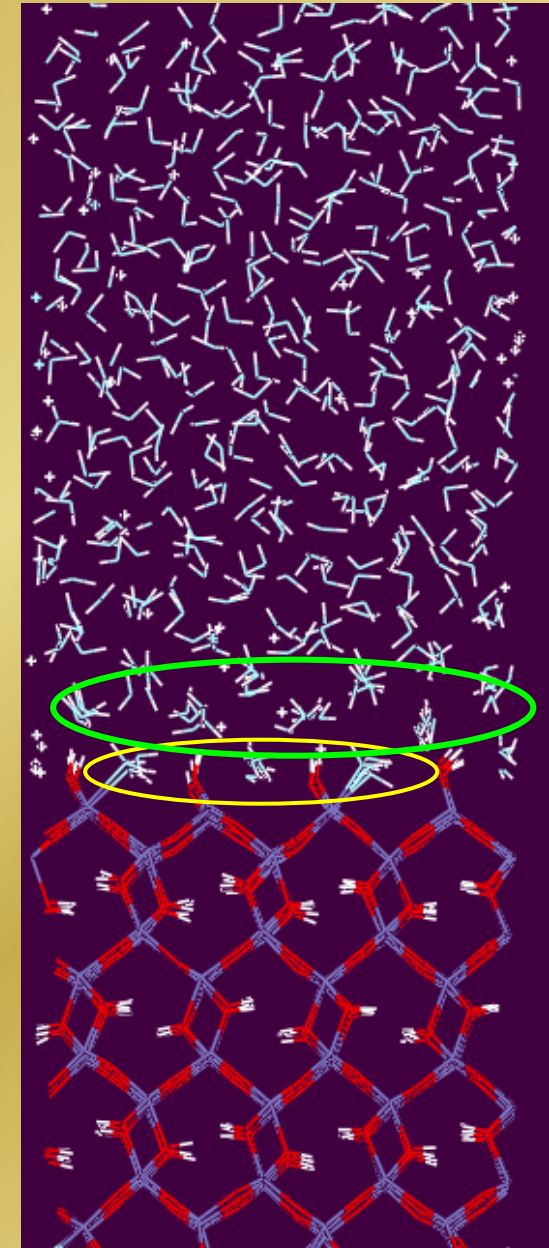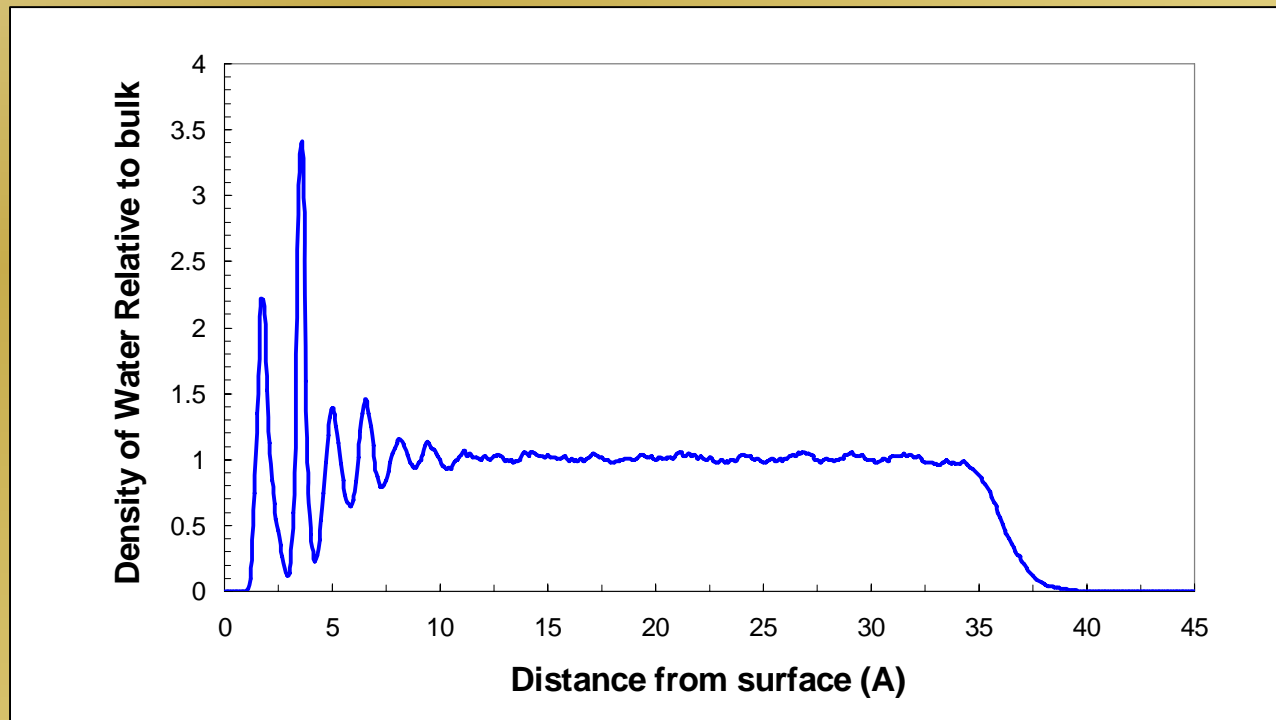
This approach provides us with good statistical data to determine diffusion and water exchange rates.

Snapshot of Goethite/Solvent interface using MD-simulation on the HPCx.
A. Marmier, D. Cooke, S. Kerisit and S.C. Parker
Bath University.

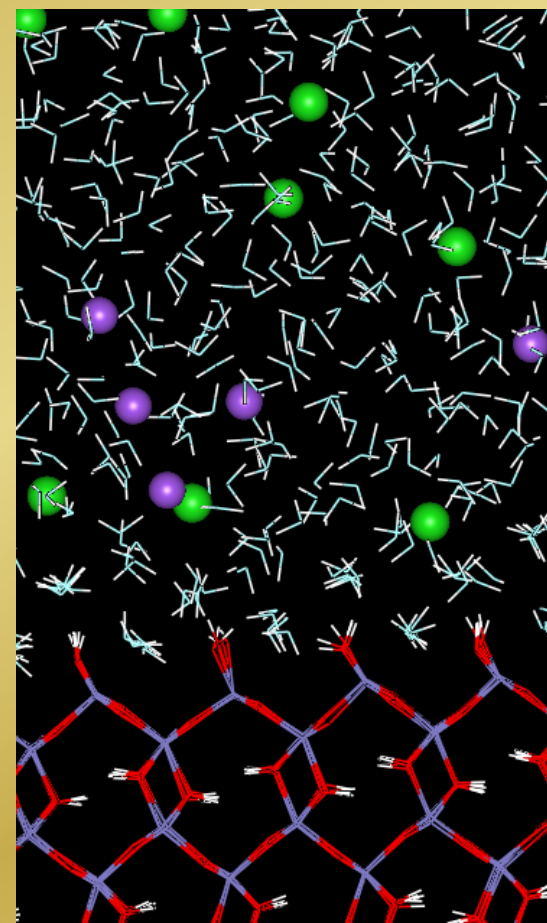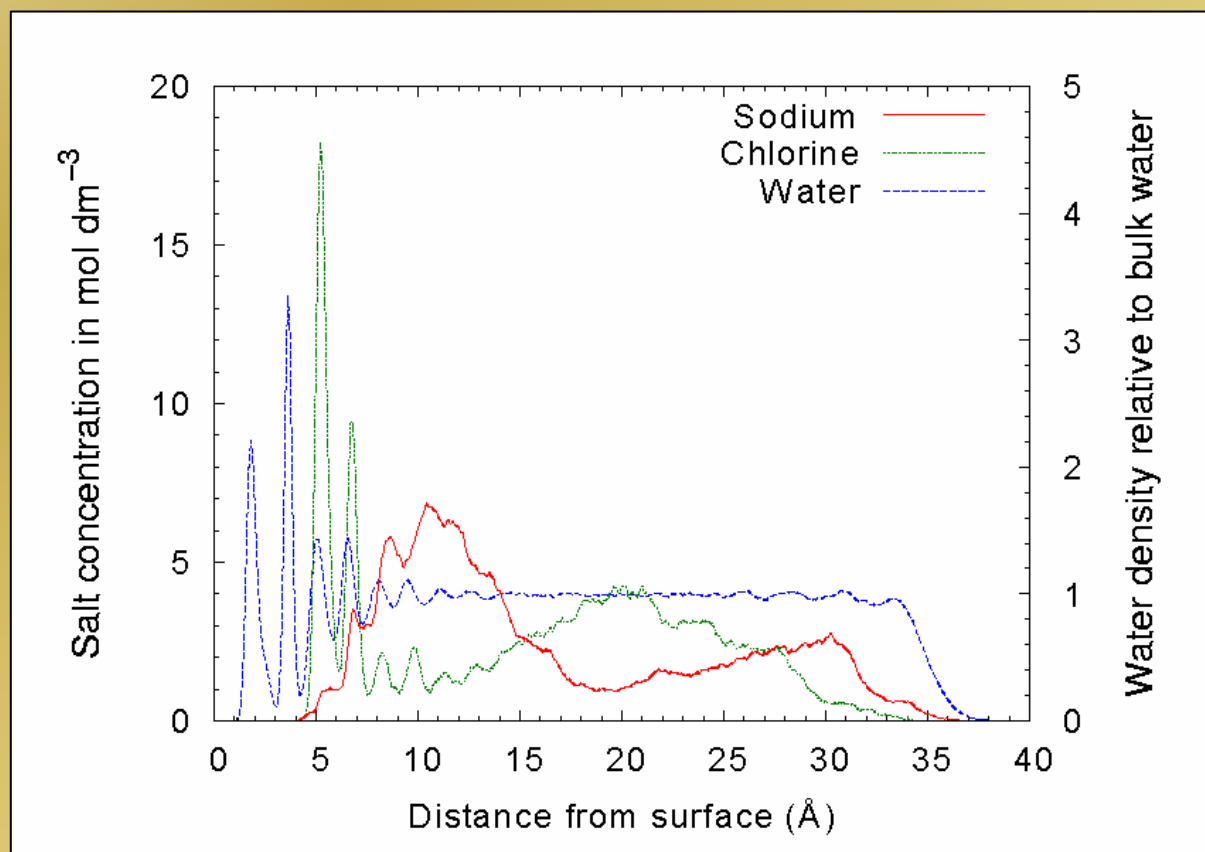# The Effect Of Water

Residence time

OH rows

$\tau > 500$ps

2nd layer $\tau \sim 50$ ps
1st layer $\tau \sim 300$ ps

1.2M Salt Solution

Residence Times
Cl⁻ site II $\tau \sim$ 10 ps
Cl⁻ site I $\tau \sim$ 150 ps

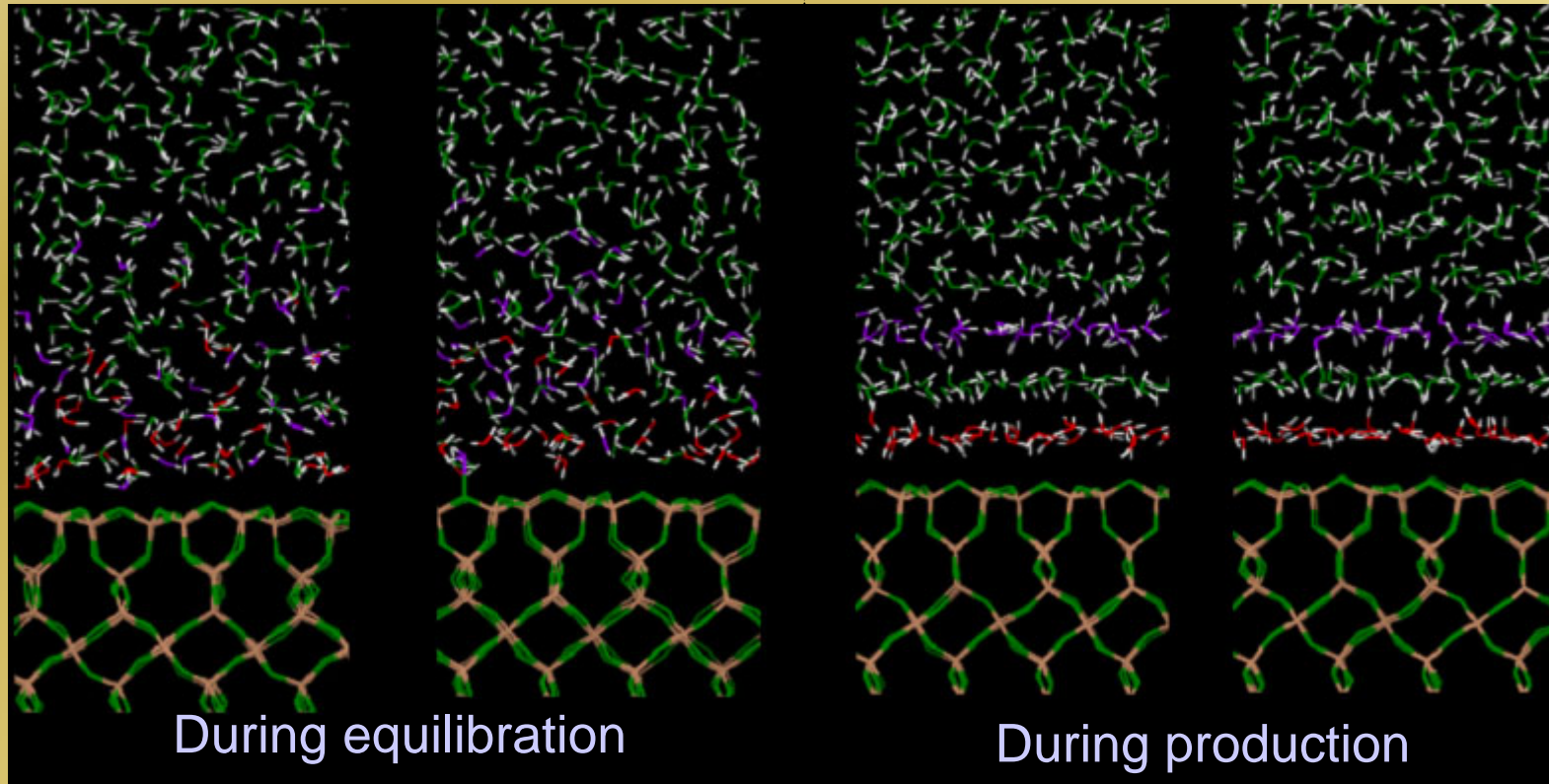t = 10 ps   t = 15 ps   t = 80 ps   t = 120 ps
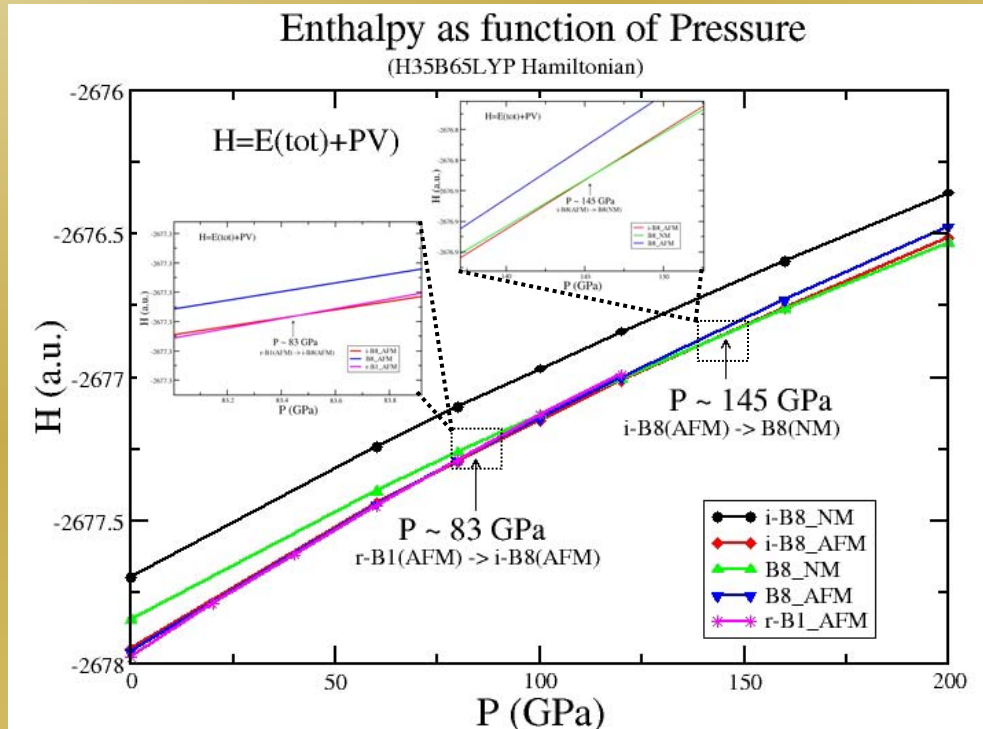
During equilibration   During production

❑Our calculated results indicate that once the system reaches equilibration, the ordered-layers of water molecules form and there is no water molecule exchange between the neighboring mono-layers.

# Phase Diagram and Crystal Structures

by UCL-team

Enthalpy as function of Pressure
(H35B65LYP Hamiltonian)

H=E(tot)+PV)

P ~ 145 GPa
i-B8(AFM) -> B8(NM)

P ~ 83 GPa
r-B1(AFM) -> i-B8(AFM)

- i-B8_NM
- i-B8_AFM
- B8_NM
- B8_AFM
- r-B1_AFM

To determine phase transitions we need to:
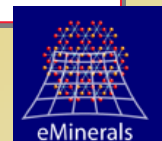• **optimise the geometries for all the possible crystal structures at various pressures.** ⇒ ~ 240 calculations for FeO
• **for up to 10 computational methods (Hamiltonians)**
⇒ ~240 x 10 = ~2400 calculations

r-B1(AFM) i-B8(AFM) B8(NM)

insulator insulator metallic P(GPa)

83   145
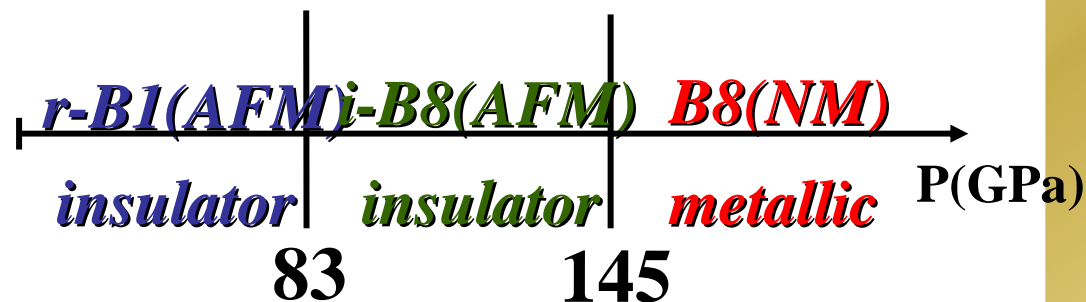
Solution:
• Condor cluster @UCL
• SRB

eMinerals

Job Submission

- Condor_submit
- Condor-G
- DAGMan scripts to submit jobs. Manages dependencies between jobs.
- Perl scripts wrapped around the codes; a way to "design" the calculations for the UCL Condor-pool. Access the SRB vaults.
- Other shell script/database variants.

Gdis:
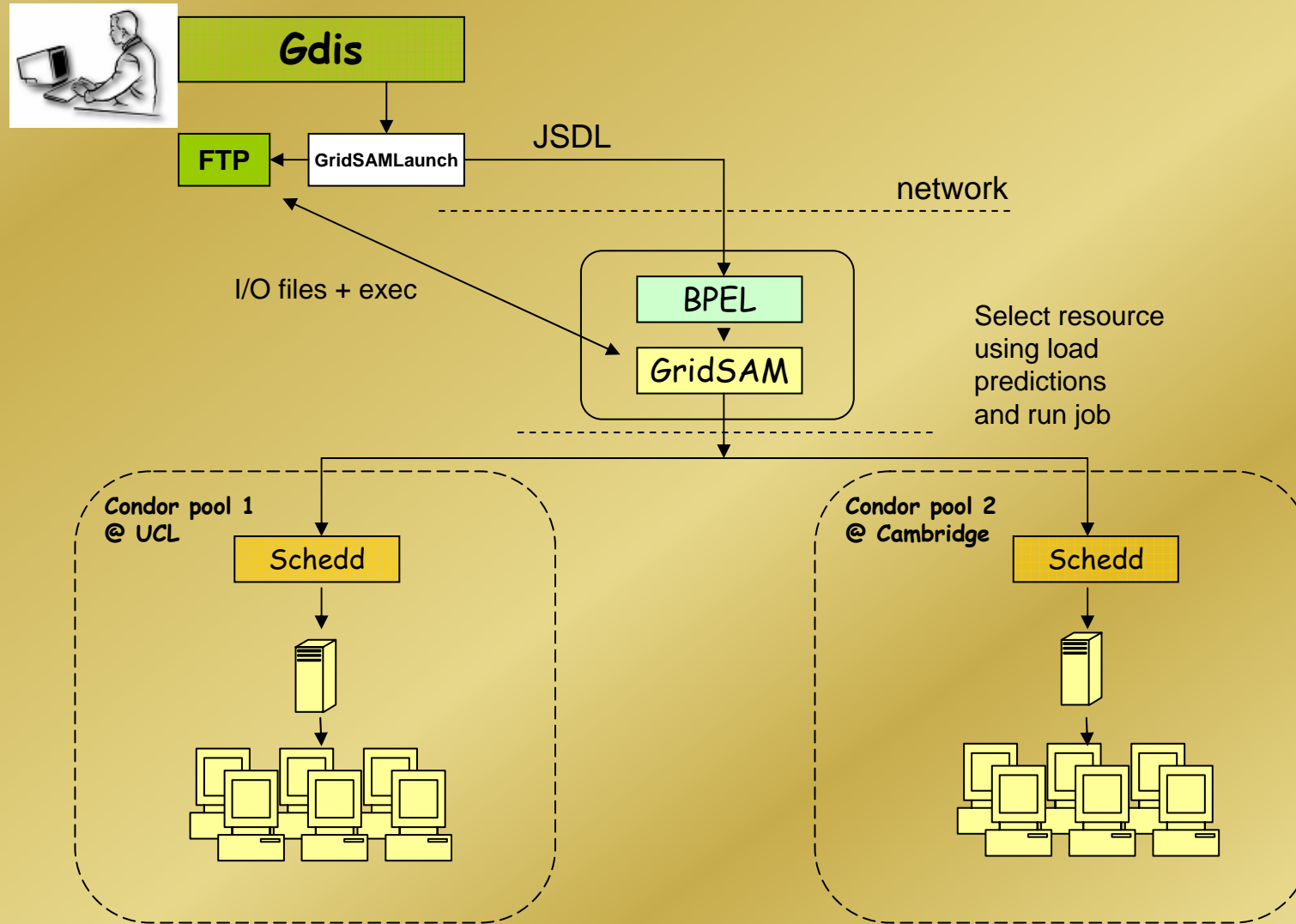## External execution request (pictured GULP)

Underlying system:

Grid execution completely transparent to the user

28
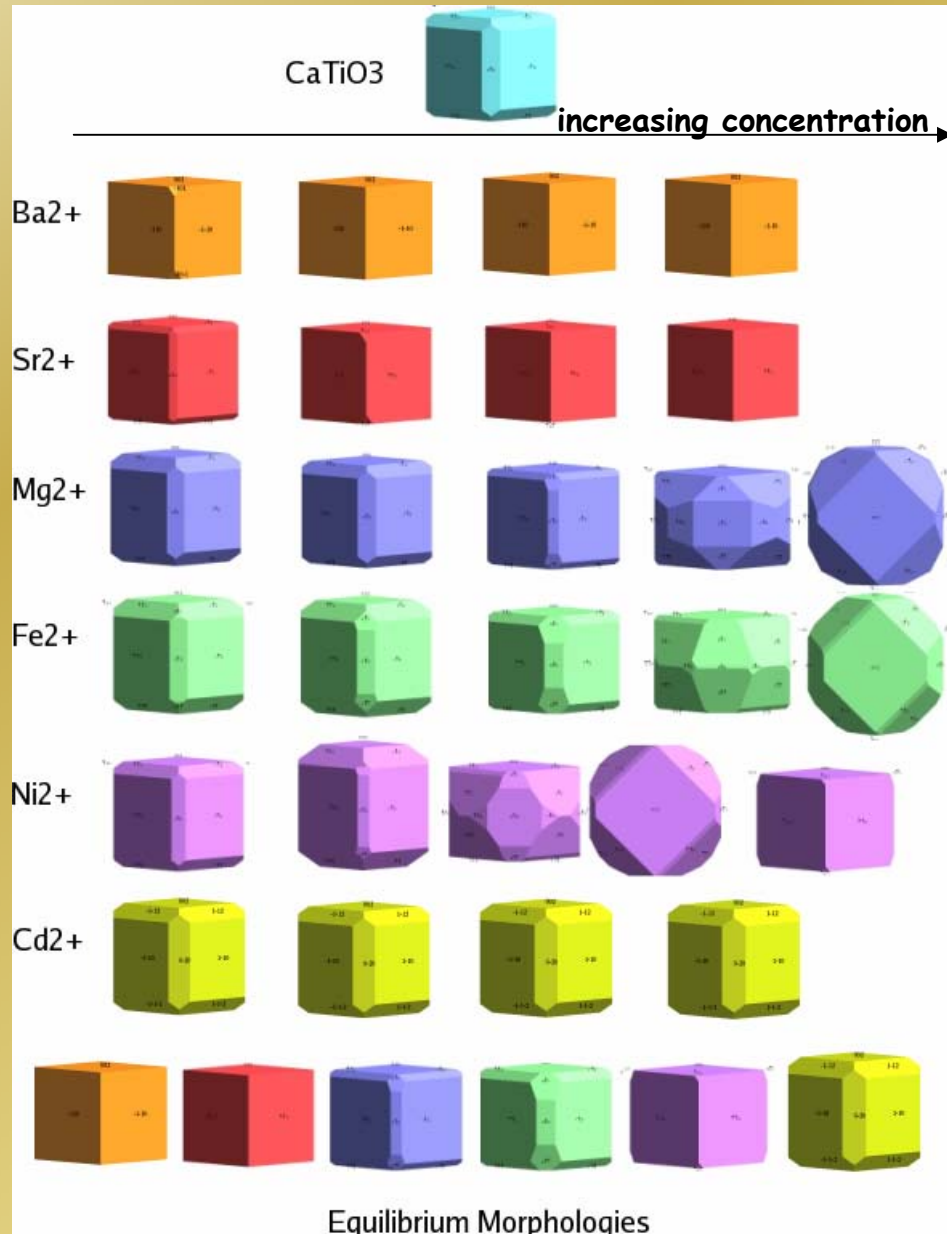
Thank you to:

Marc Blanchard

Arnaud Marmier

Zhimei Du

Maria Alfredsson

Clovis Chapman

Mineral Surfaces

CaTiO3

increasing concentration

Ba2+

Sr2+

Mg2+

Fe2+

Ni2+

Cd2+

Equilibrium Morphologies

We defined a new method to calculate surface energies which allow us to determine crystal particle shape.

We find particle shapes change with concentration of the impurity and the type of dopant.

Important to understand the reactivity and inter-actions between pollutants and minerals.