University of Kent

Kent Academic Repository

Du, Z, Alexandrov, V.N., Alfredsson, Maria, Artacho, E., Austen, K.F., Bennett, N.D., Blanchard, M., Brodholt, John P., Bruin, R.P., Catlow, C.R.A. and others (2006) ***A virtual research organization enabled by eMinerals minigrid: an integrated study of the transport and immobilization of arsenic species in the environment.*** **In: Cox, S.J., ed. Proceedings of the UK e-Science All Hands Meeting 2006. . pp. 481-488. , Nottingham, UK ISBN 0-9553988-0-0.**

Downloaded from

https://kar.kent.ac.uk/115288/ The University of Kent's Academic Repository KAR

The version of record is available from

https://www.dcc.ac.uk/news/uk-e-science-all-hands-meeting-hits-records

This document version

Author's Accepted Manuscript

DOI for this version

Licence for this version

UNSPECIFIED

Additional information

Versions of research works

Versions of Record

If this version is the version of record, it is the same as the published version available on the publisher's web site. Cite as the published version.

Author Accepted Manuscripts

If this document is identified as the Author Accepted Manuscript it is the version after peer review but before type setting, copy editing or publisher branding. Cite as Surname, Initial. (Year) 'Title of article'. To be published in ***Title of Journal*** , Volume and issue numbers [peer-reviewed accepted version]. Available at: DOI or URL (Accessed: date).

Enquiries

If you have questions about this document contact ResearchSupport@kent.ac.uk. Please include the URL of the record in KAR. If you believe that your, or a third party's rights have been compromised through this document please see our Take Down policy (available from https://www.kent.ac.uk/guides/kar-the-kent-academic-repository#policies).

A virtual research organization enabled by *e*Minerals minigrid: an integrated study of the transport and immobilization of arsenic species in the environment

Z. Du[1,2], V.N. Alexandrov[11], M. Alfredsson[3], E. Artacho[6], K.F. Austen[6] , N.D. Bennett[8], M. Blanchard[4], J.P. Brodholt[3], R. P. Bruin[6], C.R.A. Catlow[4], C. Chapman[10], D.J. Cooke[5], T.G. Cooper[9], M.T. Dove[6,7], W. Emmerich[10], S.M. Hasan[11], S. Kerisit[5], N.H. de Leeuw[1,2] , G.J. Lewis[11], A. Marmier[5], S.C. Parker[5], G.D. Price[3], W. Smith[8], I. T. Todorov [8], R.P.Tyer[8] , K Kleese van Dam[8], A.M. Walker[6], T.O.H. White[6], K. Wright[4]

1. School of Crystallography, Birkbeck College, Malet Street, London, WC1E 7HX
2. Department of Chemistry, University College London, London WC1H 0AJ
3. Department of Earth Sciences, University College London, London WC1E 6BT
4. Royal Institution of Great Britain, Albemarle Street, London W1S 4BS
5. Department of Chemistry, University of Bath, BA2 7AY
6. Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ
7. National Institute for Environmental *e*Science, Centre for Mathematical Sciences, University of Cambridge, Wilberforce Road, Cambridge CB3 0WA
8. CCLRC, Daresbury Laboratory, Daresbury, Warrington, Cheshire WA4 4AD
9. The Pfizer Institute for Pharmaceutical Materials Science, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW
10. Department of Computer Science, University College London, London WC1E 6BT
11. Department of Computer Science, University of Reading, PO Box 225, Reading RG6 6AY

Abstract

We have carried out a comprehensive computational study of the structures and properties of a series of iron-bearing minerals under various conditions using grid technologies developed within the *e*Minerals project. The work has enabled by a close collaboration between computational scientists from different institutions across the UK, as well as the involvement of computer and grid scientists in a true team effort. We show here that our new approach for scientific research is only feasible with the use of the *e*Minerals minigrid. Prior to the *e*Minerals project, such an approach would have been almost impossible within the timescale available. The new approach allows us to achieve our goals in a much quicker, more comprehensive and detailed way. Preliminary scientific results of an investigation of the transport and immobilization of arsenic species in the environment are presented in the paper.

1. Introduction

The remediation of contaminated waters and land poses a grand challenge on a global scale. The contamination of drinking water by arsenic has been associated with various cancerous and non-cancerous health effects and is thus one of the most pressing environmental concerns [1]. It is clearly important to understand the mechanisms of any processes that reduce the amount of active arsenic species in groundwater, which can be achieved by selective adsorption. It is generally considered that iron-bearing minerals are promising absorbents for a wide range of solvated impurities. There is a serious need for a detailed understanding of the capabilities of different iron-bearing minerals to immobilize contaminants under varying conditions, in order to guide strategies to reduce arsenic contamination. We have chosen to use a computational approach to study the capabilities of iron-bearing minerals to immobilize active arsenic species in water.

This large, integrated project requires input from personnel with diverse skills and rich experience, as well as techniques and infrastructure to support a large scale computing effort. The complex calculations required include workflows, high-throughput and the ability to match different computational need against available resources. Furthermore, data management tools are required to support the vast amount of data produced in such a study. This is clearly a real challenge for the *e*-science

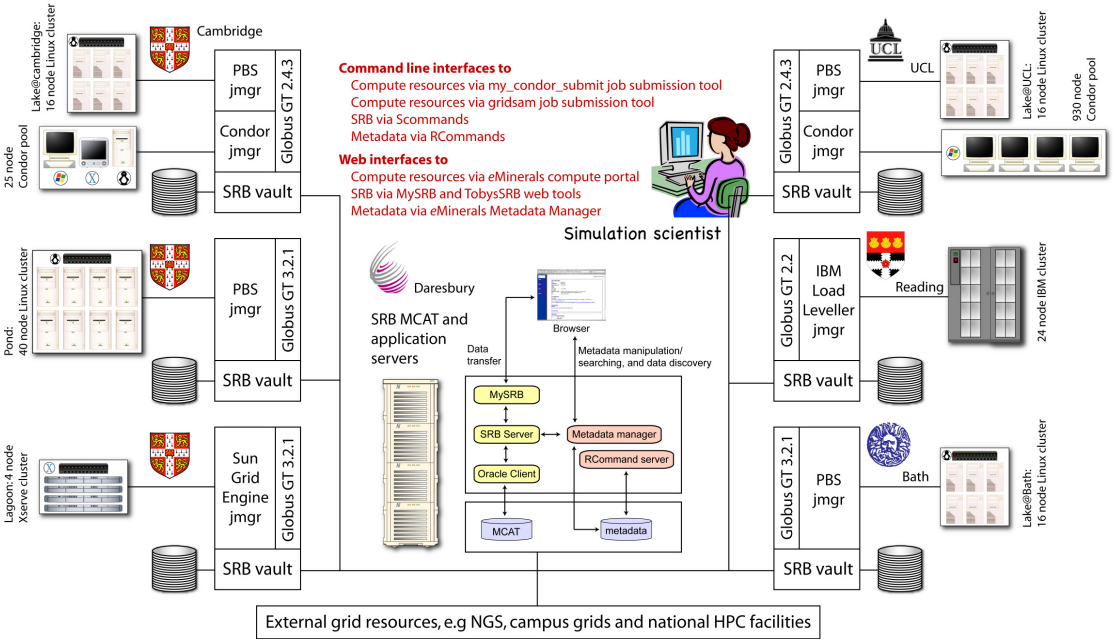


Figure 1 Components of *e*Minerals minigrid. It contains heterogeneous computer resources: 3 Linux-based clusters situated at Bath, Cambridge and UCL; 1 Linux-cluster with 8GB per node at Cambridge; 1 24-node IBM parallel machine at Reading; 3 Condor-pools located at UCL, Cambridge and Bath. Besides, external facilities *e.g.* NGS, CSAR and HPCx are also accessible. The Storage Resource Broker (SRB) enables data stored at various sites to be seen by the users as if within one single file.

community. The aim of the *e*Minerals project [2] is to incorporate grid technologies with computer simulations to tackle complex environmental problems. During the first phase of this project, *e*Minerals minigrid has been developed and tested. In addition, a functional virtual organisation has been established, based on the sharing of resources and expertise, with supporting tools.

We can now fully explore the established infrastructure to perform simulations of environmental processes, which means having to deal with very complicated simulation systems close to 'real systems' and under varying conditions. Here we report on a case study using the grid technologies developed in the *e*Minerals project to conduct a large integrated study of the transport and immobilization of arsenic in a series of iron-bearing minerals, where the computational scientists work as a team to tackle one common problem. The whole team operates as a task-oriented virtual organization (VO) and each member of the VO will use his own expertise to deal with one or several aspects of the project. A close collaboration between all team members is inevitable in such a comprehensive study, which enables the scientific studies to be carried out at different levels, using different methodologies and investigating many different iron-bearing minerals. This new approach is aimed at expanding the horizons of simulation studies and meeting the needs for a quick, comprehensive and detailed investigation into the mechanisms of arsenic adsorption by various adsorbents. The investigation at such a scale would be impossible without the collaborative grid technologies.

2. Grid technologies in computational simulations

All the simulations conducted in this study were facilitated by the *e*Minerals minigrid [3]. The eminerals mini-grid is composed of a collection of shared and dedicated resources. These are spread across 6 sites, and are depicted in figure 1. We also regularly complement these resources with external resources such as those made available by the National Grid Service. More details of building and examining tools as well as our view and experience on using these tools have been discussed in ref [3,4]. Here we just give some brief description.

2.1 Communication tools

As mentioned in the introduction, this project is a large collaboration in terms of the number of people involved and the levels of calculations

needed to be carried out. Good organization and communication is therefore the key to the institutions across the UK, it would be extremely difficult to keep the whole team in communication on a daily or weekly basis if we followed traditional methods.

Within the *e*Minerals project, we have developed a new approach, taking advantage of different communication tools like: Personal Access Grid (AG) and a *Wiki,* Instant message (IM) in addition to more conventional tools (e.g. e-mails, telephone). Each tool is suitable to a particular communication required by the collaboration.

- **AG meeting:** AG does offer a valuable alternative to the expense of travelling for project meetings. The AG meetings are now acting as a valuable management tool and in the context of the project enabling us to identify the most suitable person to complete the selected simulations within a specified time. For instance, for the arsenic pollutant problem, through the AG meeting, we have decided that team members from Bath and Birkbeck focus on adsorption of arsenic species on iron oxides and hydroxides using interatomic potential based simulations, while those from the Royal Institution and Cambridge work on arsenic species adsorption on pyrite and dolomite using quantum mechanical calculations. The AG meetings also play an important role in members contributing their ideas to collaborative papers like this one.
- **The *Wiki*:** *Wiki* is a website which can be freely edited by the members of the VO. We have use *Wiki* to exchange ideas, deposit news information, edit collaborative papers. For example, we have used Blogbooks for the resource management to notify other members before submitting large suites of calculations. The downside of this tool is that *wiki* does not support instant communication, which limits the quality of its use as a collaborative tool.
- **Instant message (IM):** IM gives much better instantaneous chat facilities than email and *wiki*. It is particular useful for members of the project developing new tools because it is easy to ask questions and reach agreement.

2.2 Grid environment support for workflow

All calculations conducted in this study have been organized by a meta-scheduling job submission tool called my_condor_submit success of the project. Because the members of the project are based at different (MCS) [5]. The MCS manages the simulation workflow using Condor's DAGman functionality and integrates with Storage Resource Brokers (SRB) for data management. The Condor interface has proved quite popular, and facilitates the submission and management of large numbers of jobs to globus resources. In addition, it enables the use of additional Condor tools and in particular the DAG-Man workflow manager. SRB has provided seamless access to distributed data resources. As shown in figure1, there are 5 SRB data storage vaults spread across 4 sites within the project amounting to a total capacity of roughly 3 Terabytes. A metadata annotation service (RCommands service)[6] hosted by the CCLRC, and database back end, was used to generate and search metadata for files stored in the SRB vaults.

The use of MCS together with SRB allows us to handle each simulation following a simple and automated three-step procedure. The input files are downloaded from the SRB and MCS decides where to run the job within the *e*Minerals minigrid, depending on the available compute facilities. Finally the output files are uploaded back to the SRB for subsequent analysis. This tool certainly facilitates the work of the scientists and avoids unnecessary delays in the calculations.

Our practice has shown that the SRB is of prime importance for data management in such collaboration. It not only provides a facility to accommodate a large number of data sets, but also allows us to share information more conveniently, e.g. large files that are nigh impossible to transfer using traditional communication tools (e.g. email) due to size limitations. SRB also permits us to access the data files wherever and whenever we wish.

Here we just illustrate a couple of examples to show the benefits of using grid techniques to support workflow in a scientific study. In the case of the quantum mechanical study of the structures of goethite, pyrite and wüstite, we have to take into account that these minerals can have different magnetic structures, which requires a range of separate calculations. For example, ferric iron, which has five d-electrons, exists with magnetic numbers equal to 5 (HS) and 1 (LS), while ferrous iron, which has 6 d-electrons, can have a magnetic number 4 (HS) or 0 (LS). This means that the minerals with ferrous iron can have anti-ferromagnetic (AFM); ferromagnetic (FM); and non-magnetic (NM) structures, while minerals containing ferric iron show AFM or FM structures. For

Table 1 Electronic and magnetic structures as predicted by the hybrid-functionals reported in the text as well as the PW91 (GGA) Hamiltonian and experiments. HS=high spin, LS=low spin, M= metal and I=insulator.

Mineral	hybrid	Exp	GGA	hybrid	GGA	Exp
FeO	HS	HS[9]	HS	I	M	I[14]
FeS_2	LS	LS [10]	LS	I	M	I[15]
$FeSiO_3$	HS	-	HS	I	I	-
Fe_2SiO_4	HS	HS[11]	LS	I	M	I[16]
Fe_2O_3	HS	HS[12]	LS	I	M	I[17]
α-FeOOH	HS	HS[13]	HS	I	I	I[18]

each mineral we consider 5 to 10 different hybrid-functionals for several magnetic structures, which means that we run 20 to 30 compute intensive calculations per mineral. As all calculations are independent of each other, they are carried out on the UCL Condor-pool (> 1000 processors) using the MCS job submission tool. As such, the calculations can start almost immediately and are completed within a couple of months, whereas, prior to this eScience technology, this type of study might have taken a year or longer to conclude.

As another example, the study of arsenic incorporation in FeS_2 pyrite has required accurate geometry optimizations of supercells at a quantum mechanical level. Due to the nature of these calculations, the national computing facility (HPCx) was used. In addition, many smaller and independent calculations were carried out for convergence tests and especially for obtaining the total energy of all the different reaction components. This task was suited perfectly to the coupled use of the *e*Minerals minigrid and SRB via the MCS tool.

3. Science outcomes

One of the major environmental concerns in recent years has been the widespread contamination by arsenic of aquifers used for drinking water, for example in Bangladesh. It is clearly of immense importance to reduce the presence of active arsenic species in the water and attention is focused on the sorption of these and other contaminants onto minerals, which are present in the environment of the aquifers.

The common goal of this project is to investigate the transport and immobilisation mechanisms of arsenic species in various iron-bearing minerals, which are thought to be promising adsorbents [7]. We report here our preliminary results, namely, the theoretical description of the bulk minerals, surface stabilities and hydration processes.

3.1 Quantum mechanical studies of the structures of Goethite, Pyrite and Wüstite

The modelling of iron-bearing minerals is a particular challenge in mineral physics as the electronic and magnetic structures of many of these minerals are badly or even wrongly represented by traditional density functional theory (DFT). Most of the minerals we have studied are predicted to be metals; although experimentally they are reported as insulators (see Table 1 for details). In addition, DFT gives the incorrect spin state for Fe_2SiO_4 and Fe_2O_3 when the GGA functional is used, thus give rise to the wrong magnetic structures of the minerals.

Our aim is to compare GGA and hybrid-functional calculations of a range of iron-bearing minerals to determine if the minerals are well described within the DFT formalism or if they need to be described by more advanced quantum mechanical techniques, e.g. hybrid-functionals. Here we have chosen to discuss three minerals in more detail: a) Goethite (α-FeOOH), b) Pyrite (FeS_2) and c) Wüstite (FeO).

a) Goethite

In goethite the Fe-species are in oxidation state (III) (ferric-iron), and as shown in Table 1 we predict both the magnetic and electronic structures correctly with both GGA and hybrid-functionals for this mineral. However, the lattice parameters optimised with GGA are in better agreement with experiment than the values obtained using the hybrid-functionals. Comparing the internal geometries we find that both the hybrid-functionals as well as the GGA Hamiltonian give values in agreement with experiment. Both computational techniques on the other hand underestimate the internal

O-H bond distance and the hydrogen bond distance. Our calculations suggest that α-FeOOH is adequately described in DFT and there is no need for alternative techniques to study this material.

b) Pyrite

Pyrite contains ferrous iron, and from Table 1 we see that DFT fails to predict this mineral as insulator. However, the magnetic structure for pyrite (LS) agrees with experiment. Pyrite has also been studied using plane-waves to describe the electron density (e.g. ref. 8), while we are using localised Gaussian-basis functions. In the previous study pyrite is correctly reported as an insulator. We also find that both the hybrid-functionals and GGA overestimate the lattice parameters compared to the experimental value. We believe this is again due to the description of the electron density by the Gaussian-basis functions, which can be improved. Hence, our conclusion from this study is that pyrite can be described by plane-wave DFT methods and does not need to be described by hybrid-functionals.

c)Wüstite

FeO is a classical example where DFT is known to fail to predict the electronic structure, as shown in Table 1. If we concentrate on the structural properties of wüstite on the other hand we find that GGA underestimates, while the hybrid-functional described by 40% Hartree-Fock exchange overestimates the lattice parameters. This is also reflected in the internal geometries. Hence, our conclusions are that wüstite is better described by hybrid-functionals, but some properties, like the geometrical properties are well described with GGA. However, the magnetic and electronic structures require hybrid-functionals to be correctly described.

Our study showed that minerals containing ferric iron are often better described within DFT than minerals containing ferrous iron. However, ferrous iron in LS configurations, such as pyrite, is also well described within DFT, while minerals containing ferrous iron, which show magnetism (i.e. HS configuration) are better described by hybrid-functionals. This result is a reflection of the known shortcomings of DFT and its representation of electron correlation; high-spin ionic states are always poorly represented within the DTF approximation, so we expect the structural features of HS ferric iron to be captured considerably worse, and requiring the additional accuracy provided by hybrid functional approaches, while for LS ferrous iron, DFT alone gives a reasonable result.

3.2 Arsenic incorporation in pyrite FeS_2

Pyrite (FeS_2) the most abundant of all metal sulphides, plays an important role in the transport of arsenic. Under reducing conditions, pyrite can delay the migration of arsenic by adsorption on its surfaces, as well as by incorporation into the bulk lattice. Pyrite can host up to about 10 wt % of arsenic [19]. Under oxidizing conditions, pyrite dissolves, leading to the generation of acid drainage and releasing arsenic into the environment. Although it is key information, the location and speciation of arsenic in pyrite remains a matter of debate. The pyrite has a NaCl-like cubic structure with an alternation of Fe atoms and S_2 groups. X-ray adsorption spectroscopic studies showed that arsenic substitutes for sulphur, forming AsS di-anion groups rather than As_2 groups [20]. On the other hand a recent experimental study has proposed that arsenic can also act like a cation, substituting for iron. The different arsenic configurations have been investigated using first-principles calculations.

Calculations have been executed within the DFT framework. In order to work with arsenic concentrations comparable with natural observations, calculations were performed on 2x2x2 pyrite supercells containing up to two arsenic atoms (< 4 wt. % As). The arsenic has been successively placed in iron and sulphur sites. In the later case, we have investigated the three following substitution mechanisms: formation of AsS groups, formation of As_2 groups and substitution of one As atom for one S_2 group. These different configurations have been compared by considering simple incorporation reactions under both oxidizing and reducing conditions. Solution energies suggest that, in conditions where pyrite is stable, arsenic will preferentially be incorporated in a sulphur site forming AsS groups (Fig 2). The incorporation of arsenic as a cation is energetically unfavourable in pure FeS_2 pyrite. Previous studies have shown that above an arsenic concentration of about 6 wt%, the solid solution becomes metastable and segregated domains of the arsenopyrite are formed in the pyrite lattice [21]. Even for the low concentrations modelled here, the substitution energies indicate that the arsenic tends to cluster. Our results also show that, in oxidising conditions, the presence of arsenic

Table 2 Surface energies for iron (hydr)oxide minerals including both dry and hydroxylated surfaces

Fe_2O_3									
Surface	001	012a	012b	012c	100	101	110	111a	111b
Dry surface energy (Jm^{-2})	1.78	1.87	2.75	2.35	1.99	2.34	2.02	2.21	2.07
Hydrated surface energy (Jm^{-2})	0.90	0.38	0.28	0.38	0.27	0.04	0.20	0.33	0.28

FeOOH						
Surface	010	100	110	001	011	101	111
Dry surface energy(Jm^{-2})	1.92	1.68	1.26	0.67	1.18	1.72	1.33
Hydrated surface energy (Jm^{-2})	0.51	1.17	0.68	0.52	0.34	1.32	1.12

$Fe(OH)_2$						
Surface	001	010	011	101	110	111
Dry surface energy (Jm^{-2})	0.04	0.38	0.35	0.35	0.64	0.60

may accelerate the dissolution of pyrite with the en environmental consequences that implies (acid rock drainage and release in soluaiton of toxic metals).

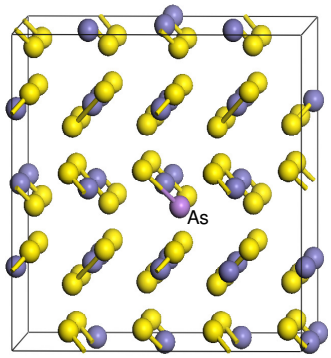


Figure 2 Relaxed structure of the 2x2x2 supercell of pyrite containing one AsS group.

3.3 Iron (hydr)oxide mineral surfaces

Iron (hydr)oxides play an important role in many disciplines including pure, environmental and industrial chemistry, soil science, and biology. Iron (hydr)oxide minerals are thought to be promising adsorbents to immobilize active arsenic and other toxic species in groundwater. There are eleven known crystalline iron (hydr)oxide compounds and the focus of our work here is initially on three representative systems, namely the pure hydroxide $Fe(OH)_2$, the mixed oxyhydroxide goethite FeOOH, and the iron oxide hematite Fe_2O_3.

In order to investigate the adsorption mechanisms of arsenic species on the iron (hydr)oxide minerals, we have first carried out a large number of interatomic potential-based simulations to examine the surface structures and stabilities of these minerals. We have presented the calculated surface energies for both dry and hydrated surfaces are listed in Table 2

The calculated surface energies of the three minerals show that in the case of dry Fe_2O_3, the iron terminated {001} surface is the most stable surface whereas the {012b} surface is the least stable one. Surface structure analysis indicated that the atoms on the {001} surface have relatively high coordination compared to other surfaces, which makes this surface less reactive. In general, the surface energies of the hydroxylated surfaces are lower than those of the corresponding dry surfaces. Upon hydration, the iron-terminated {001} surface becomes the least stable surface, although the reconstructed dipolar oxygen-terminated surface now becomes highly stable, due to the adsorbed water molecules filling oxygen vacancies at the surface.

Like hematite, the hydrated surfaces of goethite are more stable than the dry ones. In $Fe(OH)_2$, the surface energies for all surfaces are lower compared to those of Fe_2O_3 and FeOOH, which is mainly due to the fact that $Fe(OH)_2$ is an open layered structure.

Overall our calculated energies as well as structure analysis indicate that all the surfaces where the surface atoms are capped by OH groups have relatively low surface energies, which implies that the presence of hydroxyls groups helps to stabilise the surface.

3.4 Aqueous solutions in the vicinity of iron hydroxide surfaces

Although environmentally relevant immobilisation processes concern the adsorption from solution, the exact structure of aqueous solutions in contact with surfaces is not yet completely elucidated. The distribution and local concentration of the various species is difficult to observe experimentally. Coarse grained Surface Complexation Models do not include explicitly surface effects, but conversely, ultra precise *ab initio* calculations are unable to cope with the amount of water required. The intermediate solution, the use of classical atomistic modelling techniques, was also traditionally hampered by the fact that realistic ionic concentrations require the treatment of many water molecules (at a factor of 50 water molecules per ion at the already high concentration of 1 mol l^{-1}).

However, developments in computer power have now made it possible for simulations of both surface and solution at atomic resolution and in large enough quantity to produce statistically meaningful results. We have carried out many Molecular Dynamics simulations (DL_POLY code) of (Na^+/Cl^-)/ goethite interfaces, in an aqueous solution at different ionic strengths and surface charges. Our main observation is that the distribution of ions near the surface is not accurately described by the classical models of the electrical double layer.

It is considered that any surface has a structuring effect on the liquid it is in contact with, as can be observed in the density oscillations in figure 3. This density rippling in turn controls the salt concentrations. There is a direct correlation with the water density up to 10Å from the surface, but relatively unexpected,

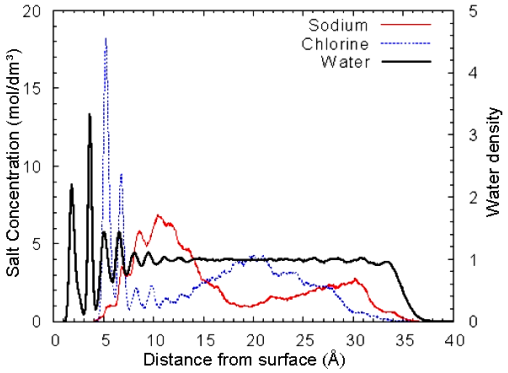


Figure 3 Salt concentrations and water density dependence on the distance from the surface of goethite.

broad, long-range oscillations continue further away. The explanation lies in the electrostatic potential, as pictured in figure 4. The structuring effect of the surface on the electrostatic potential of pure water has a longer range than what could be inferred from the simpler density curves. The addition of ions in solution only serves to reinforce this effect.

Real surfaces are likely to be charged. But the corresponding simulations show that the effect of the charged surface on the electrostatic potential in the solvent does not significantly differ from the neutral surfaces.

Additional calculations of surfaces of different minerals (calcite $CaCO_3$ and hematite Fe_2O_3) confirm these findings and suggest that the long range oscillatory behaviour of salt concentration is a consequence of the structuring presence of a surface on the electrostatic potential of the water.

We conclude that although the traditional double (stern)-layer models are correct in assuming that the ion distribution is controlled by the electrostatic potential, they fail to reproduce the distribution at medium/high salt concentration because the electrostatic contribution of the structured (layered) solvent is not taken into account.

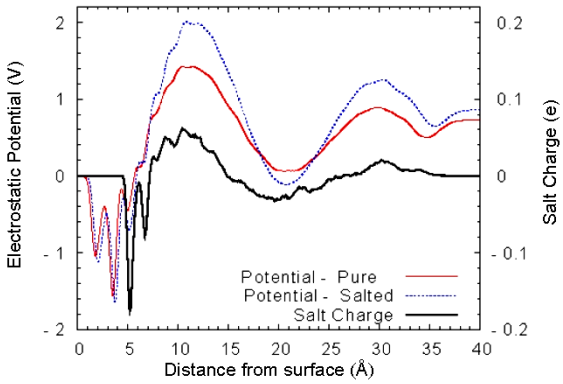


Figure 4 Electrostatic potential (in pure and salted solution) and charge dependence on the distance from the surface of goethite.

4. Conclusions and future work

Modelling of complex processes that occur in the environment is extremely challenging since simulations of large systems are required and complicated by the effects of many physical and chemical factors (e.g. T, P, pH). Although this large collaborative work is still in its early stages, it has already shown its promise to solve complex scientific problems with the support of grid technologies.

In the near future, we will extend the study to investigate the immobilization of a number of arsenic species by various iron-bearing minerals. A large number of calculations will be carried out to investigate the adsorption mechanisms of arsenic species of different oxidation state (e.g. As(III) and As(V)) on different iron-bearing mineral surfaces as well as studying the influence of varying conditions on the adsorption process. The outcome of the project will be a detailed atomic-level understanding of the chemical and physical processes involved in the immobilization of arsenic species by a variety of important iron minerals, which will benefit a wide range of communities, such as water treatment and environment agencies; academic and industrial surface scientists; mineralogists and geochemists.

Acknowledgements
This work was funded by NERC via grants NER/T/S/2001/00855**,** NE/C515698/1 and NE/C515704/1.

References

[1] D. J. Vaughan, "Arsenic", *Elements*, 2 71(2006).
[2] M. T. Dove and N. H. Leeuw, "Grid computing and molecular simulations: the vision of the *e*Minerals project", *Mol. Sim.*, **31**, 297 (2005).
[3] M. Calleja et al., "Collaborative grid infrastructure for molecular simulations: The *e*Minerals minigrid as a prototype integrated computer and data grid", *Mol. Sim.*, **31**, 303 (2005).
[4] M. T. Dove et al., "The eminerals collaboratory: tools and experience", *Mol. Sim.*, **31**, 329 (2005).
[5] R.P. Bruin, et al., "Job submission to grid computing environments", *All Hands Meeting* (2006).
[6] R.P. Tyer et. al., "Automatic metadata capture and grid computing", *All Hands Meeting* (2006).
[7] K.G. Stollenwerk, "Geochemical processes controlling transport of arsenic in groundwater: A review of adsorption". In: A.H. Welch, K. G. Stollenwerk (eds) Arsenic in groundwater: Geochemistry and Occurrence, Kluwer Academic publishers, Boston, pp67-100 (2003).
[8] M. Blanchard, M. Alfredsson, J.P. Brodholt, G.D. Price, K. Wright and C.R.A. Catlow, "Electronic structure study of the high-pressure vibrational spectrum of FeS2 pyrite". *J. Phys. Chem. B*, **109**, 22067 (2005).
[9] N.C. Tombs and H.P. Rooksby, "Structure of monoxides of some transition elements at low temperatures", *Nature*, **165**, 442 (1950).
[10] R.W.G. Wyckoff, *Crystal structures*, **1**, 346 (1963).
[11]K. Fujino, S. Sasaki, Y. Takeuchi and R.Sadanaga, "X-ray determination of electron distributions in forsterite, fayalite and tephroite", *Acta Cryst.*, **B37**, 513 (1981).
[12] R.L. Blacke, R.E. Hessevick, T. Zoltai, L.W. Finger, "Refinement of hematite structure", *Amer. Mineral.*, **51**, 123 (1966).
[13] A.F. Gaultieri and P. Venturelli, "In situ study of the goethite-hematite phase transformation by real time synchrotron powder diffraction", *Amer. Mineral.*, **84**, 895 (1999).
[14] P.S. Bagus, C.R. Brundle, T.J. Chuang and K. Wandelt, "Width of D-level final-state structure observed in photoemission spectra of fexo", *Phys. Rev. Lett*., **83**, 1229 (1977).
[15] I. Opahle, K. Koepernik and H. Escrig, "Full-potential band-structure calculation of iron pyrite", *Phys. Rev. B*, **60**, 14035 (1999).
[16] Q. Williams, E. Knittle, R. Reichlin, S. Martin and R. Jeanloz, "Structural and electronic-properties of Fe_2 SiO_4 –fayalite at ultrahigh pressures-amorphization and gap closure", *J. Geophys. Res. [Solid Earth]* **95**, 21549 (1990).
[17] A. Fujimori, M. Saeki, N. Kimizuka, M. Taniguchi and S. Suga, "Photoemission satellites and electronic-structure of Fe_2O_3", *Phys. Rev. B*, **34**, 7318 (1986).
[18] M. Ziese and M.J. Thornton *Materials for spin electronics*, (eds), Springer, (2001).
[19] P.K. Abraitis, R.A.D. Pattrick, D.J. Vaughan "Variations in the compositional, textural and electrical properties of natural pyrite: a review". *Int. J. Miner. Process.,* **74,** 41 (2004).
[20] K.S. Savage, T.N. Tingle, P.A. O'Day, G.A. Waychunas and D.K. Bird, "Arsenic speciation in pyrite and secondary weathering phases", *Appl. Geochem.,* **15**, 1219 (2000).
[21] M. Reich and U. Becker, "First-principles calculations of the thermodynamic mixing properties of arsenic incorporation into pyrite and marcasite". *Chem. Geol.,* **225,** 278 (2006).