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Publication date:
2011

Document Version
Publisher's PDF, also known as Version of record

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Citation (APA):
Sø, H. U. (2011). Adsorption of arsenic and phosphate onto the surface of calcite as revealed by batch experiments and surface complexation modelling. Kgs. Lyngby, Denmark: Technical University of Denmark (DTU).

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Helle Ugilt Sø

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Helle Ugilt Sørensen

PhD Thesis
March 2011

DTU Environment
Department of Environmental Engineering
Technical University of Denmark

Helle Ugilt Sø

**Adsorption of arsenic and phosphate onto the surface of calcite
as revealed by batch experiments and surface complexation modelling**

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The thesis will be available as a pdf-file for downloading from the homepage of the department: www.env.dtu.dk

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Printed by: Vester Kopi
Virum, March 2011

Cover: Torben Dolin

ISBN: 978-87-92654-30-4

Preface

This thesis presents the outcome of a PhD project carried out at Department of Environmental Engineering, Technical University of Denmark. The project was supervised by Associate Professor Rasmus Jakobsen at Department of Environmental Engineering, DTU, and Senior Researcher Dieke Postma and Senior Researcher Flemming Larsen at The National Geological Survey of Denmark and Greenland.

The following three scientific journal papers are part of this thesis:

- I. Sørensen H. U., Postma D., Jakobsen R. and Larsen F. (2008) Sorption and desorption of arsenate and arsenite on calcite. *Geochim. Cosmochim. Acta* **72**, 5871-5884.
- II. Sørensen H. U., Postma D., Jakobsen R. and Larsen F. (2011) Sorption of phosphate onto calcite; results from batch experiments and surface complexation modeling. *Geochim. Cosmochim. Acta*, in press.
- III. Sørensen H. U., Postma D., Jakobsen R. and Larsen F. (2011) Competitive adsorption of arsenate and phosphate onto calcite; experimental results and modeling with CCM and CD-MUSIC. *Geochim. Cosmochim. Acta*, submitted.

In the thesis these texts are cited by their roman numerals, e.g. Sørensen et al. (II). The papers are included as appendices in the thesis.

The papers are not included in this www-version but can be obtained from the Library at DTU Environment, Department of Environmental Engineering, Technical University of Denmark, Miljøvej, Building 113, DK-2800 Kgs. Lyngby, Denmark (library@env.dtu.dk).

March 2011, Helle Sørensen

Acknowledgements

I would like to thank my three wonderful supervisors: Dieke, Rasmus and Flemming. You have been very supportive throughout the duration of the project and always had time for me when I needed it. For that I am very grateful. **Dieke**, you always do a thorough job, but keep the elegant balance of not falling into the endless hole of insignificant details. You know how to help me when I am stuck or need to see my project from a different view because you are able to see it in a bigger perspective and to pin point the significance of my work. **Rasmus**, you are such a warm and welcoming person, and during my many talks with you we have come up with many constructive ideas that helped me get going. **Flemming**, your optimism, enthusiasm and foundation in the real world has helped this project on track.

I also want to thank my great colleagues at DTU Environment, especially all the PhD students, for making it a joy going to work.

Helle Sø

March 2011

En stor tak til min familie og venner for deres støtte.

En særlig tak til Rune, min dejlige mand og faste holdepunkt, og Balder, min vidunderlige søn.

Summary

The adsorption of phosphate, arsenate (As(V)) and arsenite (As(III)) onto synthetic calcite was studied in a series of batch experiments. The adsorption of the three ions was studied separately followed by studies of the competition between arsenate and phosphate. The experimental data was utilized to set up models for sorption of arsenate and phosphate onto calcite. This was done to enhance the understanding of the governing processes controlling adsorption as well as to develop a tool to predict the fate of arsenate and phosphate in a calcareous environment.

The adsorption was studied in eleven different calcite-equilibrated solutions that varied in pH, P_{CO_2} , ionic strength and activity of Ca^{2+} , CO_3^{2-} and HCO_3^- . To avoid the precipitation of phosphate or arsenic-containing minerals the experiments were conducted using a short reaction time (generally 3 h) and a low concentration of phosphate ($\leq 50 \mu\text{M}$) and arsenic ($\leq 33 \mu\text{M}$).

The results show that little or no arsenite adsorbs onto calcite within 24 h at initial arsenite concentration of $0.67 \mu\text{M}$. In contrast, both arsenate and phosphate adsorb readily and quickly onto calcite, with arsenate adsorbing faster than phosphate (adsorption is complete after 1 and 2-3 hours, respectively). Also desorption is fast and complete for both ions within 0.5 h. The reversibility of the sorption process indicates that neither arsenate nor phosphate is readily incorporated into the calcite crystal lattice under our experimental conditions.

The phosphate adsorption affinity for calcite is greater as compared to arsenate and the phosphate sorption isotherms are more strongly curved. However, the amount of both arsenate and phosphate adsorbed varied with the solution composition in the same manner. In particular, adsorption increased as the CO_3^{2-} activity decreased (at constant pH) and as pH increased (at constant CO_3^{2-} activity). The dependency on the carbonate activity indicates competition for sorption sites between carbonate and arsenate/phosphate, whereas the pH dependency is likely a response to changes in arsenate and phosphate speciation.

The primary effect of the ionic strength on phosphate sorption onto calcite is its influence on the activity of the different aqueous phosphate species. For the adsorption of arsenate onto calcite, the effect of the ionic strength is more pronounced and cannot fully be accounted for by changes in the aqueous activity of the different arsenate species.

Studies on competitive adsorption of arsenate and phosphate onto calcite show that the adsorption of arsenate onto calcite is strongly reduced by the presence of phosphate, whereas phosphate adsorption is only slightly reduced by arsenate addition. Simultaneous and sequential addition (3 hours apart) yields the same reduction in adsorption, underlining the high reversibility of the system. The reduction in adsorption of both arsenate and phosphate is most likely due to competition for the same sorption sites at the calcite surface, considering the similarity in sorption edges, pKa's and geometry of the two anions.

The adsorption of arsenate and phosphate in the single sorbate systems was modelled successfully using either the constant capacitance model (CCM) for calcite or the CD-MUSIC model for calcite. Generally the models capture the variation in arsenate and phosphate adsorption onto calcite as a function of solution composition. However, it was necessary to include two types of sorption sites in the CCM to reproduce the convex shape of the sorption isotherm, with the fraction of strong sites being greater in the phosphate model compared to the arsenate model.

By combining the models for single sorbate systems the competitive adsorption of phosphate and arsenate onto calcite in a binary sorbate system could be predicted with the CD-MUSIC model. This is in contrast to the CCM (also based on the single sorbate systems) which under-predicted the competitive effect. This clearly shows the importance of competition studies in validating multi-component models.

Extrapolation of the experimental results to calcite bearing aquifers suggests a large variability in the mobility of arsenic. Under reduced conditions, arsenite, which does not adsorb onto calcite, will dominate and, hence, arsenic will not be affected by the presence of calcite. In contrast, when conditions are oxidizing, arsenate is the predominant species and, because arsenate adsorbs onto calcite, arsenic mobility will be significantly lower. However, the presence of competing ions must be considered. Phosphate is often present at concentration levels sufficient to significantly reduce arsenate adsorption and this suggests that adsorption of arsenate onto calcite is of minor importance in most groundwater aquifers. This underlines the importance of including competitive effects when estimating the mobility of an ion in the environment.

Dansk resumé

I dette projekt er adsorption af fosfat, arsenat (As(V)) og arsenit (As(III)) til syntetisk kalcit blevet undersøgt i en række batchforsøg. Adsorptionen af de tre ioner blev først undersøgt individuelt, hvorefter konkurrencen mellem arsenat og fosfat blev belyst. Data fra det eksperimentelle arbejde blev benyttet til at opstille modeller for adsorption af fosfat og arsenat til kalcit. Dette blev gjort både for at øge forståelsen af de styrende processer for adsorptionen og for at udvikle et værktøj, som kan bruges til at forudsige arsenat og fosfats skæbne i kalkholdige jord- og grundvandsmiljøer.

Der blev udført batchforsøg med elleve forskellige opløsninger, alle i ligevægt med kalcit, men med forskellig pH, P_{CO_2} , ionstyrke og aktivitet af Ca^{2+} , CO_3^{2-} and HCO_3^- . For at undgå udfældning af mineraler med fosfat og arsen blev forsøgene gennemført med korte reaktionstider (generelt af 3 timers varighed) og med lave koncentrationer af fosfat ($\leq 50 \mu M$) og arsen ($\leq 33 \mu M$).

Resultaterne viser, at meget lidt eller intet arsenit adsorberes til kalcit inden for 24 timer ved startkoncentrationer på $0,67 \mu M$. Dette står i modsætning til både arsenat og fosfat, der begge adsorberes hurtigt. Arsenat adsorberes hurtigere end fosfat (reaktionen er forløbet færdig efter hhv. 1 og 2-3 timer). Begge ioner desorberes også let og hurtigt (indenfor en halv time). Reversibiliteten af sorptionsprocessen viser, at hverken arsenat eller fosfat let integreres i kalcitkrySTALLERNES gitterstruktur under vores eksperimentelle forhold.

Adsorptionsgraden af fosfat er større end for arsenat, og sorptionsisotermerne for fosfat er mere afbøjede. Men både mængden af adsorberet arsenat og fosfat er afhængig af opløsningens sammensætning på samme måde. Adsorptionen øges, når aktiviteten af CO_3^{2-} falder (ved konstant pH) og når pH stiger (ved konstant CO_3^{2-} aktivitet). Afhængigheden af karbonat-aktiviteten indikerer, at der er konkurrence om sorptionspladserne mellem karbonat og arsenat/fosfat, hvorimod afhængigheden af pH sandsynligvis skyldes, at specieringen af både arsenat og fosfat er afhængig af pH og at det ikke er alle arsenat- og fosfatspecier, der adsorberer til kalcit.

Ændring i ionstyrke påvirker adsorptionsgraden for både arsenat og fosfat. For fosfat kan dette henføres til ændringer i aktiviteten af de vandige fosfat-komplekser. Ændringer i ionstyrken påvirker i større grad adsorptionen af arsenat, og disse ændringer kan kun delvist tilskrives ændringer i aktiviteten af de

vandige arsenat-komplekser. Den yderligere effekt er muligvis elektrostatisk af natur.

Undersøgelser af konkurrencen mellem arsenat og fosfat for adsorption til kalцит viser, at adsorptionen af arsenat nedbringes markant når der er fosfat tilstede, hvorimod adsorptionen af fosfat kun påvirkes lidt, når der er arsenat i systemet. Der blev opnået samme adsorptionsgrad uafhængig af, om de to ioner blev tilsat samtidig eller med tre times mellemrum, hvilket understreger den høje reversibilitet af adsorptionen af både arsenat og fosfat. Reduktionen af både arsenat og fosfat skyldes højst sandsynlig konkurrence om de samme sorptionspladser, da både sorptionskanter, pKa'er og geometri ligner hinanden meget for de to anioner.

Adsorptionen af arsenat og fosfat i enkelt-ion systemer kunne modelleres med både den konstante kapacitans model (CCM) for kalцит og med CD-MUSIC modellen for kalцит. Overordnet gengiver modellerne adsorptionsgradens afhængighed af opløsningens sammensætning. Det var dog nødvendigt at indføre to forskellige sorptionspladser i CCM modellen for at kunne gengive afbøjningen på sorptionsisotermerne, hvor andelen af "stærke" pladser i modellen for fosfat var større end i modellen for arsenat.

Ved at sammensætte modellerne baseret på enkelt-ion systemer var det muligt at forudsige konkurrencen i dobbelt-ion systemet ved brug af CD-MUSIC modellen. Derimod forudsagde CCM modellen (også baseret på enkelt-ion systemer) en mindre grad af konkurrence end der blev observeret eksperimentelt. Dette viser hvorledes konkurrence studier kan bruges til at validere fler-komponent modeller.

De eksperimentelle resultater kan overføres til kalkholdige grundvandsmagasiner og antyder, at der vil være en stor variation i arsens mobilitet. Under anaerobe forhold vil arsen hovedsagelig være at finde som arsenit, der ikke adsorberes til kalцит og derfor vil mobiliteten ikke påvirkes af kalцит. Under aerobe forhold dominerer arsenat, som adsorberes til kalцит, og mobiliteten vil være markant lavere. I naturlige systemer må tilstedeværelsen af konkurrerende ioner tages med i overvejelserne. I grundvandsmagasiner er koncentrationsniveauet af fosfat ofte tilstrækkelig til at mindske adsorptionen af arsenat markant. Dette kan betyde, at adsorption af arsenat til kalцит er af ringe betydning for mobiliteten af arsen i kalkholdige grundvandsmagasiner, og viser hvor vigtigt det er at inkludere konkurrencen fra andre stoffer, når et stofs mobilitet skal vurderes.

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1 Introduction

The two elements arsenic (As) and phosphorous (P) are both found in the aquatic environment, arsenic primarily in the form of arsenite (As(III)) and arsenate (As(V)) and phosphorus in the form of phosphate (PO_4). Where phosphorus is essential to all living things, arsenic is highly poisonous and a known carcinogenic (Kohn et al., 2002; Smith et al., 2009).

The primary exposure of humans to arsenic is through water, with the highest arsenic concentrations found in groundwater. Areas with high levels of arsenic in groundwater include Argentina, Bangladesh, Chile, China, Hungary, India, Mexico, Romania, Taiwan, USA, and Vietnam (Smedley and Kinniburgh, 2002), with the South East Asian deltas being the most severely arsenic affected regions worldwide (Smedley, 2007). High concentrations of arsenic in groundwater are considered to be one of the world's most challenging inorganic drinking water contaminants (Smedley and Kinniburgh, 2002) and understanding the mobility of arsenic in groundwater aquifers is of high importance.

Phosphorus plays a central role in biological systems, in soils and aquatic sediments. It is an important element in plant nutrition and is often the limiting growth factor and is therefore added to agricultural fields as a fertilizer on a large scale. In combination with soil erosion and the release of wastewaters enriched in phosphorus this has led to an increase in the phosphate concentration in freshwater aquatic environments as well as in the oceans (Filippelli, 2008). The result has been the eutrophication of freshwaters and the coastal marine environment with a subsequent degradation of water quality and toxic algae blooms. The disturbance of the terrestrial phosphorous cycle by human activity (Filippelli, 2008) requires a proper understanding of the chemical processes regulating the aqueous phosphate concentration in order to predict the effects of our actions and measures.

One of the mechanisms controlling the bioavailability and mobility of both arsenic and phosphorus is their uptake and release by soils and sediments. The uptake of arsenic and phosphate by minerals may proceed via adsorption (the coordination of the ion to the mineral surface), co-precipitation (the ion substitutes for lattice ions and is thus incorporated into the mineral structure) and precipitation of arsenates or phosphates (Elzinga et al., 2006). Often arsenic and phosphate are present in concentrations so low that precipitation of arsenates or phosphates does not occur. Rather, adsorption is the initial step, after which co-

precipitation or formation of solid solutions can occur and adsorption is thus the basis for any solid phase uptake.

When predicting the mobility and bioavailability of arsenic and phosphate in the environment it is therefore important to understand the reactions of the ions with individual soil minerals. Calcite (CaCO_3) is a ubiquitous mineral in soils and aquifers, ranging from small amounts in some aquifer sediments to being the main constituent of limestone aquifers. For Denmark, the fate of arsenic in carbonate aquifers is of special interest as approximately one half of the Danish drinking water is abstracted from calcite bearing chalk and limestone aquifers. Previous studies have shown that phosphate, arsenite and arsenate can adsorb onto calcite (Suzuki et al., 1986; Román-Ross et al., 2006; Alexandratos et al., 2007). Thus, calcite can act as both a source and sink for arsenic and phosphate in soils and sediments thereby influencing the arsenic and phosphate fluxes. However, further knowledge on the adsorption of arsenic and phosphate onto calcite is needed; there is especially a need for models that can predict the fate of the ions in the natural environment.

Many different ions are present in groundwater and often more than one ion will compete for the same sorption sites at the mineral surfaces, resulting in increased concentration levels and mobility of the ions. Phosphate, for which concentrations in groundwater generally by far exceed those of arsenic, is known to compete with arsenate for sorption sites on iron oxides (Manning and Goldberg, 1996a; Jain and Loeppert, 2000; Gao and A Mucci, 2001; Zhao and Stanforth, 2001; Dixit and Hering, 2003) as well as on the clay minerals kaolinite, montmorillonite and illite (Manning and Goldberg, 1996b). The competition between arsenate and phosphate for sorption sites on the calcite surface has not been studied previously.

1.1 Objective

The overall objective of this thesis has been to enhance our understanding of the geochemistry of arsenic and phosphate in calcareous groundwater aquifers. This was approached by:

- studying adsorption of arsenic and phosphate onto calcite experimentally in single sorbate systems as well as binary sorbate systems

- setting up models for adsorption of arsenate and phosphate onto calcite to enhance the understanding of the governing processes controlling adsorption and to develop a tool for predicting the fate of arsenate and phosphate in a calcareous environment.

The first objective was met by studying the affinity of arsenic and phosphate for the calcite surface as a function of the ionic strength, pH and the activity of Ca^{2+} , CO_3^{2-} and HCO_3^- . The adsorption dependency on the solid:liquid ratio as well as the ability to desorb was examined. Finally, experiments aimed at examining the competition for sorption sites between arsenate and phosphate were carried out. All experimental work was carried out as batch experiments with synthetic calcite and solutions pre-equilibrated with calcite.

The second objective was met by implementing reactions for arsenate and phosphate adsorption in the two different models for the calcite-water interface: the constant capacitance model (CCM) first presented by van Cappellen et al. (1993) and further elaborated by Pokrovsky et al. (2000) and Pokrovsky and Schott (2002) and the CD-MUSIC model developed by Wolthers et al. (2008).

2 Arsenic

Arsenic (As) belongs to group 5A in the periodic table and it is classified as a heavy metalloid. Arsenic has not been proven to be an essential element for humans. On the contrary arsenic is highly poisonous and a known carcinogen (WHO, 2004; Smith et al., 2009). The toxicity of arsenic depends on its chemical form, its oxidation state and the solubility in the biological media. Generally the inorganic form is more toxic than the organic form and arsenite is more toxic than arsenate (Viraraghavan et al., 1999). Among the adverse health effects caused by arsenic poisoning is keratosis, cardiovascular diseases and lung, skin and bladder cancer (Smith and Steinmaus, 2009).

Arsenic is widely distributed throughout the Earth's crust. Arsenic is found as a major constituent in more than 200 minerals. The majority are ore minerals or alteration products of ore minerals and their abundance is limited. Arsenic is also found as a minor constituent in common rock-forming minerals. Due to the similarity in the chemical behaviour of arsenic and sulphur (S), arsenic is often found in sulphide minerals where it substitutes for S in the mineral structure. The most abundant sulphide mineral is pyrite that can be formed under reducing conditions in the sedimentary environment. Pyrite is unstable under aerobic conditions and arsenic will be released upon oxidation of the mineral. The chemical behaviour of arsenic is also similar to phosphorus (P) and arsenic is therefore found in many phosphate minerals, especially as a substitute for phosphorus in hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. Arsenic is also found in oxides and hydrous metal oxides, especially iron, manganese and aluminium oxides, either in the mineral structure or as an adsorbed species. The abundance of sulphides and oxides is much greater than of phosphate minerals and their contribution to the concentration of arsenic in sediments is therefore correspondingly larger (Smedley and Kinniburgh, 2002).

Arsenic is released to the aquatic environment by natural erosion processes (Viraraghavan et al., 1999) and most of the arsenic contamination of aquifers results from mobilization of arsenic under natural conditions. High arsenic concentrations are common in areas with geothermal activity. However, arsenic contamination is not exclusive to these areas, as arsenic can also be released to the aquatic environment through dissolution of minerals with built in arsenic, e.g. oxidation of sulphide minerals due to lowering of the water table, or reductive dissolution of iron oxides with arsenic as part of the mineral structure, or desorption from the surface of iron oxides due to changes in the chemical

composition of the groundwater (Smedley and Kinniburgh, 2002). Humanity has also contributed to the arsenic contamination through industrial discharges, mining activity, use of arsenic herbicides, wood preservation and crop desiccants, combustion of fossil fuels and as an additive in livestock feed. (Viraraghavan et al., 1999; Smedley and Kinniburgh, 2002).

Under natural conditions the concentration of arsenic in groundwater is normally below 10 µg/l (0.13 µM) and often less than 1 µg/l, but natural groundwater concentrations up to 5000 µg/l (67 µM) are found. For geothermal waters concentrations up to 50,000 g/l have been recorded. Groundwater arsenic is found under both reducing and oxidizing conditions as well as in aquifers affected by geothermal, mining and industrial activity. The majority of provinces affected by high arsenic concentrations are the result of natural occurrences of arsenic (Smedley and Kinniburgh, 2002).

2.1 Geochemistry of arsenic

Arsenic is found in four oxidation states, -3 (arsine), 0 (arsenic) +3 (arsenite) and +5 (arsenate), and in the aquatic environment both the organic and inorganic form is found. Several bacterial species and fungi can methylate inorganic arsenic by an initial reduction to arsenite and the addition of methyl groups. However, methylated arsenic is commonly below 1 µg/l and the predominant form of arsenic in natural aquatic systems is inorganic (Viraraghavan et al., 1999). The two dominant oxidation states for inorganic arsenic are the trivalent arsenite at moderately and strongly reduced conditions and the pentavalent arsenate in the aerobic environment. Cherry et al. (1979) suggested that the speciation of arsenic could be used to determine the dominant redox conditions if periods of years or longer are available for equilibration. However, more recent studies do not support this, as the redox kinetics are slow and the redox potential tends to be controlled by the major elements (O, C, N, S and Fe) (Welch et al., 1988; Masscheleyn et al., 1991; Smedley and Kinniburgh, 2002; Postma et al., 2007). Due to the slow redox kinetics, both arsenate and arsenite are found in most arsenic bearing groundwaters.

The speciation of arsenate and arsenite is determined by the pH as both arsenate and arsenite protonate/deprotonate depending on the pH of the solution. Between pH 3 and 11 the dominant forms of arsenate are the negatively charged H_2AsO_4^- and HAsO_4^{2-} , whereas below pH 9 the neutrally charged arsenite species H_3AsO_3^0 is dominant. This is also illustrated in Fig. 1. The geometric form of the

arsenite molecule is a trigonal pyramid, whereas arsenate forms a tetrahedron (Cheng et al., 1999).

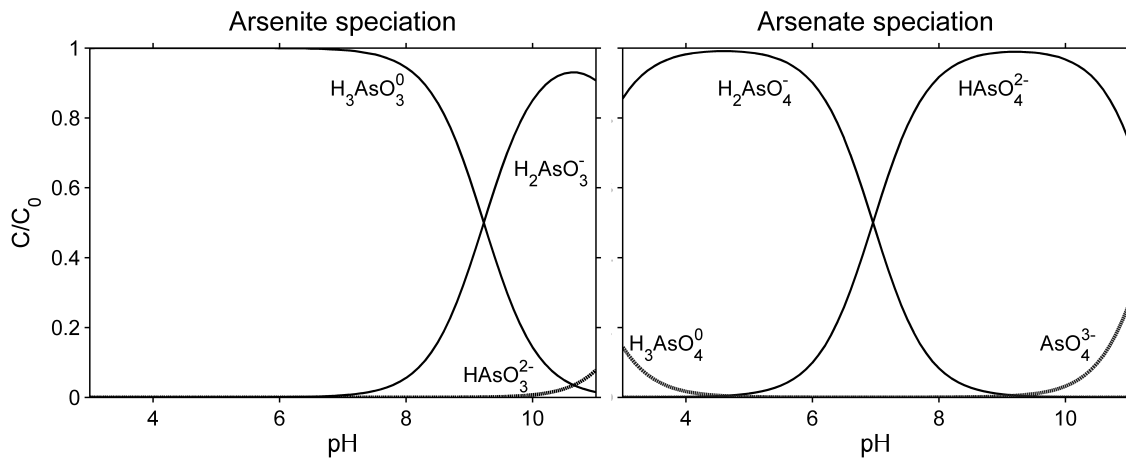


Fig. 1. Speciation of arsenite (As(III)) and arsenate (As(V)) as a function of pH as calculated with PHREEQC and the pK_a 's listed in Table 1.

2.2 Aqueous complexation

In solutions ions can form aqueous complexes with co-solutes. Formation of such complexes will lower the activity of most dissolved ions, which will lead to an increased solubility of minerals that include a complex-forming ion (Appelo and Postma, 2005) and it might decrease the adsorption of the ion onto mineral surfaces.

Arsenite can form aqueous complexes with carbonates. Kim et al. (2000) reported that the release of arsenic from sandstone was strongly correlated to the concentration of bicarbonate in the water. This was interpreted as dissolution of arsenic sulfide minerals followed by formation of arseno-carbonate complexes. However, the significance of the arseno-carbonate complexes for the mobilization of arsenic is disputed by Neuberger and Helz (2005). They confirm the formation of aqueous arsenite-carbonate complexes, but underline that the concentration of bicarbonate has to be elevated (> 0.04 M) for the complex $As(OH)_2CO_3^{2-}$ to exceed 1% of the arsenite concentration. Neuberger and Helz (2005) therefore conclude that arseno-carbonate complexes are not significant in natural aquatic environments.

In a sulfidic environment arsenite forms complexes with sulfide (thioarsenites). Four different thioarsenites dominate the arsenic speciation at sulfide concentrations above $50 \mu\text{M}$ at neutral pH (Wilkin et al., 2003). Such complexes might influence the mobility of arsenite under sulfate reducing conditions in

systems where the amount of reactive iron oxides is low compared to available sulfate.

Langmuir et al. (2006) propose the formation of aqueous arsenate complexes with the metals Ca, Fe, Mg and Mn. The presence of these complexes was derived from modelling, graphical methods and a comparison with the corresponding metal-phosphate complexes. Raposo et al. (2004) did not find experimental evidence for the formation of aqueous arsenate complexes with neither Ca nor Mg. This contradicts the experimental evidence presented by Mironov et al. (1995), who had experimentally shown the formation of aqueous Ca-arsenate complexes. The stability constants of these complexes were later adjusted to 23°C by Bothe and Brown (1999). Whether arsenate does or does not form aqueous complexes with Ca is important when studying the interaction between arsenate and calcite. Due to the similarity in the geochemical behaviour of arsenate and phosphate, the existence of calcium-arsenate complexes is very likely and we have therefore chosen to include these complexes in our geochemical calculations. The stability constants are given in Table 1.

Table 1. Equilibrium constants for the aqueous speciation of arsenite, arsenate and phosphate.

Reaction	logK
Arsenite	
$\text{H}_3\text{AsO}_3^0 \leftrightarrow \text{H}_2\text{AsO}_3^- + \text{H}^+$	-9.23 ^a
Arsenate	
$\text{H}_3\text{AsO}_4^0 \leftrightarrow \text{H}_2\text{AsO}_4^- + \text{H}^+$	-2.24 ^a
$\text{H}_2\text{AsO}_4^- \leftrightarrow \text{HAsO}_4^{2-} + \text{H}^+$	-6.96 ^a
$\text{HAsO}_4^{2-} \leftrightarrow \text{AsO}_4^{3-} + \text{H}^+$	-11.50 ^a
$\text{Ca}^{2+} + \text{H}_2\text{AsO}_4^- \leftrightarrow \text{CaH}_2\text{AsO}_4^+$	1.30 ^b
$\text{Ca}^{2+} + \text{HAsO}_4^{2-} \leftrightarrow \text{CaHAsO}_4^0$	2.66 ^b
$\text{Ca}^{2+} + \text{AsO}_4^{3-} \leftrightarrow \text{CaAsO}_4^-$	4.36 ^b
Phosphate	
$\text{H}_3\text{PO}_4^0 \leftrightarrow \text{H}_2\text{PO}_4^- + \text{H}^+$	-2.168 ^c
$\text{H}_2\text{PO}_4^- \leftrightarrow \text{HPO}_4^{2-} + \text{H}^+$	-7.207 ^c
$\text{HPO}_4^{2-} \leftrightarrow \text{PO}_4^{3-} + \text{H}^+$	-12.346 ^c
$\text{Ca}^{2+} + \text{H}_2\text{PO}_4^- \leftrightarrow \text{CaH}_2\text{PO}_4^+$	1.408 ^c
$\text{Ca}^{2+} + \text{HPO}_4^{2-} \leftrightarrow \text{CaHPO}_4^0$	2.736 ^c
$\text{Ca}^{2+} + \text{PO}_4^{3-} \leftrightarrow \text{CaPO}_4^-$	6.459 ^c

^a From Langmuir et al.(2006),

^b From Bothe and Brown (1999)

^c From the wateq4f database in PHREEQC (Parkhurst and Appelo, 1999).

3 Phosphorus

Phosphorous (P) belongs to group 5A in the periodic table and is classified as a non-metal. Phosphorous is essential to all biological activity in its dissolved form and phosphate minerals are a major structural component in vertebrates, with the phosphate mineral apatite being the main mineral in the human body (Kohn et al., 2002).

Phosphorous is widespread throughout the Earth's crust and found in many different geological environments; in igneous, metamorphic, and sedimentary rocks, as well as in low temperature sedimentary environments and as a precipitate from hydrothermal solutions. The most abundant phosphate minerals are in the apatite group, with fluorapatite and hydroxylapatite being the most common in nature. The apatite minerals all consist of phosphate (PO_4) coordinated to Ca in a hexagonal structure, but with different elements at the corners of the hexagonal cell depending on the specific apatite mineral, e.g. F in fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), OH in hydroxylapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) and Cl in chlorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$) (Kohn et al., 2002).

In the natural environment P is released through weathering of minerals, primarily apatite, via both physical and chemical weathering. The biological available P obtained through soil development (chemical weathering) is extensively recycled in the soils between biota and soil, before it is transported via rivers to the oceans. Human activities have greatly impacted the phosphorous cycle, due to extensive mining activity, as apatite is used in the production of fertilizers, detergents and phosphoric acid. The P derived is also utilized in motor fuels, insecticides and rust removers. The human activities, including application of fertilizers, deforestation and removal of P from the terrestrial cycle through sewage and waste handling, have doubled the P load from land to the oceans (Kohn et al., 2002; Filippelli, 2008).

3.1 Geochemistry of phosphate

The geochemistry of phosphate (PO_4) is in many aspects similar to that of arsenate. In the pentavalent oxidation state, in an aqueous solution, both P and As form a tetrahedron with four oxygen atoms. The arsenate oxyanion is slightly larger than phosphate, with the O-O distance being 2.6-2.8 Å for arsenate (Alexandratos et al., 2007) compared to 2.45 Å for phosphate (Khare et al., 2004). The phosphate ion undergoes stepwise protonation as pH decreases, as illustrated

in Fig. 2 The deprotonation of phosphate is displaced slightly towards higher pH compared to arsenate, with a pK_{a2} of 6.96 for arsenate and 7.21 for phosphate.

Like arsenate, phosphate forms complexes in aqueous solutions. Complexes are formed with both the major ions Ca, Mg, Na, K, Fe(II) and Fe(III) and trace ions such as Cu, Co, Cr(VI) and Sr (Parkhurst and Appelo, 1999). The stability constants for the Ca-phosphate complexes are listed in Table 1. The geochemical analogy between arsenate and phosphate has been utilized to calculate formation constants for aqueous arsenate complexes in lack of experimental data (e.g. Langmuir et al., 2006).

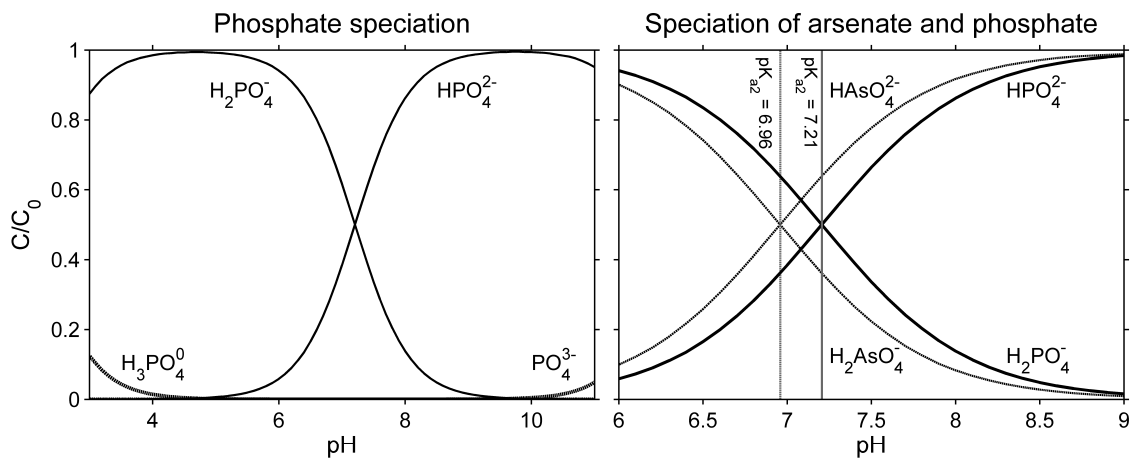


Fig. 2. Speciation of phosphate (solid black lines) and arsenate (grey lines) as a function of pH as calculated with PHREEQC and the pK_a 's listed in Table 1. The pK_{a2} of arsenate and phosphate are indicated by the vertical lines. The shift in the speciation of phosphate is displaced slightly towards higher pH compared to arsenate.

4 Calcite

Calcite (CaCO_3) is one of the most common minerals in the environment. It is predominant in the sedimentary environment and is primarily formed at relatively shallow depth and forms rocks in both shallow and deep water settings. It is an important mineral in the aquatic environment due to its important role in regulating the pH and alkalinity (Morse and Mackenzie, 1990). Calcite is used for a wide range of industrial purposes, e.g. paper production, building materials, agriculture, paints, plastics, ceramics, glasses, pharmaceuticals and cosmetics (Baltrusaitis and Grassian, 2009; Villegas-Jiménez et al., 2009).

Three different polymorphs of CaCO_3 are found in sediments and organisms: calcite, aragonite and vaterite. As they are polymorphs, they have different crystal structures and symmetry: calcite is trigonal-rhombohedral, aragonite is orthorhombic and vaterite is hexagonal. Calcite is the most abundant and ubiquitous form of the CaCO_3 polymorphs. It is the most stable polymorph at most temperatures and pressures encountered in the environment and aragonite and vaterite will therefore, over time, transform to calcite. Aragonite is also an abundant mineral, though not as common as calcite, whereas vaterite is rarely found in natural systems, and always under conditions where it is metastable with respect to calcite and aragonite (Morse and Mackenzie, 1990).

The lowest energy surface of calcite is the $\{1014\}$ plane of the calcite crystal that also characterises the rhombohedral morphology. This surface is the most stable and rhombohedral crystals are therefore also the most dominant morphology of calcite observed in the natural environment (Kerisit et al., 2006; Perry et al., 2007).

The synthetic CaCO_3 powder used in our batch experiments was confirmed to be calcite by X-ray diffraction (Sø et al., I). Scanning electron microscope images of the calcite revealed its morphology, as shown in Fig. 3 (Sø et al., II). The calcite crystals are rhombohedral and thus expose the $\{1014\}$ surface. The crystals have an average size of around $10\ \mu\text{m}$ (based on the images), but with many smaller crystals attached to the larger crystals. Generally the crystals have many irregularities in the form of pits, islands, stepped surfaces and rounded corners, the latter most likely resulting from mechanical abrasion.

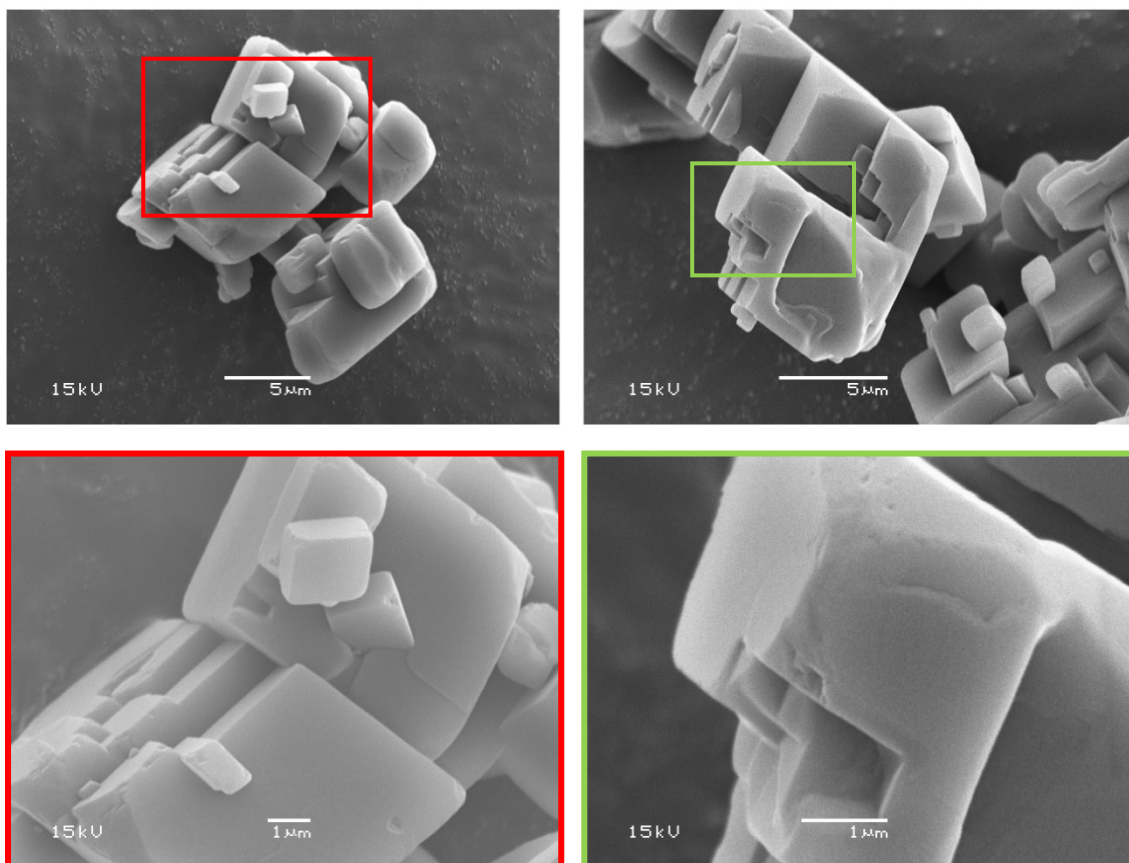
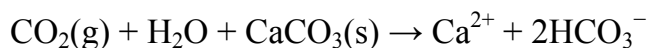


Fig. 3. Scanning Electron Microscopy (SEM) of the calcite used in this thesis. The two pictures at the bottom are close-up views of the marked areas in the pictures above. The SEM images were obtained by placing the dry calcite on carbon tape and coating it with gold. From Sørensen et al. (II).

Calcite is a widespread mineral phase in groundwater aquifers, where it functions as a buffer for groundwater pH and regulates alkalinity via its relatively rapid precipitation/dissolution kinetics. In the calcite-water-CO₂ system, the dissolution of calcite is coupled to the carbonate system as illustrated by the reaction below (Appelo and Postma, 2005).



This equilibrium reaction has been exploited in the experimental work of this thesis, where all experiments were carried out at equilibrium with calcite, but with different solution compositions by using different partial pressures of CO₂, and/or adding either calcium (as CaCl₂) or carbonate (as NaHCO₃). Another method often used in studies of adsorption onto calcite is addition of strong acid or base at constant CO₂ (often the atmosphere). At the same partial pressure of CO₂ the two approaches yield the same solutions with respect to pH and the activity of Ca²⁺, CO₃²⁻ and HCO₃⁻.

4.1 The calcite solid-solution interface

The surface of calcite has been widely studied, both in vacuum, under humid conditions and in bulk aqueous solutions; both experimentally and by modelling. The surface chemistry and adsorption on calcite depend on the conditions (vacuum/humid/aqueous solution) due to the difference in the interfacial free energy and chemical potential (Baltrusaitis and Grassian, 2009). Thus in this context, it is only relevant to focus on studies in aqueous solutions.

In the rhombohedral structure of calcite each Ca atom is octahedrally coordinated to six oxygen atoms, each from different CO₃ groups. The charge of Ca (+2) is shared between six oxygen atoms resulting in a charge of about +1/3 charge unit per bond. In the CO₃ group each O is coordinated to two Ca atoms and the CO₃ group is in this way coordinated to six Ca atoms with a charge of -1/3 charge unit per bond. The stoichiometry of Ca atoms and carbonate groups at the {1014} cleavage plane is 1:1 with a density of 5 Ca atoms/nm² (Möller and Sastri, 1974). This plane of calcite consists of alternating rows of Ca and CO₃ groups, with Ca, C and one O per CO₃ group in the same plane and the two remaining oxygen atoms equally above and below that plane. At the {1014} surface of calcite only one Ca-O bond per Ca is broken and none of the C-O bonds are broken. A surface Ca is thus under-coordinated as it is missing one oxygen atom and the unsatisfied charge of Ca is approximately +1/3, whereas the under-coordinated CO₃ group is missing one Ca atom resulting in an unsatisfied charge of -1/3 (Stipp, 1999).

To compensate for the under-coordination at the surface the crystal lattice is slightly restructured. In the aqueous environment the crystal structure at the surface undergoes slight relaxation, as shown with atomic force microscopy (Liang et al., 1996). Greater details of the lattice distortion were obtained using specular and non-specular X-ray scattering, showing a small displacement of the Ca and CO₃ groups and slight rotations of the CO₃ groups in the first and second layer of the crystal. The ions were displaced slightly towards the bulk crystal in the first layer and slightly towards the solution in the second layer (Geissbühler et al., 2004).

The distortion of the crystal structure is less pronounced in aqueous solutions compared to calcite crystals in vacuum, as some of the charge imbalance resulting from under-coordination is compensated by water, where the Ca ion coordinates to the oxygen in the water and the CO₃ forms hydrogen bonds with

the water. In this way the presence of water stabilizes the surface and reduces the surface energy (Wright et al., 2001).

Both experimental and modelling studies show that the water at the calcite surface is highly structured, with one or two hydrated layers; however, the precise structure and number of hydrated layers is debated.

X-ray reflectivity experiments reveal an adsorbed monolayer of hydroxyl species bonding to the Ca atoms at a distance of 2.50 ± 0.12 Å above the surface Ca atoms. The oxygen atoms were assumed to be placed on top of the Ca atoms. The technique is relatively insensitive to hydrogen atoms and the hydroxyl species might be OH, OH₂ or OH₃ or a combination of the three (Fenter et al., 2000). Atomistic computer simulations of the calcite surface with a single layer of water molecules (Wright et al., 2001) also showed that the oxygen of the water is placed above the Ca atom, with a Ca-O_w distance of 2.55 Å (thus slightly larger than the C-O distance of 2.37 Å in the crystal lattice), in agreement with Fenter et al. (2000).

By use of specular and non-specular X-ray scattering it was possible to determine both the vertical and lateral positions of water. A two-component hydrated layer at the calcite surface was observed, with no additional layering of water beyond the hydration layer (Geissbühler et al., 2004). The layer consists of two water molecules having distinct heights of 2.3 ± 0.1 and 3.45 ± 0.2 Å. The lower water molecules are laterally displaced with respect to the surface Ca atoms, thus contrasting the simulations by Wright et al. (2001).

Raiteri et al. (2010) based their study on a force-field description of the interaction-energy. The model reproduces the thermodynamics of the aqueous calcium carbonate system (the free energies of components in solution, the energy difference for the calcite-aragonite phase transition, and the dissolution enthalpy for calcite). The model result showed two monolayers of water at a Ca-O_w distance of approximately 2 and 3.5 Å. The distances are comparable to the experimental results of Geissbühler et al. (2004), though Geissbühler et al. (2004) describe it as a two-component layer rather than two separate layers. The first layer of water molecules is situated with the O's approximately above the Ca atoms and the H's forming weak hydrogen bonds with the CO₃ groups. The second layer is situated with the H's approximately above the CO₃ groups forming strong hydrogen bonds with the CO₃ groups (see Fig. 4).

Raiteri et al. (2010) also modelled dissolution and growth at the flat {1014} surface and showed that direct dissolution from the flat surface was highly

improbable. Applying the model to adsorption of Ca^{2+} and CO_3^{2-} onto the flat surface revealed that CO_3^{2-} ion only weakly binds to the flat surface, whereas association of Ca^{2+} with the surface was only predicted in the presence of a previously adsorbed CO_3^{2-} ion. They thus concluded that growth and dissolution of calcite most likely occurs from defects, such as kink sites. This is in agreement with microscopy studies (Dove and Hochella, 1993; Paquette and Reeder, 1995; Reeder, 1996; Teng et al., 1998; Teng et al., 1999; Teng, 2004) that have shown that dissolution and growth primarily take place at high energy defect sites, such as step-edge kink sites, under conditions near equilibrium.

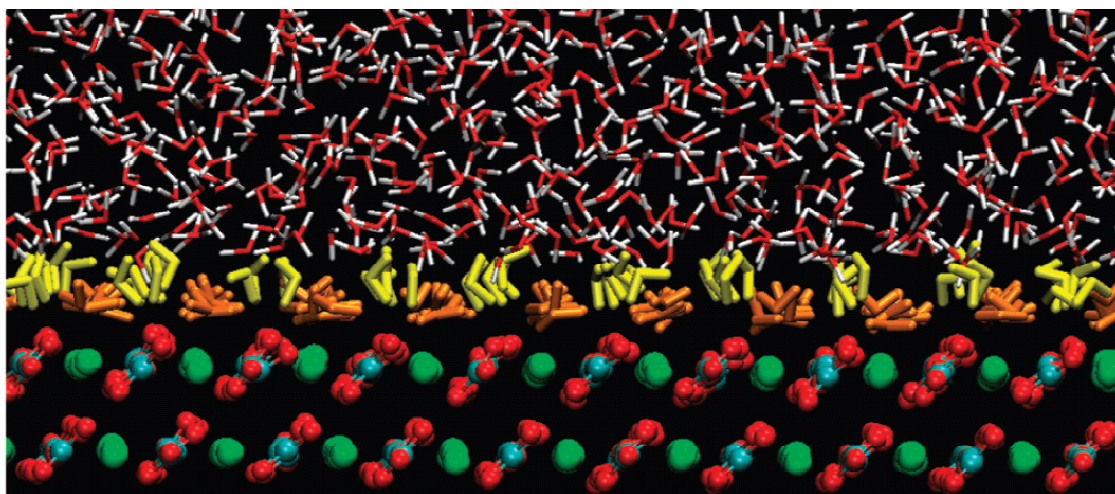


Fig. 4. NVT simulation of the water structure at the $\{1014\}$ calcite surface. Oxygen, carbon, calcium, and hydrogen coloured red, blue, green, and white, respectively. The first layer of water is shown in orange, the second layer in yellow. From Raiteri et al. (2010) with permission from American Chemical Society.

Macroscopic investigations of the calcite-solution interface have studied the electrical properties of the calcite surface and its dependency on solution composition. This has been done via electrokinetic methods, with micro electrophoresis and streaming potential being the most frequently used (Madsen, 2001). Literature reviews have shown large differences in the experimental results (Madsen, 2001; Wolthers et al., 2008). Madsen (2001) demonstrates that there is no clear difference between the type of electrokinetic methods, nor the solid:liquid ratio and the review underlines the problem of limited experimental protocols in terms of specifying pH-adjustments, stirring rates and sample histories.

The measured ζ -potential is not a measure of the potential at the surface, but the potential at a certain distance from the surface and is defined as a slipping plane separating the charged surface from the solution (Madsen, 2001). Based on the response in the ζ -potential to the solution composition the potential determining ions are deduced. Several studies have shown that in pure aqueous solutions the lattice ions Ca^{2+} and CO_3^{2-} are the potential determining ions (Foxall et al., 1979; Thompson and Pownall, 1989; Pierre et al., 1990; Cicerone et al., 1992). However, others also include H^+ , OH^- , CaOH^+ and HCO_3^- (Somasundaran and Agar, 1967; Mishra, 1978; Amankonah and Somasundaran, 1985; Somasundaran et al., 1985; Stumm, 1992; van Cappellen et al., 1993; Moulin and Roques, 2003). Madsen (2001) concludes, based on the literature review, that Ca^{2+} and CO_3^{2-} are the only potential determining ions and that the effect of pH and partial pressure of CO_2 is only indirect, in the sense that they determine the activities of Ca^{2+} and CO_3^{2-} in the solution.

Despite the awareness of Ca^{2+} and CO_3^{2-} being potential determining ions, adsorption of these ions was not observed in the microscopic studies (Fenter et al., 2000; Geissbühler et al., 2004). As pointed out by Fenter et al. (2000) the method is largely insensitive to the speciation at step edges and kink sites and adsorption of Ca^{2+} and CO_3^{2-} at these sites could not be excluded. If an ion is potential determining it needs to be within the slipping plane (often also termed the shear plane), but not necessarily adsorbed directly to the surface. This line of thought is the background for the conceptual model for the calcite surface presented by Stipp (1999), where the potential determining ions are situated just above the hydrolyzed layer. As the charge of the calcite surface is delocalized both by the hydrated layer and the adsorbed Ca^{2+} and CO_3^{2-} , the density of adsorbed Ca^{2+} and CO_3^{2-} is less than at the calcite surface.

5 Adsorption onto calcite

Calcite is considered a potentially important sink for both anions and cations due to the reactive nature of calcite and its ubiquity in groundwater aquifers. Several studies on the mobility of both anions and cations have therefore focused on adsorption and co-precipitation with calcite.

The studies have utilized a wide range of methods, including several spectroscopic techniques (Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), extended X-ray absorption fine structure (EXAFS), differential interference contrast (DIC) surface imaging, synchrotron micro-X-ray fluorescence (μ -XRF), X-ray adsorption near-edge structure (XANES)) as well as macroscopic studies (batch experiments and flow-through reactors) (e.g. Stipp et al., 1992; Martin-Garin et al., 2003; Alexandratos et al., 2007; Yokoyama et al., 2009). Also the time frame of the experiments varies greatly, between minutes to several years (Elzinga et al., 2006).

5.1 Uptake

Adsorption of both cations (Ba, Cd, Co, Cu, Fe(II), Mn, Ni, Pb, Sr, and Zn) and anions (As(V), As(III), Cr(VI), Ga(III), P(V), Se(IV), S(VI)) on calcite has been reported, e.g. (Cowan et al., 1990; Zachara et al., 1991; van der Weijden and Comans, 1997; Pokrovsky et al., 2004; Elzinga et al., 2006; Román-Ross et al., 2006; Tang et al., 2007; Mettler et al., 2009; Sørensen et al., I, II). The affinity of the ions for calcite varies greatly. For divalent metals Zachara et al. (1991) showed that the uptake generally depends on the ionic radii. The cations Ba and Sr, having greater ionic radii than Ca, have a very low affinity for calcite, whereas Cd, Mn, Zn, Co and Ni, all with smaller ionic radii than Ca, have a stronger affinity for calcite. The largest uptake was seen for Cd, having an ionic radius very close to that of Ca, and the affinity decreased with decreasing ionic radius as the general trend. A similar comparative study has not been made for the uptake of anions on calcite. However, as noted by Sørensen et al. (III), the difference in the uptake of the oxyanions arsenate and phosphate on calcite might be related to the size of the two anions, with phosphate being closer in size to that of carbonate.

In contrast to Román-Ross et al. (2006), who reported adsorption of arsenite onto calcite, Sørensen et al. (I) observed no significant adsorption of arsenite onto calcite in batch experiments, as illustrated in Fig. 5. The two studies were conducted at the same pH. Unfortunately, no experimental details other than the pH were provided

by Román-Ross et al. (2006) and thus, the reason for the discrepancy can not readily be identified. The adsorption of arsenite onto calcite was studied by Sørensen et al. (I) in three different solutions. Despite a great variation in the concentration of Ca (0.15-23.9 mM) and alkalinity (0.29-8.63 meq/l) among the three solutions and a calcite surface area of up to 130 m²/l no significant adsorption of arsenite was observed.

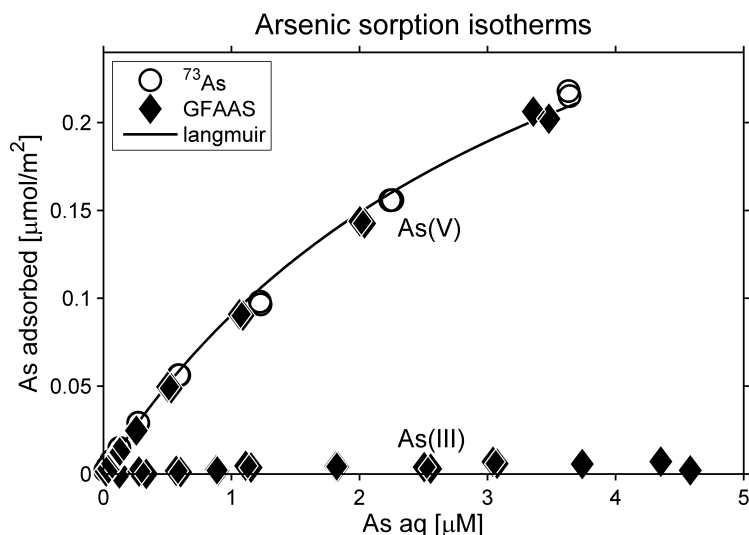


Fig. 5. Sorption data and isotherm for arsenate (As(V)) and arsenite (As(III)) onto calcite at a calcite surface area of 28 m²/l (pH 7.53 and pCO₃²⁻ 6.50). The two data sets for arsenate were measured as the activity of ⁷³As and the total aqueous arsenate concentration by graphite furnace AAS. The concentration of arsenite was measured by graphite furnace AAS. The line is a Langmuir isotherm fitted to the experimental data ($b = 0.28$ l/μmol and $S_{\max} = 0.42$ μmol/m²). From Sørensen et al. (I) with permission from Elsevier Ltd.

5.2 Desorption

Desorption studies have been conducted for several of the ions, and the reversibility is generally used as an indicator of the uptake being adsorption rather than precipitation or solid-state diffusion. Complete desorption of arsenate and phosphate from calcite was observed by Sørensen et al. (I, II) and Millero et al. (2001), whereas Suzuki et al. (1986) and van der Weijden and Comans (1997) observed a maximum of 70% desorption of phosphate depending on the initial concentration. At very low concentrations phosphate was irreversibly incorporated into the calcite lattice, but as the initial phosphate concentration increased, Suzuki et al. (1986) observed an increase in the extent of desorption. The concentrations employed by Sørensen et al. (II) were higher than used by Suzuki et al. (1986) and the complete desorption shown by Sørensen et al. (II) is thus in line with

the trend reported by Suzuki et al. (1986). A small fraction might be irreversibly incorporated into the calcite lattice, but if it is within the experimental uncertainty it would not be observed.

The uptake of Zn on calcite has been reported to be fully reversible over a 1000 h period (Tertre et al., 2010), whereas Zachara et al. (1991) reported only 80% desorption. In the same study Zachara et al. (1991) showed that >80% of Co and Ni desorbed, whereas the reversibility of Mn and Cd uptake was only 10-25%. The difference in reversibility was linearly correlated to the single ion hydration energy, which indicated that Mn and Cd dehydrate upon adsorption, whereas Zn, Co and Ni do not. The reversibility of Cd uptake by calcite has also been studied by other groups, e.g. (Stipp et al., 1992; van der Weijden et al., 1994; Martin-Garin et al., 2003; Ahmed et al., 2008), all showing desorption hysteresis. An increase in Cd uptake with time has been linked to decreasing reversibility and the process was by Stipp et al. (1992) characterized as solid-state diffusion into the calcite crystal lattice. The reversibility of Cd uptake is also dependent on solution composition, with the highest degree of reversibility observed at low aqueous Ca concentrations (van der Weijden et al., 1994) and the highest degree of reversibility is thus linked to the highest fractional adsorption of Cd. The correlation between fractional adsorption and reversibility was also found for Pd uptake on calcite (Rouff et al., 2005). In their study complete desorption at pH 8.2 was reported, whereas hysteresis was observed at higher and lower pH, due to co-precipitation. The variation in co-precipitation, and thus also reversibility, with solution composition was ascribed to differences in fractional adsorption of Pb in combination with variations in the rate of near-surface dynamic exchange of Ca and CO₃ species among the different solutions (Rouff et al., 2005).

The great variation in uptake reversibility among the different ions and solution composition underlines the importance of conducting desorption studies to better understand the processes, which again is an important prerequisite for setting up models and predicting the fate of the ions in the environment.

5.3 Incorporation into the calcite lattice

Co-precipitation experiments with calcite and trace ions have shown that the calcite crystal lattice is capable of incorporating many different ions in the crystal structure. As the ions are often different in size and charge than the Ca and CO₃ group, the incorporation of the trace ion often leads to distortion of the crystal structure. Cations substitute for Ca in the calcite lattice, as for example observed

for Cu (Schosseler et al., 1999), Co, Zn, Pb and Ba (Reeder et al., 1999), whereas anions substitute for the CO₃ group.

Despite the difference in the geometry of the CO₃ group (trigonal planar) and selenite, (trigonal pyramidal), the selenite ion (SeO₃) is incorporated in the calcite lattice during co-precipitation experiments, resulting in an expansion of the calcite unit cell (Aurelio et al., 2010). Selenite becomes incorporated in the calcite surface at the CO₃ sites when freshly cleaved calcite crystals are added to solutions, near calcite saturation, containing selenite (Cheng et al., 1997). An equivalent experiment with selenate (SeO₄) showed no significant incorporation in the calcite surface (Cheng et al., 1997). However, previous studies of co-precipitation with the tetrahedral shaped selenate ion have shown that selenate can be incorporated into the calcite lattice substituting for the carbonate group (Lamble et al., 1995; Staudt et al., 1994; Reeder et al., 1994).

Arsenite (AsO₃), a trigonal pyramid like selenite, substitutes for the carbonate group in the calcite crystal both in co-precipitation experiments (Román-Ross et al., 2006) and under experimental conditions similar to the experiments with selenite described above (Cheng et al., 1999). At identical experimental conditions, the tetrahedral arsenate (AsO₄) was not incorporated in the calcite surface (Cheng et al., 1999). These results are, however, contradicted by a later study of Yokoyama et al. (2009), who found that arsenate was incorporated into the calcite lattice to a much larger degree than arsenite (a factor of 200) and that the arsenic incorporated in the experiment with arsenite was in fact arsenate even though the aqueous phase contained >96% arsenite. The incorporation of arsenate in the calcite lattice during co-precipitation has also been shown by Alexandratos et al. (2007). Besides arsenate and selenate, tetrahedral anions like sulphate (SO₄) and chromate (CrO₄) may also be incorporated at carbonate sites during co-precipitation with calcite, despite the fact that the incorporation of tetrahedral ions requires a significant distortion or disruption of the crystal structure (Staudt et al., 1994; Tang et al., 2007).

The large degree of uptake reversibility for most of the anions and cations indicates that co-precipitation or recrystallization of calcite is necessary for the incorporation of ions into the crystal structure. This is also supported by the study by Elzinga et al. (2006), who detected no sign of incorporation of Cu, Zn and Pb over a 2½ year reaction period in solutions in equilibrium with calcite. The ions remained coordinated to the calcite surface as inner-sphere complexes over the entire period (Elzinga et al., 2006), despite that all three divalent metals can be incorporated in the calcite lattice (Schosseler et al., 1999; Reeder et al.,

1999). Due to the reactive and dynamic nature of calcite, co-precipitation or recrystallization of calcite is not unlikely to take place in the natural environment, where the degree of calcite saturation may vary, leading to a more effective trapping of the ions by incorporation into the crystal lattice.

5.4 Coordination of ions at the calcite surface

The coordination of anions and cations when binding to the calcite surface has not been as extensively studied. In line with incorporation, the cations adsorb at Ca sites coordinating to the CO₃ group, whereas the anions adsorb at the carbonate sites coordinating to Ca. The cation Pb(II) forms mononuclear inner-sphere complexes at the calcite surface, coordinating to the carbonate group (Rouff et al., 2004) and Schosseler et al. (1999) showed that Cu dehydrates upon adsorption and coordinates to three or four carbonate groups, most likely at steps or kink sites. The anion arsenate also forms inner-sphere complexes on calcite, coordinating to two or three Ca atoms (Alexandratos et al., 2007).

5.5 Sorption dependence on solution composition

The adsorption of both anions and cations onto calcite is dependent on the solution composition. This dependency is often shown graphically as a plot of the sorption edge: adsorption as a function of either pH or the activity of Ca²⁺ or CO₃²⁻. The use of the pH has its origin in the vast literature on oxides, where the sorption edge usually is plotted as a function of pH, as H⁺ and OH⁻ are the potential determining ions (pdi's). The pdi's are considered to influence adsorption in two ways; i) because the pdi's affect the particle surface charge and ii) by competing with the ion for sorption sites at the surface. For calcite there is a consensus that Ca²⁺ or CO₃²⁻ are the potential determining ions, whereas the role of H⁺, OH⁻ and HCO₃⁻ is debated (see section 4.1). By transferring the knowledge gained from adsorption studies on oxides to calcite, adsorption onto calcite should be studied as a function of either Ca²⁺ or CO₃²⁻ as the primary focus. However, the influence of pH must not be neglected, as H⁺ and OH⁻ might also be pdi's, but also because pH influences the speciation of anions through protonation and deprotonation reactions and the speciation of cations by affecting the formation of hydroxy complexes.

Adsorption of anions or cations in the calcite-water-CO₂ system is, in all its simplicity, a complex system to study, as the parameters of the system are linked. The activity of Ca²⁺ is inversely correlated to the activity of CO₃²⁻ in a solution in equilibrium with calcite and it is therefore not possible to change one while

keeping the other constant. The pH affects both the carbonate system as well as the protonation of the anion and the formation of hydroxy complexes of the cation. In addition the speciation of many anions is also influenced by the activity of Ca^{2+} via Ca-complexation, while many cations are influenced by the activity of CO_3^{2-} via carbonate-complexation.

This interdependency of parameters can partly be overcome by for example varying the activity of Ca^{2+} at constant pH and in another series of experiments exploring the opposite, as done by Suzuki et al. (1986). It was found that phosphate adsorption increased with increasing activity of Ca^{2+} (at constant pH), but also that adsorption increased with increasing pH (at constant activity of Ca^{2+}). The effect of Ca^{2+} on phosphate adsorption was greater than the effect of pH. This thorough approach is unfortunately rarely seen in the literature.

The study of phosphate adsorption onto calcite by Sørensen et al. (II) is in line with the work done by Suzuki et al. (1986), but explores a lower pH interval (6.5-9.1 compared to 7.5-10.5), including five solutions at pH 7, covering a wide range in the activity Ca^{2+} ($\text{pCa}^{2+} = 2.0\text{-}5.1$) and CO_3^{2-} ($\text{pCO}_3^{2-} = 3.4\text{-}6.6$). The adsorption of phosphate greatly depends on the solution composition, as illustrated in Fig. 6 that plots the amount of adsorbed phosphate as a function of the activity of CO_3^{2-} and HCO_3^- respectively. Overall, a negative log-log relation between phosphate sorption and the carbonate activity is seen, whereas the relation with bicarbonate is less clear. The decrease in sorption of phosphate onto calcite with increasing carbonate activities is probably due to an increasing competition between phosphate and carbonate for sorption sites at the calcite surface.

The relationship between phosphate adsorption and the activity of CO_3^{2-} (or Ca^{2+}) was also shown by Suzuki et al. (1986), who also reported a secondary effect of pH, with increasing adsorption as pH increased (at constant Ca^{2+} activity). This is also seen from Fig. 6: near $\log\{\text{CO}_3^{2-}\} = -5.5$ the amount of phosphate adsorbed increases towards higher pH values. The most probable explanation for this is the increase in the activity of more deprotonated phosphate species with increasing pH.

An identical experimental setup for the study of phosphate adsorption by Sørensen et al. (II) was also used to study adsorption of arsenate onto calcite (Sørensen et al., I). The dependence of arsenate adsorption on the activity of CO_3^{2-} is strikingly similar to what is seen for phosphate, indicating that the mechanisms and parameters controlling arsenate and phosphate adsorption are the same. However, the sorption affinity of phosphate for calcite is much stronger than that of arsenate.

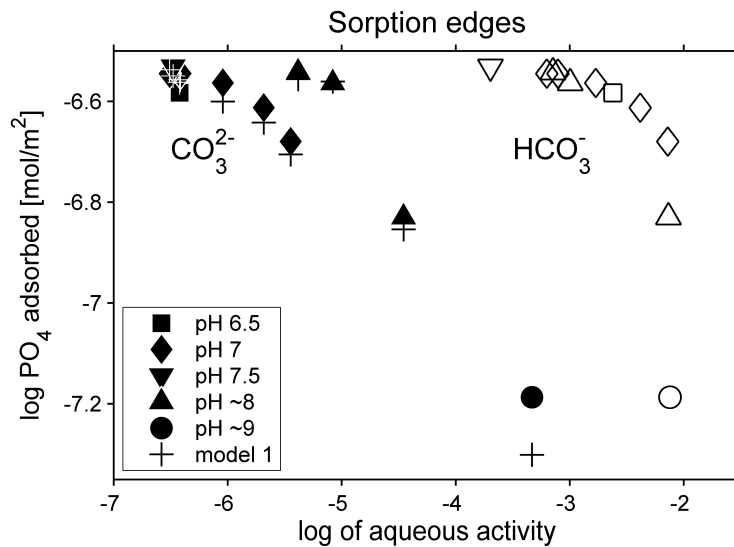


Fig. 6. Adsorption of phosphate as a function of the activity of CO_3^{2-} (closed symbols) and HCO_3^- (open symbols) at initial PO_4 concentrations of $6.7 \mu\text{M}$ in calcite-equilibrated solutions. Constant capacitance model results are shown as crosses. From Sørensen et al. (II) with permission from Elsevier Ltd.

Zachara et al. (1991) studied sorption of the divalent metals Co, Ni, Mn, Cd and Zn in calcite-equilibrated solutions and showed that their extent of sorption was negatively log-log linearly correlated to the aqueous activity of Ca^{2+} . The strong dependence on the activity of Ca^{2+} was interpreted as competition for sorption sites between Ca^{2+} and the divalent metal ions. Accordingly adsorption could be modelled as simple ion exchange between Ca^{2+} and the uncomplexed divalent metal ion (Me^{2+}). Also van der Weijden et al. (1994) showed that adsorption of Cd depends on solution composition, with sorption of Cd^{2+} increasing as the aqueous activity of Ca^{2+} was decreasing. Also here it was possible to model the adsorption dependence on solution composition as ion exchange between Cd^{2+} and Ca^{2+} , with a logK value comparable to the value of Zachara et al. (1991).

The adsorption of the anion $\text{Ga}(\text{OH})_4^-$ was studied by Pokrovsky et al. (2004), while Cowan et al. (1990) studied sorption of the anion selenite (SeO_3^-) in calcite-equilibrated solutions with and without the anion phosphate and the cation magnesium. The sorption of the anions decreased with increasing pH, while the opposite was observed for the cation (Mg). The concomitant change in the activity of Ca^{2+} and CO_3^{2-} prevents an interpretation of whether the adsorption is influenced by pH or the activity of $\text{Ca}^{2+}/\text{CO}_3^{2-}$ or a combination of the two parameters.

5.6 Competitive adsorption

More than one ion might compete for the same sorption sites on the calcite surface and this may increase the aqueous concentrations and mobility of the adsorbing ions. Only three studies have investigated competitive sorption onto calcite. Van der Weijden and Comans (1997) studied competitive adsorption of phosphate and Cd, while Cowan et al. (1990) studied the adsorption of selenite in the presence of either phosphate, sulfate, or magnesium, and Sørensen et al. (III) studied the arsenate-phosphate system. In all cases mutually reduced adsorption was observed in the anion-anion systems, whereas no effect on selenite adsorption was observed in the presence of magnesium (anion-cation system).

The process of sequential addition is relevant to study as this is likely to happen in the natural environment where the mineral surface will be exposed to one ion before the other. If sequential exposure changes the degree of adsorption it has to be taken into consideration when estimating the mobility of the ion in the environment. Studies of arsenate and phosphate adsorption onto iron oxides have shown that adding the two ions sequentially results in surface coverages different from adsorption experiments where the two ions are added simultaneously (Liu et al., 2001; Zhao and Stanforth, 2001; Zhang et al., 2008). When added sequentially, the first ion, to some extent, inhibits the adsorption of the second ion. This is in contrast to adsorption onto calcite, where no difference in adsorption was observed between the simultaneous and sequential addition for neither the phosphate-Cd system (van der Weijden and Comans, 1997) nor the phosphate-arsenate system (Sørensen et al., III) in batch experiments. This is illustrated in Fig. 7 for the arsenate-phosphate system, where arsenate being the first ion in panels a and b, and phosphate the first ion in panels c and d. After 3 hours with a binary sorbate system the aqueous concentration of both arsenate and phosphate reaches a steady state, as no further changes were observed the following 21 hours (data not shown).

When phosphate is added as the first ion, a peak in the phosphate concentration is observed after addition of arsenate (Fig. 7d). This is not the case when arsenate is added as the first ion (Fig. 7a) and the continuous increase in the arsenate concentration during the first hour after phosphate addition clearly indicates that the concentration of arsenate did not peak between measurements. The peak in the phosphate concentration indicates that some rearrangement in the binding of phosphate takes place when arsenate is adsorbed, e.g. the coordination mode of phosphate changes or phosphate is moved from sites of high arsenate affinity to sites of lower arsenate affinity.

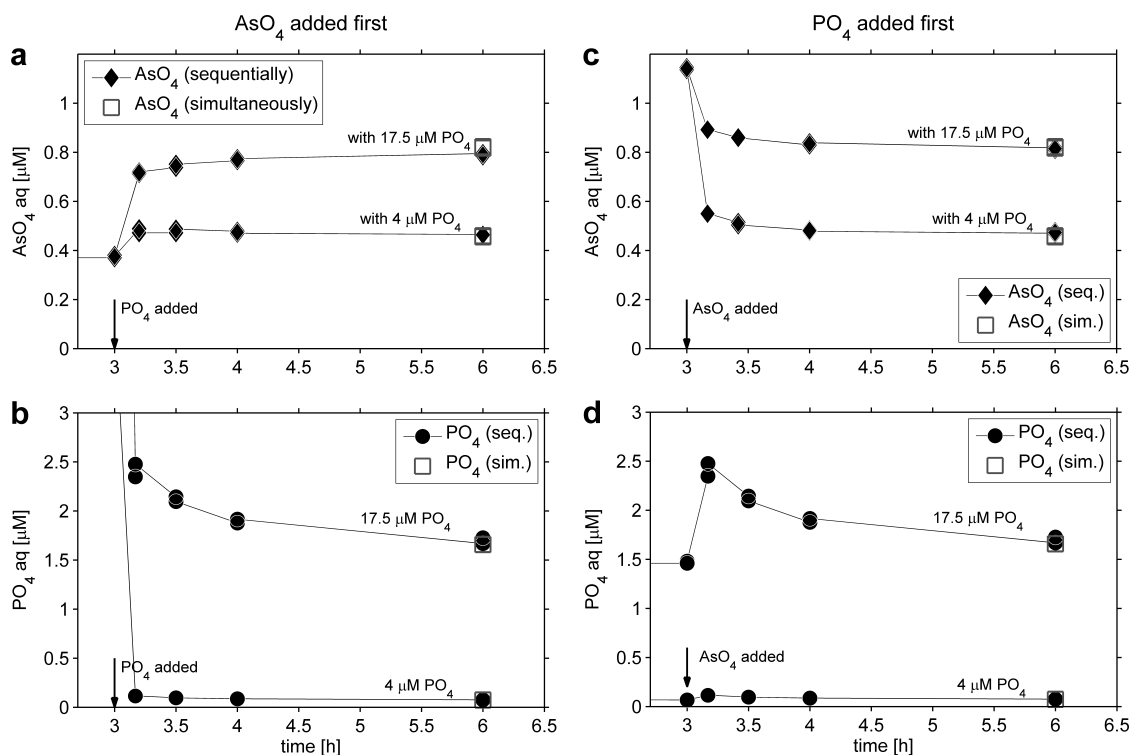


Fig. 7. Competitive adsorption of arsenate and phosphate onto calcite. Solid symbols, the two ions are added sequentially (3 hours apart), with the first ion added at time=0. Open symbols, the two ions are added simultaneously. Total AsO₄ concentration: 1.1 μM and total PO₄ concentration: 4 or 17.5 μM. a) + b) Arsenate added first. c) + d) Phosphate added first. From Sørensen et al. (III).

Simultaneous addition of arsenate and phosphate revealed that the adsorption of arsenate is strongly reduced by the presence of phosphate, whereas phosphate adsorption is only slightly reduced by arsenate addition, as illustrated in Fig. 8. The different response can be ascribed to the far stronger adsorption of phosphate onto calcite as compared to arsenate. The similarity in size, geometry and pK_a's of arsenate and phosphate indicate a possibility for competition. The mutually reduced adsorption in the binary system combined with the fact that arsenate and phosphate display very similar sorption edges (Sørensen et al., I, II), provides evidence that arsenate and phosphate are preferentially bonding to the same surface sites at the calcite surface and that the reduction in adsorption is caused by direct competitive adsorption. The higher affinity for phosphate adsorption relative to arsenate and the peak in phosphate concentration when arsenate is added to the batches (Fig. 7d) indicates that phosphate more readily than arsenate adsorbs to other sites than the preferential sites for both arsenate and phosphate and phosphate adsorption is therefore not as strongly reduced in the binary sorbate system.

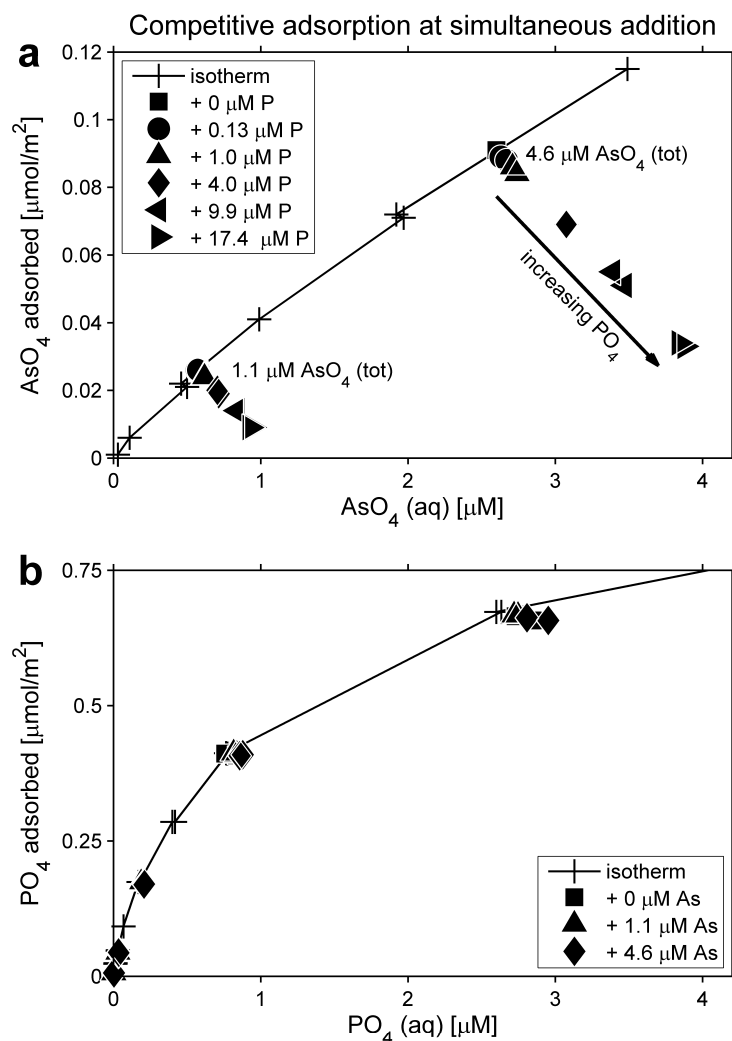


Fig. 8. Competitive adsorption of arsenate and phosphate onto calcite at simultaneous addition (pH 7.0, $p\text{CO}_3^{2-}$ 6.45). **a)** The effect on arsenate adsorption in the presence of phosphate (0.13-17.4 μM PO₄). The sorption isotherm and 0 μM PO₄ represents the single ion system. When phosphate is present the sorption of arsenate is reduced. **b)** The small effect on phosphate adsorption when arsenate is present. The sorption isotherm and 0 μM As represents the single ion system. Note the difference in scale between a) and b). From Sørensen et al. (III).

6 Models of surface complexation on calcite

Application of models can be a useful tool when investigating the calcite-water-CO₂-sorbant system, both to understand the adsorption process in greater detail, and also to predict the behaviour of the sorbant in the natural environment. Several models have been applied to describe adsorption onto calcite. For adsorption of phosphate this includes different types of Langmuir models (House and Donaldson, 1986; Millero et al., 2001), anion-exchange models (Cowan et al., 1990; van der Weijden and Comans, 1997), the constant capacitance model (Hinedi et al., 1992; Sørensen et al., II, III), and the CD-MUSIC model (Sørensen et al., III).

The ion-exchange model has, besides phosphate adsorption, also been applied to describe adsorption of the cations Ba, Co, Mn, Sr, Zn, Cd, and Ni (Zachara et al., 1988; Zachara et al., 1991; Martin-Garin et al., 2003; Kjoller et al., 2006) and the anion SeO₃ (Cowan et al., 1990). In the models the cations exchange with Ca²⁺, whereas the anions exchange with CO₃²⁻ and HCO₃⁻. The applications of the ion-exchange models have been successful in describing the adsorption dependence on solution composition. The ion-exchange models are grey-box models that do not include the vast information on the calcite surface-solution interface as gained from spectroscopic studies or the charging behaviour gained from macroscopic studies (see Section 4.1). However, both the constant capacitance model and the CD-MUSIC models attempt to describe the surface complexation of calcite in the calcite-water-CO₂ system based on observations from both spectroscopic, microscopic and macroscopic studies of the calcite-water interface and were therefore chosen in the present work to model adsorption of arsenate and phosphate onto calcite (Sørensen et al., I, II, III).

6.1 The constant capacitance model

The constant capacitance model (CCM) for calcite was first presented by van Cappellen et al. (1993) and further elaborated upon by Pokrovsky et al. (2000) and Pokrovsky and Schott (2002).

The CCM is the simplest electrostatic model with the relationship between surface charge, σ , and surface potential, Ψ , described as a simple capacitor. The change over distance in potential at the solid-solution interface is illustrated in Fig. 9. In the CCM for calcite the capacitance, C , is dependent on the ionic strength, I , and the empirical constant, α :

$$\Psi = \frac{\sigma}{C} \quad \text{and} \quad C = \frac{\sqrt{I}}{\alpha}$$

The very rapid dissolution and precipitation kinetics of calcite hinder surface potential titrations and the relationship between surface charge and surface potential for calcite was therefore based on acid-base titrations for rhodochrosite (MnCO_3) and siderite (FeCO_3). A high capacitance was necessary to describe the high charge build-up and the weak dependence on ionic strength for these minerals and was applied to calcite without modifications.

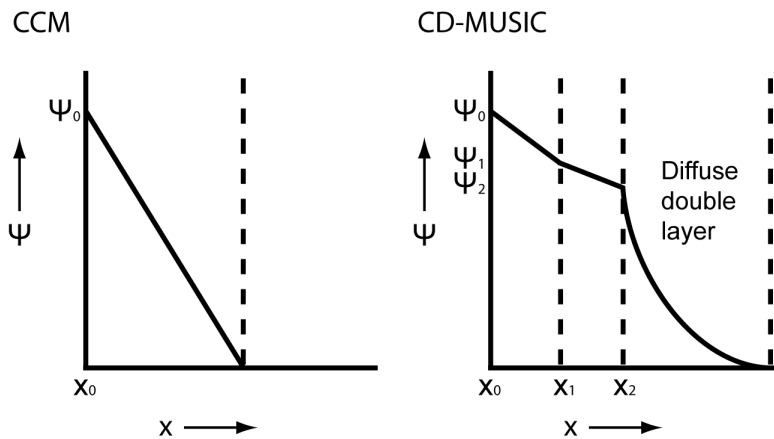
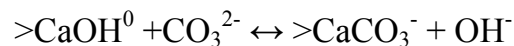


Fig. 9. Schematics of the variation in potential at the solid-solution interface in the CCM and CD-MUSIC model. The surface is located at x_0 and x is the direction towards the solution.

Like other surface complexation models the CCM uses an equilibrium approach. Surface species are described analogous to aqueous complexes by chemical reactions with mass and charge balance and equilibrium constants. In the CCM for calcite there are two primary hydration sites, $>\text{CaOH}^0$ and $>\text{CO}_3\text{H}^0$, ($>$ denotes the calcite lattice) having a 1:1 stoichiometry. These sites were defined based on the X-ray photoelectron spectroscopic (XPS) measurements of the calcite surface by Stipp and Hochella (1991). In the model the sites have the same density as Ca and CO_3 groups in the $\{1014\}$ cleavage plane and they react with other ions in the calcite-water- CO_2 solution, e.g.:



The reactions were based on an analogy with aqueous acid-base and complexation equilibria of carbonic acid and Ca^{2+} in solution. The intrinsic surface stability constants were also based on this analogy, but were adjusted to fit experimental data. Van Cappellen et al. (1993) made minor adjustments to

obtain a zero-potential in agreement with the experimental results by Mishra (1978). Further adjustments were made by Pokrovsky et al. (2000) for the model to fit the isoelectric point obtained in several different studies using electrophoresis and streaming potential techniques. In addition, Pokrovsky et al. (2000) carried out diffuse reflectance infrared (DRIFT) spectroscopy measurements of the calcite surface to determine the composition and density of surface hydroxyl and carbonate groups and found that it correlated well with the surface speciation predicted by the CCM for calcite.

Fenter et al. (2000) studied the calcite surface in calcite equilibrated solutions using specular X-ray reflectivity measurements and compared the findings to the surface speciation predicted by the CCM (as given in van Cappellen et al. (1993) and Pokrovsky et al. (2000)). The experimental results revealed a monolayer of hydroxyl species (OH or OH₂) at pH 8.3 and the measurements at pH 6.8 and 12.1 could be explained by including protonation reactions in the surface speciation at terrace areas. The experimental results agreed with the CCM at pH 8.3 and 12.1, predicting the dominant surface species to be >CaOH₂⁺ and >CO₃⁻. However, the higher concentration of >CO₃Ca⁰ at pH 6.8, predicted by the model, was not observed experimentally.

6.1.1 Application of the constant capacitance model

The CCM for calcite has been used to model adsorption of both cations (Cd²⁺, Ni²⁺ and Fe²⁺) and anions (Ga(III), arsenate and phosphate) onto calcite. Lakshtanov and Stipp (2007) successfully applied the model to a single Ni²⁺ sorption isotherm obtained from batch experiments. Pokrovsky et al. (2004) studied adsorption of Ga(III) in a wide range of solutions and initial Ga(III) concentrations in batch experiments and was able to model the experimental results with a single Ga(III)-adsorbing complex having a stability constant, logK, between 6.6 - 7.45.

Cd²⁺ adsorption onto calcite in two different solutions was studied in a stirred flow-through reactor (Martin-Garin et al., 2003). The model reproduced the experimental results nicely when the site density of both >CaOH⁰ and >CO₃H⁰-sites was increased from 8.3 μmol/m² to 11 μmol/m² and the capacitance was decreased from 17 F/m² to 9 F/m². How changing these parameters might otherwise affect the original model was not discussed.

Mettler et al. (2009) measured adsorption of Fe²⁺ onto calcite in batch experiments in a single solution. They modelled the results using the CCM without surface charge corrections. In contrast to the studies described above, the

Fe^{2+} adsorption isotherm was not log-log linear. To reproduce the experimental results, the total site densities of both $>\text{CaOH}^0$ and $>\text{CO}_3\text{H}^0$ -sites were decreased from $8.3 \mu\text{mol}/\text{m}^2$ to $5 \mu\text{mol}/\text{m}^2$ and it was noted that this might indicate that a more complex binding than a 1:1 surface ligand to metal complex is involved.

Sø et al. (I, II) studied adsorption of arsenate and phosphate onto calcite in a wide range of solutions with different compositions and initial arsenate and phosphate concentrations in batch experiments. Similar to the adsorption of Fe^{2+} , non log-log linear sorption isotherms were observed. The model nicely captured the variation in adsorption as a function of solution composition. However, using monodentate adsorption in the model yielded almost straight adsorption isotherms, unlike the experimental data. Modelling phosphate adsorption as bidentate surface complexation improved the model fit, though a discrepancy between the experimental and modelled sorption isotherms still persisted.

Lowering the fraction of sites available for phosphate adsorption, analogue to the modelling of Fe^{2+} adsorption (Mettler et al., 2009), was tested. However, the approach was discarded as it was found that the fraction of sites greatly depended on the available dataset (Sø et al., II). Because Mettler et al. (2009) only measured an adsorption isotherm in one solution they were not able to investigate this issue.

Curved model sorption isotherms that matched the experimental data were obtained by introducing two types of $>\text{CaOH}^0$ sites; “strong sites” with a low density and “weak sites” with a higher density (Fig. 10), an approach that has been used to model adsorption onto iron oxides (Dzombak and Morel, 1990). Different stability constants were defined for adsorption onto “strong” and “weak” sites for phosphate and arsenate, whereas all other stability constants were kept identical for the two types of sites. Because phosphate adsorbs stronger and shows more curved adsorption isotherms compared to arsenate, the number of “strong” sites needed to model phosphate adsorption was four times the number needed to model arsenate adsorption.

The division into “strong” and “weak” sites is discussed in Sø et al. (II). It is proposed that the “strong” sites might be considered as the corners, edges and step sites at the calcite surface. If this a correct description of the processes taking place at the calcite surface, then the use of two sites also needs to be implemented in the basic model of the calcite-solution interface. On the other hand, the two types of sites might also originate as a modelling artefact. The constant capacitance model was developed as a special case for high ionic

strength, where the diffuse double layer can be neglected. Lützenkirchen (1999) showed that the applications of the CCM on oxides at low ionic strength are in some cases successful, but only with capacitances that are too high to be physically reasonable. He therefore concluded that at low ionic strength the CCM should be considered as a data fitting model without mechanistic implications. The necessity to introduce two types of sites to fit the experimental data might be a sign that the framework of the CCM is too simple to describe the system.

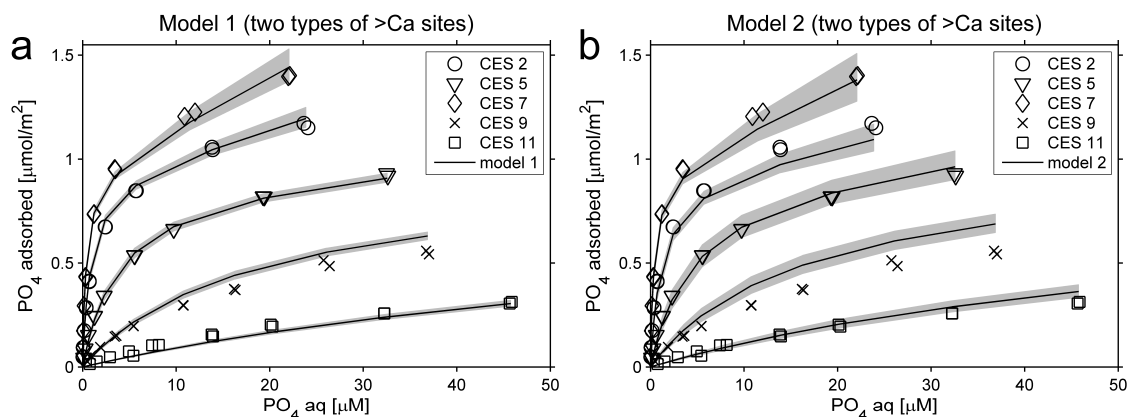


Fig. 10. Modelling adsorption of phosphate onto calcite with the CCM (lines) compared to experimental data (symbols). Both model 1 and 2 uses two types of $>\text{CaOH}^0$ sites for sorption of phosphate, but differ in the complexes formed. The grey area illustrates the 95% confidence interval. From Sørensen et al. (II) with permission from Elsevier Ltd.

6.2 The CD-MUSIC model

The charge distribution multisite ion complexation (CD-MUSIC) model was originally developed for the iron hydroxide goethite (Hiemstra and van Riemsdijk, 1996). Recently, the framework of the model was applied to model the calcite-solution interface by Wolthers et al. (2008). The CD-MUSIC model differs from the CCM for calcite in its structural representation of the mineral surface, the location of the adsorbing ions and the description of the electrostatic interface from the mineral surface out into the solution.

As the CCM, the CD-MUSIC model for calcite operates with both $>\text{Ca}$ and $>\text{CO}_3$ -sites. However, the CD-MUSIC model distinguishes between sites at faces, corners and edges and therefore has a total of six different sites. The formal charge of the different sites is calculated based on the valence bond concept by Pauling (Pauling, 1929) and is based on the coordination of atoms in the lattice structure and the atoms exposed at the surface. The charge of the $>\text{Ca}$ -

site is +1/3 (face site), +2/3 (edge site) and +1 (corner site). The same, but negative, charges are given to the $>\text{CO}_3$ -sites.

Like the CCM for calcite, the CD-MUSIC model comprises both sorption of lattice ions and the hydration of the sorption sites. The constants for sorption of lattice derived ions (Ca^{2+} , CO_3^{2-} and HCO_3^-) are the same as in the CCM by van Cappellen et al. (1993), but the CD-MUSIC model has new constants for the protonation of $>\text{CO}_3$ and the hydration of $>\text{Ca}$. The same stability constants are applied to the face, corner and edge sites, as it was not possible with the available data to distinguish adsorption affinities for the different sites. The sites therefore only differ in their charge (Wolthers et al., 2008).

The electrostatic interface from the mineral surface out into the solution is described with the three plane model shown in Fig. 9. The 0-plane cuts through the oxygen atoms in the surface carbonate groups, inner-sphere complexation reactions take place in the 0-plane and 1-plane, whereas outer-sphere complexes are located in the 2-plane with the head end of the diffuse double layer located at the 2-plane. The charge development between the 0-plane, 1-plane and 2-plane is described as two serial capacitors with individual, constant capacitances and the diffuse double layer is described with the Gouy-Chapman model.

The charge of an adsorbing ion is assigned to either one plane or the charge is distributed between two planes. In the CD-MUSIC model for calcite the location of the adsorbing ions inherent to the calcite-water- CO_2 system is based on geometric considerations. Adsorbed Ca^{2+} is for example located in the 1-plane and hence its charge is also placed in this plane, whereas adsorption of CO_3^{2-} is adsorbed in the 0-plane and 1-plane, with its charge distributed between the two planes (Wolthers et al., 2008).

In the calibration of the CD-MUSIC model for calcite, available experimental data in the literature on ζ -potentials and total net surface charges was used. The potential calculated for the 2-plane (Ψ_2) was assumed to represent the measured ζ -potentials (Wolthers et al., 2008). The shear plane, where the ζ -potential is measured, might be located slightly further away from the surface than the 2-plane, nevertheless, the difference in potential is not considered to be significant.

At the isoelectric point, the potential at the shear plane is 0, as is the potential at the surface. The simplicity of the CCM only allows calculation of the potential at the surface, and the model was therefore calibrated on the isoelectric point. The more detailed description of the potential development in the CD-MUSIC model allowed for a large range of data being used to calibrate the model.

6.2.1 Application of the CD-MUSIC model

The CD-MUSIC model for calcite was used successfully to model adsorption of both arsenate and phosphate onto calcite (Sø et al., III), see **Fig. 11**. This is the first study that uses the CD-MUSIC model for calcite to model adsorption of ions not inherent to the calcite-water system.

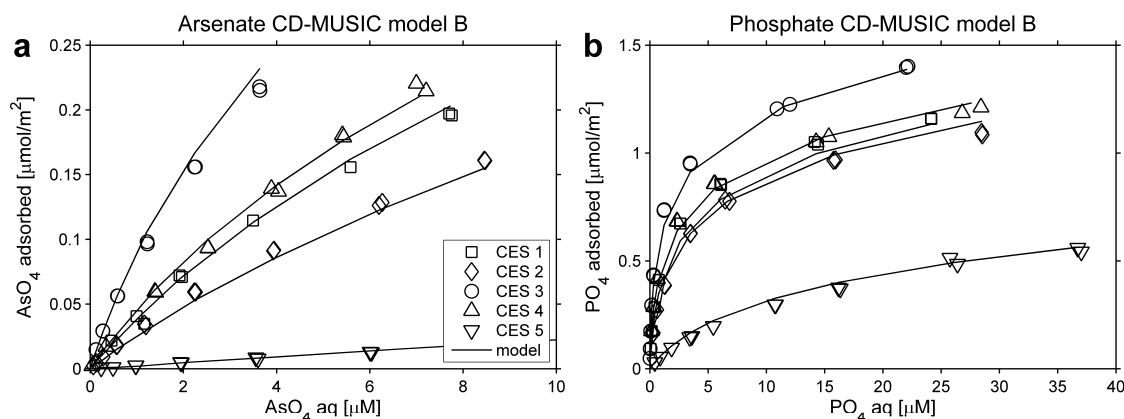


Fig. 11. Modelling arsenate and phosphate adsorption onto calcite with the CD-MUSIC model (lines) compared to experimental data (symbols). Both arsenate and phosphate sorption is in this version modelled with monodentate-binuclear coordination (B in Fig. 12). From Sø et al. (III).

The calcite crystals used by Sø et al. (III) are relatively large (around 10 μm, see Fig. 3) and the face sites therefore form the large majority. The face, edge, and kink sites only differ in their charge in the original model by Wolthers et al. (2008), and to limit the number of adjustable parameters only adsorption of arsenate and phosphate onto face sites were considered.

Employing the capacitances of the original model ($C_1 = C_2 = 100 \text{ F/m}^2$) yielded almost straight adsorption isotherms for arsenate and phosphate. As lowering the capacitances yielded more curved adsorption isotherms, calculated capacitance values based on the distances between the planes and the relative permittivity of water were implemented in the model ($C_1 = 1.3\text{-}3 \text{ F/m}^2$ and $C_2 = 4.5 \text{ F/m}^2$). A similar approach has been used to adjust the capacitances in the CD-MUSIC model for goethite (Hiemstra and van Riemsdijk, 2006). The change in capacitance did not significantly affect the original model, as the small change in the calibration parameter (the potential at the 2-plane, Ψ_2) was insignificant as compared to the scatter of the experimental data and the general fit of the model to data originally used to calibrate the model (Sø et al., III).

Adsorption of both arsenate and phosphate was modelled as inner-sphere coordination, with four different coordination modes tested, see Fig. 12. Coordination mode B, C and D all yielded satisfactory fits to the experimental data; see Fig. 11 for coordination mode B. Besides coordination mode D, which is not in agreement with EXAFS measurements of arsenate adsorption onto calcite (Alexandratos et al., 2007), it was not possible to select one coordination mode over the others.

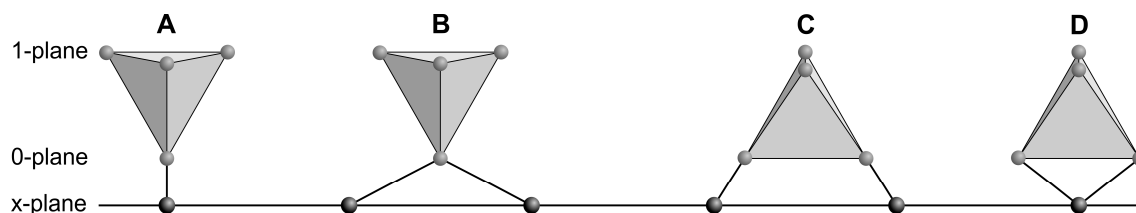


Fig. 12. The four different coordination modes for arsenate and phosphate used for optimization of the CD-MUSIC model. A: monodentate-mono-nuclear, B: monodentate-bi-nuclear, C: bidentate-bi-nuclear and D: bidentate-mono-nuclear. A, B and C are corner-sharing, while D is edge-sharing. The x-plane is located at the calcite surface, with the black spheres representing Ca atoms. From Sørensen et al. (III).

The charge of the adsorbing ion was distributed between the 0-plane and 1-plane and included in the model optimization as an adjustable parameter. To limit the variation in the charge distribution, the resulting charge on the oxygen atom in the 0-plane was calculated. A charge between $\pm 1/3$ was allowed, as this charge was considered likely to be neutralized by hydrogen bonding (Sørensen et al., III). The charge distribution strongly affected the curvature of the adsorption isotherms and was a powerful parameter in the optimization. In the final models the charge of the oxygen atom in the 0-plane was in most cases negative and at/or close to $-1/3$.

Two models for arsenate adsorption and four models for phosphate adsorption all modelled the experimental data well (Sørensen et al., III). Two adsorbing species were used in all six models, and except for one model for phosphate surface complexation the Ca-complexed species (CaHAsO_4^0 and CaAsO_4^- or CaHPO_4^0 and CaPO_4^-) were used as the adsorbing species. Further studies of the binding mechanism for adsorption of arsenate and phosphate are needed to constrain the models; especially knowledge on the coordination mode and charge distribution.

6.3 Modelling competitive adsorption

The literature on competitive adsorption onto calcite is limited and modelling studies of competitive adsorption onto calcite are even more sparse. Cowan et al. (1990) successfully modelled the competition between phosphate and selenite onto calcite with the ion exchange model. However, the model for phosphate was based on data from the binary sorbate system and was not verified for the single sorbate system.

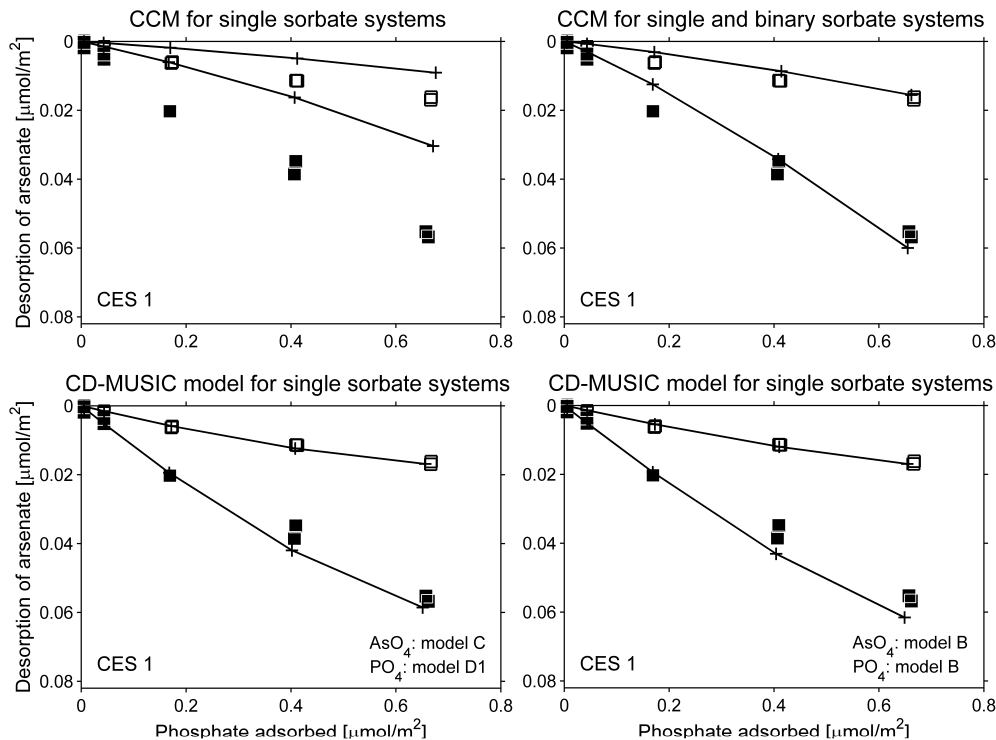


Fig. 13. Modelling competitive adsorption of arsenate and phosphate onto calcite compared to experimental data. The desorption of arsenate is calculated as $As(ads)_{p=0} - As(ads)_{p=i}$. Open symbols: 1.1 μM As, closed symbols: 4.6 μM As, lines: model predictions. From Sørensen et al. (III).

Competitive adsorption of arsenate and phosphate onto calcite was modelled by Sørensen et al. (III) with the constant capacitance model (CCM) and the CD-MUSIC model (Fig. 13). Applying the CCM's based on single sorbate systems (arsenate and phosphate individually) resulted in a poor model prediction of the competitive adsorption, as the modelled competitive effect was smaller than what was observed experimentally (Fig. 13 top left). Modelling competitive adsorption of arsenate and phosphate onto goethite with the CCM based on single sorbate systems has also proven to be difficult, with correct predictions of only some of the observed features (Manning and Goldberg, 1996a; Gao and Mucci, 2001; Gao and Mucci, 2003).

It was possible to model competitive adsorption of arsenate and phosphate onto calcite with the CCM when the model constants were derived from both single and binary sorbate systems (Sø et al., III), see Fig. 13 top right. However, a model that needs to be fitted on competitive data is not appealing, as it most likely will be necessary to recalibrate the model each time a new ion is added to the model. A more elegant solution would be to combine models for single sorbate systems in order to successfully model the competitive effect in a multi-component system.

Modelling the competitive adsorption of arsenate and phosphate onto goethite based on constants that were derived from the single sorbate system has been successful using the CD-MUSIC model (Hiemstra and van Riemsdijk, 1999; Stachowicz et al., 2008). Applying the CD-MUSIC model for calcite to model competitive adsorption of arsenate and phosphate onto calcite was also successful (see Fig. 13 bottom panel) (Sø et al., III). Based on the single sorbate system two models for arsenate adsorption and four models for phosphate adsorption were found to model the experimental data well. Four combinations of different arsenate and phosphate models were tested on the competitive data and all combinations modelled the competitive effect equally well. It was therefore not possible, based on the competitive data, to select one model over the others.

The CD-MUSIC model successfully predicts the competitive effect of the binary system based on models in the single ion system, whereas the CCM based on the single sorbate systems under-predicted the competitive effect. The main difference between the two models is that the CCM uses two types of adsorption sites, whereas the CD-MUSIC model has a more detailed description of the electrostatic interface from the mineral surface out into the solution. The ability to predict the competitive effect is connected to these differences, as adsorption in the CD-MUSIC model is largely controlled by changes in the charge at the calcite surface, whereas the distribution between the strong and weak sites is important in the CCM. Only when the number of sorption sites for arsenate is sufficiently limiting, the CCM predicts a competitive effect comparable to the observed competition. Most likely, both electrostatic effects and site heterogeneity affect the adsorption of phosphate and arsenate onto calcite and a model combining the two mechanisms would be most correct (Sø et al., III). The CD-MUSIC model could be expanded with adsorption of arsenate and phosphate onto edge and corner sites, to take the heterogeneity of the surface into account, but as mentioned there are no data available to constrain such an approach.

7 Mobility of arsenic and phosphate in groundwater aquifers

Extrapolation of the results of the experimental work in this thesis and earlier studies indicates how the presence of calcite in groundwater aquifers will affect the mobility of arsenite, arsenate and phosphate.

Under reducing conditions, arsenic will be present primarily as arsenite. Román-Ross et al. (2006) reported adsorption of arsenite onto calcite, indicating that the mobility of arsenite will be affected by the presence of calcite. This is contradicted in the results from this thesis (Sø et al., I), showing that arsenite does not adsorb significantly onto calcite and the mobility of arsenite in a calcite bearing aquifer will therefore not be affected. To clarify this issue further studies are needed.

Under oxidizing conditions, arsenic will be present as arsenate. Because arsenate adsorbs onto calcite (Alexandratos et al., 2007, Sø et al., I) the presence of calcite in the aquatic environment will affect the mobility of arsenate. Adsorption of phosphate onto calcite is in many ways similar to that of arsenate, though phosphate adsorption affinity is even higher than it is for arsenate and the mobility of phosphate will correspondingly be affected more than arsenate by the presence of calcite. The results from the experimental work of this thesis show that calcite can act as a quickly responding source and sink for both arsenate and phosphate (Sø et al., I, II). The high reversibility of the system is further demonstrated in the binary sorbate system (Sø et al., III) and underlines that the adsorption of both arsenate and phosphate onto calcite is a highly dynamic system within the short time frame of our experiments. The large degree of sorption reversibility enhances the availability of arsenate and phosphate, where a decrease in the aqueous concentration would lead to release of the ion from the calcite surface. It should be noted, that the short sorption time employed in our experiments could contribute to a larger apparent degree of sorption reversibility than might be observed in nature, where longer sorption periods may lead to precipitation or incorporation into the calcite lattice during recrystallization.

Based on calculated retardation factors (a measure of the velocity of an ion relative to the groundwater velocity) Sø et al. (I) found that calcite will be an important factor in controlling the mobility of arsenate in aquifers where calcite is dominant, e.g. limestone or chalk, where calcite can act as a sink or a possible source for arsenate. The degree of retardation will greatly depend on the

groundwater composition, and the availability will thus be influenced by changes in solution. Concerning aquifers with low calcite content Sørensen et al. (I) concluded that the importance of calcite depends on whether other minerals such as iron oxides, that are highly effective in adsorbing arsenate, are present in the aquifer.

The analysis of the significance of the adsorption of arsenate onto calcite for the mobility of this ion in groundwater aquifers by Sørensen et al. (I) does not include the competitive effect of phosphate. The strong lowering in the extent of arsenate adsorption in the presence of phosphate (Sørensen et al., III) suggests that adsorption of arsenate onto calcite is of minor importance in most groundwater aquifers, because phosphate is often present at concentration levels sufficient to significantly reduce arsenate adsorption. This clearly points to the difficulties of extrapolating simple laboratory studies to the inherently complex natural environment, but also points to the importance of considering as many relevant factors as possible when predicting the fate of a solute in the environment.

8 Conclusions

Arsenite does not adsorb significantly onto calcite within 24 h. In contrast, the extent of uptake of both arsenate and phosphate on the surface of calcite is high, fast and completed within 2-3 hours. Because the process is easily reversed by lowering the aqueous arsenate and phosphate concentration, the process is characterized as adsorption rather than surface precipitation.

The degree of phosphate adsorption is higher than for arsenate and the sorption isotherms for phosphate are more strongly curved. The adsorption of both arsenate and phosphate onto calcite depends on solution composition in the same way: adsorption increases as the activity of CO_3^{2-} decreases (at constant pH) and as pH increases (at constant CO_3^{2-} activity). Changes in ionic strength also influence the degree of adsorption. For phosphate this can generally be accounted for by the concomitant changes in the activity of aqueous phosphate species, whereas there is an additional (electrostatic) effect on arsenate.

The adsorption of arsenate onto calcite is strongly reduced by the presence of phosphate, whereas phosphate adsorption is only slightly reduced by arsenate addition. The observed reduction is independent of the sequence of addition, even when the ions are introduced into the system three hours apart. The reduction in sorption of both arsenate and phosphate is most likely due to competition for the same sorption sites, considering the similarity in sorption edges, pKa's and geometry of the two anions.

The experimental results of the single sorbate systems were successfully modelled using either the constant capacitance model (CCM) or the CD-MUSIC model. The changes in adsorption as a function of the solution composition are well captured by both models. However, introducing two types of sorption sites was necessary in the CCM for the model to reproduce the convex shape of the experimental sorption isotherms, with the distribution between the two types of sites being different for the model of arsenate and phosphate. The competitive effect of arsenate and phosphate could also be modelled satisfactorily with the CD-MUSIC model. In contrast, the CCM under-predicted the competition based on individually fitted models. This shows the importance of competitive studies in validating multi-component adsorption models.

Based on single sorbate studies the mobility of arsenate in calcite bearing, especially chalk-type, aquifers will be greatly reduced due to adsorption onto calcite, whereas adsorption onto calcite in aquifers with low calcite content will

affect the mobility of arsenate to a lesser extent. The mobility of arsenite, on the other hand, will not be affected by the presence of calcite. A change in the aquifer redox conditions, between oxidizing and reducing, can therefore greatly influence the mobility and availability of arsenic. However, based on the binary sorbate studies the strong reduction in adsorbed arsenate suggest that sorption of arsenate on calcite is of minor importance in most groundwater systems, where phosphate is normally present at much higher concentrations. This underlines the importance of experimentally studying the competition between different ions for sorption sites in order to realistically estimate the mobility of a given solute in the environment.

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10 Papers

- I. Sørensen H. U., Postma D., Jakobsen R. and Larsen F. (2008) Sorption and desorption of arsenate and arsenite on calcite. *Geochim. Cosmochim. Acta* **72**, 5871-5884.
- II. Sørensen H. U., Postma D., Jakobsen R. and Larsen F. (2011) Sorption of phosphate onto calcite; results from batch experiments and surface complexation modeling. *Geochim. Cosmochim. Acta*, in press.
- III. Sørensen H. U., Postma D., Jakobsen R. and Larsen F. (2011) Competitive adsorption of arsenate and phosphate onto calcite; experimental results and modeling with CCM and CD-MUSIC. *Geochim. Cosmochim. Acta*, submitted.

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ISBN 978-87-92654-30-4