RUHR-UNIVERSITÄT BOCHUM

Computational adsorption experiments at the (100)-pyrite-water interface: The influence of surface defects to the H_2O-adsorption model

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Introduction:

Chemical reactions at the (100)-pyrite (FeS_2) surface play an important role in many environmental, geological and chemical processes. To understand these processes it is of essential importance to understand the adsorption properties of pyrite to organic molecules and water.

In this study the adsorption model of water at the (100)-pyrite surface near iron and sulphur defect sites is presented and compared to experimental results. We present molecular dynamic simulations using the forcefield COMPASS. The simulations were carried out with the program package Materials Studio 5.0, particularly the program "Forcite", from Accelrys Inc. A surface cell, that was determined from GIXRD previously, was used as a start model for the simulations.

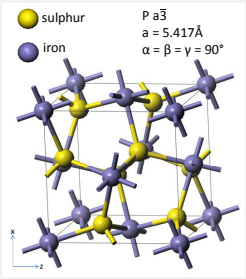


Fig. 1: Bulk structure of pyrite.

Methods:

- Materials Studio 5.0
- Forcite
- Forcefield simulations (COMPASS)
- Molecular dynamic (MD) and mechanic (MM) simulations
- Dynamic calculations for H_2O-molecules at defect sites

- iron defect sites
- sulphur defect sites
- three layer defect at the surface slab

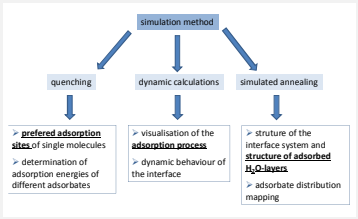
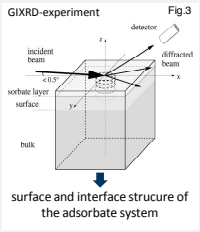


Fig. 2: Schematic view of used simulation methods and their results.

Previous GIXRD-results:

CTR-scans (crystal truncation rod) were carried out at the ESRF (ID03) using GIXRD (see Fig.3). The (100)-pyrite-water interface was determined using the program ROD. The cell is bulk terminated and shows only small relaxations, no reconstruction and an increasing amount of defects from the bottom to the topmost layer of the surface slab.



surface and interface strucure of the adsorbate system

Surface structure of pyrite

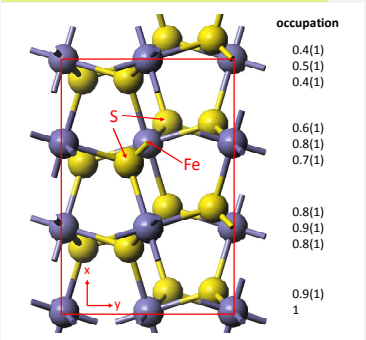


Fig. 4: Final model of the pyrite surface cell under aqueous conditions with X^2=4.76 and the resulting occupation factors.

→ Fe- & S- defect surface structure

The dynamic H_2O adsorption process at a three layer defect surface

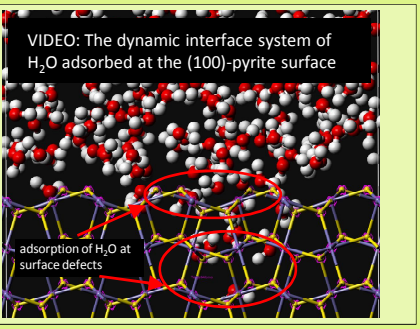
Forcefield dynamic simulations:

Molecular dynamic simulations were carried out using dynamic calculations with the program Forcite and the forcefield Compass. The simulations yield to an adsorption model that supports the GIXRD-measurements and contains the location of H_2O-layers adsorbed at the surface, the atomic positioning above the surface, and the dynamic behaviour of the adsorption process.

Tab. 1 General MD- and MM-simulation parameters.

program	Materials Studio 5.0 Adsorption locator, Forcite
force field	COMPASS
summation method: electrostatic van der Waals	Ewald atom based
geo. optimization	smart method
time step	0.2-1fs
ensemble	NVT

1. Sulphur defect sites (Fig.6)
2. Iron defect sites (Fig.7)
3. Multiple layer defects (Fig.8;9)



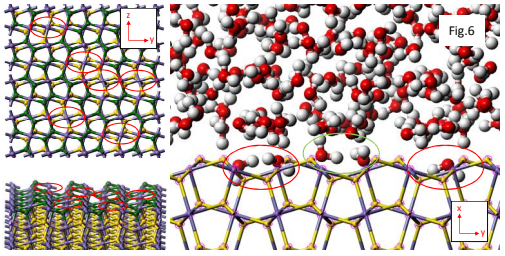
The video shows the dynamic behaviour of H_2O molecules at a multiple layer defect.

The combination of GIXRD and forcefield simulations is a powerful method to determine mineral-water interfaces and periodical ordered dynamic systems.

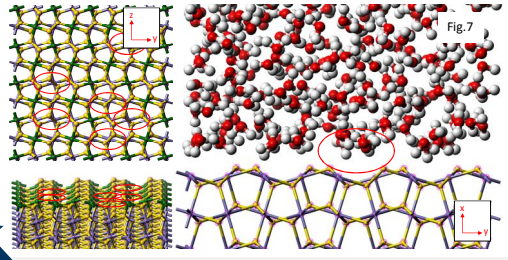
Outlook:

- adsorption model of different organic molecules in aqueous solution at the (100)-pyrite surface
- adsorption models at different pyrite surfaces
- adsorption near surface steps

1. Sulphur defect sites



2. Iron defect sites



Adsorption model for H_2O

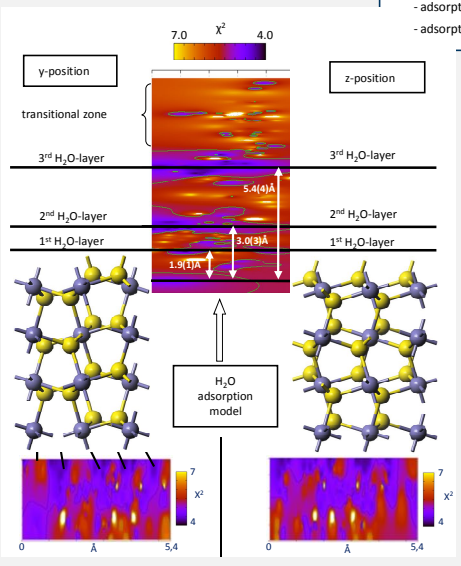


Fig. 5: Location of H_2O from X^2-dependent H_2O-distribution maps (GIXRD-results):

x-position:
- 3 layers above the surface
- transitional zone: zone above adsorbed H_2O-layers of partially ordered water
- H_2O molecules occupy vacancies at the topmost FeS_2-layer

y-position:
- 5 defined positions for H_2O
- 3 dedicated to the x-Fe position
- 2 dedicated to the x-S position

z-position:
- dynamic positions, no exact adsorption positions

→ dynamic H_2O-adsorption system

3. Multiple layer defects

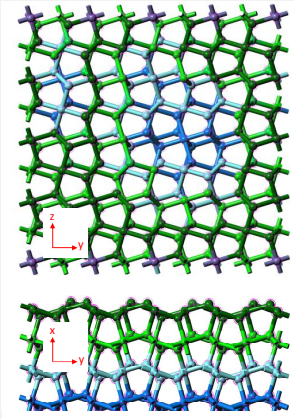


Fig. 8: Structure of the multiple layer defect of the pyrite surface. The topmost layer is shown in dark green and the bulk structure in dark blue.

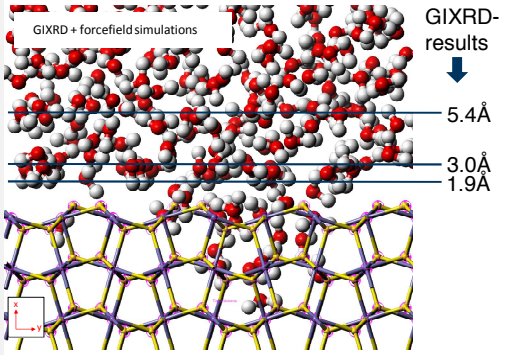


Fig. 9: Final adsorption model for H_2O at the (100)-pyrite surface (simulation) compared to experimental model (GIXRD).

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