

# First-Principles Studies of Dissolution Reactions OF Orthoclase

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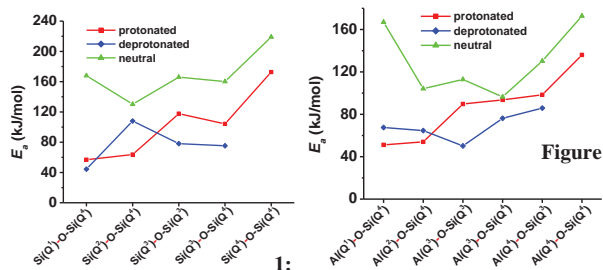
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## Introduction

Subcontinuum approaches based on first-principles theory have been successfully applied to a variety of condensed matter problems in the past, including reactivity of glass and mineral surfaces with water, to develop understanding of reaction mechanisms at the atomic scale and provide estimates of reaction rates. To develop atomistic-informed constitutive models for the dissolution rate, we chose to study a well-characterized crystalline aluminosilicate – orthoclase - as initial model system. Time resolved X-ray reflectivity was previously used to obtain the face-specific dissolution rates of orthoclase (001) surfaces under a wide range of pH and temperature conditions.[1] By studying elementary reactions of water and ions on orthoclase using first-principles methods, and combining these studies with Kinetic Monte Carlo (KMC) simulations, our goal is to develop fundamental models to understand the observed experimental dependence of dissolution rates on pH and temperature.



Calculated activation energies for different sites on the orthoclase (001) surface.

## Results and Conclusion

We have performed first-principles-based modelling of surface site distribution as a function of pH and temperature on orthoclase surfaces of two different orientations (001) and (010). Differences in the surface species distribution are found for the two surfaces, suggesting different initial dissolution behavior. To evaluate reaction pathways, we have performed first-principles calculations of reaction barriers for water reactions with neutral, protonated and deprotonated sites of constituting network formers Si and Al (Fig. 1). The calculated reaction barriers together with the surface site distribution model are used to estimate the overall dissolution rates and compare with experimental values.[1] Kinetic Monte Carlo studies were used to validate a phenomenological constitutive model. This work is aimed at better understanding of the dissolution behavior and development of predictive models for dissolution rates.

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# *In situ* monitoring of lepidocrocite bio-reduction and magnetite formation by backscattering Mössbauer spectroscopy

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Magnetite, a mixed valence Fe(II-III) oxide ( $\text{Fe}_3\text{-}\delta\text{O}_4$ ), is a commonly occurring mineral on Earth usually found in soils and sediments. Depending on the geochemical environments in which Fe(III) bio-reduction takes place, dissimilatory iron reducing bacteria (DIRB) activity can lead to diverse biogenic minerals such as magnetite. Consequently, the discovery of magnetite at depth of 6.7 km in subsurface has been used as a marker of DIRB activity [1-2]. Moreover, the quantity of extracellular magnetite induced by DIRB could be several thousand times more than magnetotactic bacteria do per unit of biomass [3-4]. Whereas, many reports have focused on magnetite precipitated by magnetotactic bacteria, very few studies have been able to demonstrate the unequivocal existence of extracellularly precipitated magnetite. This discrepancy could be explained by the higher reactivity of magnetite formed by DIRB [5]. Indeed, the reactivity and stability of magnetite is dictated partly by its stoichiometry. It was shown that stoichiometric magnetite had the lowest reduction potential in comparison with a non-stoichiometric magnetite, consistent with higher reactivity toward pollutants such as nitrobenzene compounds [6].

The miniaturized Mössbauer spectrometer (MIMOS II) was used to monitor *in situ* the mineralogical transformation of lepidocrocite ( $\gamma\text{-FeOOH}$ ) in *Shewanella putrefaciens* CIP 8040 culture under anaerobic condition using methanoate as the electron source. Magnetite ( $\text{Fe}_3\text{-}\delta\text{O}_4$ ) was the only biogenic mineral formed during the course of the incubation. The analysis of the biogenic mineral by transmission electron microscopy (TEM) revealed cube-shaped crystals with a relatively homogeneous grain size of about 50 nm. After one day of incubation, the departure from stoichiometry  $\delta$  of the biogenerated magnetite was very low ( $\delta \sim 0.025$ ) and rapidly reached values close to zero indicating the precipitation of a stoichiometric magnetite. The experimental setup used in this study could be replicated in field experiments when assessing the formation of magnetite in modern geological settings when its formation is suspected to be caused by a strong bacterial activity.

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- [5] Li et al., (2009) *Geobiology* **7**, 25-34
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