Dynamics of water dissociation on oxides surfaces: Comparison between rutile and cassiterite

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Water dissociates at the interface with oxides due to a dynamical equilibrium where protons jump from water to the surface and back. We use large-scale ab-initio molecular dynamics (AIMD) simulations to study water dynamics on rutile (110) surface (titanium dioxide) and cassiterite (110) surface (tin dioxide). We calculate the proton jump rates in both surface (Figure 1) and found that the rate on cassiterite surface is around five times more than on rutile surface. The increased proton jump rate on cassiterite results from stronger hydrogen bond formation between the surface and the water layer above the surface. The increase in strength of hydrogen bonding causes the water to come closer to the cassiterite surface as evidenced by observing a red shift in the OH vibrational stretching band. We will show that the cause of the increased hydrogen bonding strength is shown to be rooted primarily in the electronic structure difference between the two surfaces. We have traced this cause to be the increase in covalency character of the hydrogen bonding between the water and the surface bridging oxygen. We will discuss the importance of this dissociation dynamics with respect to surface reactivity, surface dissolution as well as the quantum character of the proton dynamics on these surfaces.

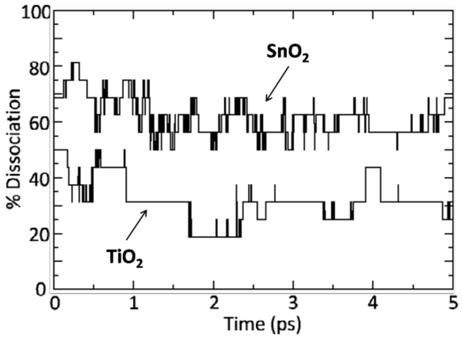

Figure 1: Percentage of water dissociated on cassiterite and rutile surfaces as a function of the simulation time. The percentage is higher and the fluctuations more frequent in cassiterite.

Can Ti phases appearance on Foresudetic Monocline be affected by CO$_2$

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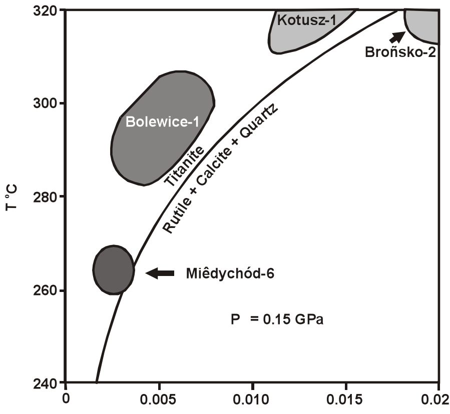
Mafic and intermediate rocks from the Foresudetic Monocline have been affected by very low and low-grade metamorphic processes [1].

The most common secondary Ti-bearing phase is titanite. It is present in most boreholes, excluding Brońsko-2. It forms usually small xenomorphic crystals in rock matrix and pseudomorphoses after pyroxenes as well as bigger subautomorphic crystals in amygdules. In the Brońsko-2 borehole rutile associated with carbonates are frequently observed in pseudomorphoses after titanomagnetite in highly microfractured, chlorite and carbonate rich rocks.



Position of the reaction calcite + quartz + rutile = titanite + CO$_2$ as a function of T and XCO$_2$ at 0.15 GPa calculated using the Perplex program of [2] from [3] with marked fields for studied drillcores.

The main factor controling appearence of titanite and rutile is amount of CO$_2$ in solutions. If CO$_2$ pressure is not high enough to fix all Ca titanite is alwatys present, while rutile is extremely rare.

[1] Sokalska E.T. (2007) PhD thesis–unpublished 1–140. [2] Connolly, J.A.D. (2005) *Earth & Planetary Science Letters,* **236**, 524–5541. [3] Hansen, E. Reimink, J. Harlow, D. (2010) Manuscript accepted for *Lithos*.