# Control of charge and orbital order at the $Fe_3O_4$(001)-surface via adsorbates: Insights from density functional theory calculations

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Besides being a potential spintronics material magnetite plays an important role in a number of environmental processes. As the surface reactivity depends critically on the electronic state of the mineral surface, we explore the interaction of water and hydrogen with the $Fe_3O_4$ (001)-surface using density functional theory (DFT) calculations with an on-site Coulomb repulsion term (GGA+*U*). The surface phase diagram compiled in the framework of *ab -initio* thermodynamics shows dissociation of isolated water molecules especially at oxygen vacancies and a crossover to a partial dissociation with chains of alternating $H_2O$ and OH groups stabilised by hydrogen bonding with increasing oxygen and water pressures [1]. The DFT results reveal that defects and adsorbates induce a unique charge and orbital order at the $Fe_3O_4$ (001) surface: While the clean, water and OH-covered surfaces exhibit an exclusively $Fe^{3+}$ surface layer with $Fe^{2+}$, $Fe^{3+}$ ordering in the deeper layers [1], hydrogen adsorption can be used to reduce the surface layer to $Fe^{2+}$ [2] with implications for the catalytic activity of the mineral surface, as well as the spin-polarization of carriers.

[1] N. Mulakaluri, R. Pentcheva, M.Wieland, W. Moritz & M. Scheffler (2009) *Phys. Rev. Lett* **103**, 176102. [2] G. S. Parkinson, N. Mulakaluri, Y. Losovyj, P. Jacobson, R. Pentcheva, & U. Diebold (2010) *Phys. Rev. B* **82**, 125413.

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# Decarbonation of subducting slab at subarc depth: Experimental modeling

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We present UHP experimental results that model $H_2O$-$CO_2$ fluid release from the natural analogues of the oceanic crust and the mantle wedge. The experiments were conducted with two layer 'sandwich' materials consisting of calcite-bearing blueschist (BS) and olivine (OL) and three layer 'sandwich' with siliceous marble layer in between BS and OL. The experiments were carried out at 2.7 GPa under the conditions of imposed temperature gradient of ac. 40-50 ºC/mm so that to keep GS at the lower temperatures conditions than the OL [1]. The maximum temperature at the top of the capsules was 1000 °C. P-T conditions at the bottom of the capsules were corresponded to so-called 'hot' subduction zones.

The experiments reveal crucial role of hyrous fluid on decarbonation of calcite (the only carbonate in the starting materials) and contrasting behaviour of $CO_2$ in different types of sandwich materials. Aqueous fluid was produced mainly by the reaction of glaucophane breakdown: glaucophane => omphacite+quartz±Ca-Na amphibole+$H_2O$ operated in the both types of sandwiches. Flux of $H_2O$ (and solutes like Si, Al etc) in the OL zone of the two layer sandwich was resulted in the development of the Al-bearing orthopyroxene layer at contact with the glaucophane zone. Some of the released $CO_2$ was stored within abundant vermicular magnesite randomly distributed among olivine crystals above the orthopyroxene layer. Such magnesite occurrences are rare in the olivine from the three layer sandwich. However, upward migration of the $H_2O$-bearing fluid through the marble in this sandwich was resulted in the formation of ultrahigh pressure metasomatic column which consists of 4 zones: Fe-Mg-Ca carbonate| dolomite | diopside | magnesite in between the marble and OL, respectively. Multiple clinochlore flakes in lower part of the OL zone also witnesses migration of the hydrous fluid.

Storage of $CO_2$ in the mantle wedge minerals at the subarc depth may have valuable effect on an imbalance in the carbon budget in subduction zones. Further investigation of the slab-mantle interaction is necessary to explain existing discrepancies.

[1] Perchuk & Korepanova (2011) *Doklady Earth Sciences* **437**, 393–395.