

Atomistic simulation of the structure and reactivity of calcite surfaces

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Atomistic simulation techniques enable us to gain insight into processes occurring at the atomic level on mineral surfaces. We will describe recent work using two atomistic techniques, namely molecular dynamics and energy minimisation, to model the surface structure and reactivity of the most abundant calcium carbonate polymorph: calcite. The questions we are addressing are, does the surface structure and stability change with temperature? And to what extent are the surfaces likely to contain hydroxyl groups? In addition, we compare techniques that use inter-atomic potentials based on the Born model of solids to describe the total interaction energy of a system with electronic structure calculations using the VASP code (Kresse and Hafner 1993, 1994).

First we will review how we generate different calcite surfaces, their structures in dry and wet conditions as well as the structural change due to the presence of impurities, and their surface energy and how they compare with ab-initio calculations. We found that atom based potentials slightly overestimate the surface energies, e.g. the surface energy of the (10.4) surface calculated to be 0.59 J.m⁻² compared to 0.42 J.m⁻² using the VASP code. In the second part of the talk, we will present our use of molecular dynamics, using the DLPOLY code (Forester and Smith 1995), to model the interactions of water with the most significant low index surfaces and with growth steps. We found that water molecules bind strongly to the surface, this implies a layering of the water molecules in the vicinity of the surface as observed for MgO (de Leeuw and Parker 1998). The final section will describe the solid state reaction of calcite surfaces with calcium hydroxide and the implications for the presence of hydroxyl groups on the calcite surfaces as observed by experimentalists. Our calculations predict that the stepped surfaces are more likely to react than the flat surfaces, for example the energy of reaction of the hydrated acute step surface is -45.5 kJ.mol⁻¹ whereas that of the (10.4) surface is +13.5 kJ.mol⁻¹.

To conclude, atomistic simulation is a useful tool for relating surface structure and reactivity and provides a good complement to experiment.

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Quantification of subduction zone metamorphic devolatilization from computed high pressure phase equilibria

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Devolatilization in subduction zones is essential to arc magmatism, seismicity and volatile recycling. Realistic modeling of metamorphic devolatilization of subducted lithologies is only possible for chemical systems that closely approximate actual bulk compositions. Volatile components are introduced into subduction zones by three contrasting lithologies: marine sediments, and hydrothermally altered mantle ultramafic rocks and oceanic metabasalts. Using free energy minimization (*Perplex* programs: erdw.ethz.ch/~jamie/perplex), phase equilibria were computed to 6 GPa (~160 km) to quantify the evolution of CO₂ and H₂O by prograde metamorphism of these lithologies. *Serpentinites*: for carbonate-bearing serpentinites (ophicarbonates) little CO₂ is released; for high-temperature (high-T) geotherms complete dehydration occurs under forearcs, and for low-temperature (low-T) geotherms major dehydration occurs under subarcs. *Siliceous limestones*: little devolatilization for all geotherms. *Marls*: with high-T geotherms devolatilization is complete under subarcs; in contrast, little devolatilization occurs with low-T geotherms. *Carbonate-free pelites and turbidites*: with high-T geotherms most dehydration occurs under forearcs, whereas along low-T geotherms substantial H₂O is released under subarcs. *Carbonate-bearing oceanic metabasalts*: decarbonation is negligible along low-T and intermediate-T geotherms and is limited along high-T geotherms; dehydration is complete under forearcs for high-T geotherms, significant under subarcs for intermediate-T geotherms, and very limited along low-T geotherms. *Carbonate-free oceanic metabasalts*: dehydration is complete under forearcs for high-T geotherms, and widespread under subarcs for intermediate-T and low-T geotherms. Because metamorphic devolatilization of subducted metabasalts and metasediments is continuous, no "pulses" of fluid release (corresponding to univariant devolatilization) are expected for these lithologies. Due to differences in the bulk compositions of volatile-bearing lithologies and in the P-T location of geotherms, generalized modeling of subduction zone volatile recycling is questionable.

References

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