Dissolution of fluorite (111) cleavage surface in acid pH: VSI, AFM and Monte Carlo simulations

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To enlarge the current understanding of fluorite (CaF_2) dissolution kinetics we have carried out a detailed study of fluorite dissolution, combining fluid-interface experiments (AFM and VSI techniques), as well as Monte Carlo simulations of fluorite cleavage (111) surface dissolution. To our knowledge, these are the first direct observations of etch pit nucleation on the (111) surface of fluorite under low but variable pH conditions.

AFM (Atomic Force Microscope) and VSI (Vertical Scanning Interferometry) were used to measure dissolution in single pass flow-through cells at pH values ranging from 1 to 3.15 in dilute HCl solutions far from equilibrium. Under these conditions, our observations show that dissolution proceeds through the formation of crystallographically-controlled triangular pits, whose coalescence results in overall surface retreat. These observations are consistent with the stepwave model [1], which predicts that at ΔG_r less that a critical value, mineral dissolution is controlled by stepwave generation and movement. Surface retreat was quantified as a function of pH, yielding an intrinsic fluorite dissolution rate constant as well as the dependence of dissolution rate on pH.

The results of Monte Carlo simulations were also found to be entirely consistent with the above observations. These fully parameterized simulations include a lattice-accurate cubic structure with Ca-F bonds and do not require any "strategic" assumptions about reaction mechanism, thus allowing us to explore and compare the changes in virtual surface microtopography and process kinetics with direct observations. Simulation results include the formation of triangular etch pits and their coalescence under far-from-equilibrium conditions.

[1] Lasaga & Lüttge (2001) *Science* **291**, 2400–2404.

The thermochemical structure of the upper mantle as inferred by seismic and gravity data

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We consider a reference mineral physics model based on current knowledge of material properties at high pressure (P) and temperature (T). The phase equilibria and the elastic properties are computed with a recent thermodynamical model covering a six oxides (NCFMAS) system. Anelastic properties are implemented with a P, T and frequency dependent law based on mineral physics knowledge. The model predicts values of physical parameters (e.g., shear velocity, density) as function of pressure (or depth), temperature and composition. Equilibrium compositions or mixtures of different compositions (e.g., MORB and Harzburgite) can be considered.

Starting from this model, we adopt a non-linear approach to obtain the average thermal and compositional structures that are able to fit global seismic data, i.e. normal modes and travel times. Then, we extend our results to 3-D inversion of long period seismic waveforms, which allow us to resolve seismic structure in the whole upper mantle. We produce several T-C models that are able to fit the seismic observations. At the same time, we predict the 3-D density structures related to the inverted T-C fields. Viscosity is evaluated with a similar physical law as seismic attenuation. We compute the synthetic geoid for all the models by using the STAGYY code and thus the misfits with observations. The analysis of the results will give a robust interpretation of the thermochemical structure of the upper mantle, will reduce the trade-off between T and C and it will point out possible problems with uncertain physical properties in the reference mineral physics model used.