Revisit calcite dissolution kinetics: Roles of ΔG, pCO₂, and dislocation

H. HERNY TENG[1] AND CHUANFANG FAN[2]

[1]Dept. Chemistry, the George Washington University, Washington, DC 20052 (hteng@gwu.edu)
[2]Department of Civil and Environmental Engineering, Rice University, Houston, TX 77005

The dissolution of calctite in a full range of saturation conditions is investigated to reveal the kinetic effect of Gibbs free energy, dislocation density, and the presence of atmospheric pCO_2. Experiments are carried out in a mixed-flow reactor at room temperature in both closed and open (to air) settings. Calcite samples are prepared by fragmentation and milling to generate variations in defect densities. Experimental observations show a highly nonlinear dependence of the dissolution rates on Gibbs free energy. However, the dissolution rates do not seem to be affected by dislocation density and also are largely independent of the presence or absence of atmospheric pCO_2 at any saturation conditions. These results suggest that: (i) the classic TST model may not be sufficient to depict the relation between dissolution rate and Gibbs free energy for calcite at all saturation conditions. The sigmoidal trend in the R-ΔG relationship indicates that, though the TST rate equation adequately describes calcite dissolution kinetics when ΔG < −12 KJ mol^{-1}, it clearly overestimates the dissolution rates when the system approaches equilibrium; (ii) the surface steps associated with increased crystal defects may be overwhelmed by those regenerated at corners and edges of calcite particles through layer-by-layer dissolution along cleavage directions; (iii) the fluctuation of atmospheric CO_2 in ambient environments bears little importance to calcite dissolution due possibly to the slow response of aqueous HCO_3^- to change of pCO_2 at low CO_2 partial pressure conditions.

H₂O storage capacity of olivine from 5-13 GPa: Consequences for dehydration melting above the transition zone

TRAVIS J. TENNER*, PAOLA ARDIA, MARC M. HIRSCHMANN AND ANTHONY C. WITHERS

University of Minnesota, Minneapolis, MN 55103, USA (*correspondence: tenn0047@umn.edu)

The onset of hydrous partial melting above the transition zone (TZ) is controlled by the H_2O storage capacity of peridotite, defined as the maximum concentration the rock can store at T and P without stabilizing a hydrous fluid or melt. H_2O solubilities of individual minerals do not constrain peridotite storage capacities as they do not account for enhanced hydrous melt stability and reduced H_2O activity facilitated by the additional components of multiply saturated peridotite. Here we present experimental determinations at 5-13 GPa along the upper mantle geotherm of H_2O contents in olivine in peridotite saturated with small amounts of hydrous melt, thereby constraining true H_2O storage capacities.

Experiments consist of layered (~2/3 KLB-1 peridotite, ~1/3 Fo 89.6 olivine), hydrated oxide analogues. Monomineralic olivine layers grow ~200 μm crystals, allowing H_2O analysis by SIMS. Experiments were conducted at 1350-1500 °C with 0.5-1.0 wt.% bulk H_2O. All experiments contained melt+ol+pyx+gt. At 1450 °C, H_2O in olivine increases from 60±20 to 500±60 ppm from 5-13 GPa, and diminishes slightly with increased T. Variable bulk H_2O has no effect, thereby justifying extrapolation to small bulk H_2O contents appropriate for incipient partial melting of peridotite near its storage capacity

Using these results together with P-dependent lherzolite modes and olivine/pyroxenet/garnet partition coefficients [1] predicts a peridotite storage capacity at 1450 °C that increases from 170 to 920 ppm from 5-13 GPa. Therefore, partial melting above the TZ would leave residues with ~1000 ppm bulk H_2O, far more than is present in MORB-source upper mantle [50-200 ppm] and near the upper limit of estimates for OIB-source upper mantle [300-900 ppm]. This is not consistent with a pervasive layer of partial melt atop the TZ, but allows for such layers in regions of local H_2O enrichment, such as near areas of recent subduction or those affected by H_2O-enriched plumes.

[1] Hirschmann *et al*. (2009), *Phys. Earth Planet. Int*. **176**, 54-68.