

Investigating the dependence of feldspar dissolution rates on Gibbs free energy in the presence of high pCO₂

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Here we report on results from an ongoing experimental investigation of the dissolution kinetics of albite feldspar at 100 °C in aqueous solutions significantly enriched in dissolved carbon dioxide (pCO₂ = 9 MPa). The purpose of this study is to measure CO₂-water-rock interactions as a function of solution saturation (ΔG), thereby providing data needed to model physico-chemical interactions associated with mobile CO₂-plumes in subsurface environments. Over the fluid saturation range of -70 to -40 kJ mol⁻¹ the dissolution rates can be characterized by a dissolution rate plateau, where the rates are roughly equal and independent of dissolved Na, Al, and Si. At higher solution saturation states, the rates begin to decrease sharply. In addition, the stoichiometry of dissolution changes from stoichiometric to non-stoichiometric, and is most probably due to the precipitation of an Al phase. Current experiments are being run to measure the kinetics at $\Delta G > -30$ kJ mol⁻¹. The present data set, even though incomplete, is in general accord with many other studies that show a sigmoidal dissolution rate-free energy relation (e.g. Hellmann and Tisserand, 2006; and refs therein). Most importantly, the data also deviate dramatically from the behavior predicted by transition state theory (TST).

Reference

Hellmann, R. and Tisserand, D., (2006) Dissolution kinetics as a function of the Gibbs free energy of reaction: An experimental study based on albite feldspar. *Geochim. Cosmochim. Acta* **70**, 364-383.

Lower mantle phase-boundary variability

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A lower mantle S-wave triplication with a Scd branch occurring between S and ScS appears to be explained by a recently discovered Perovskite (PV) to Post-Perovskite (PPV) phase-change. It is predicted to have a positive Clapeyron slope (γ) between 5 to 13 MPa/K with a small S-velocity jump (1.5 to 4%) and an even smaller 1 to 2% jump in P-velocity. Seismic observations indicate that Scd arrives earlier and stronger beneath fast regions indicating a positive γ (circum-Pacific) than slow regions (super plumes). However, it proves difficult to separate effects produced by down-welling (slab debris) from up-welling (plumes) in refining the actual physical properties. Here we model dense record sections collected from USArray and existing PASSCAL data to isolate effects produced by lower mantle structure as evidenced by P and S-waves, to better define the seismic phase-change properties beneath Central America. We find that the PV-PPV velocity jump is twice as strong beneath slow regions than fast regions requiring distinct reference heights indicative of changing chemistry. Moreover, the edges of the supposed buckled slabs delimited by both P and S-waves display very rapid changes in phase-boundary heights producing Scd multipathing. These features can explain the unstable nature of this phase with easy detection to no detection commonly observed. The fine structure at the base of the mantle beneath these edges contains particularly strong reflections indicative of local ultralow velocity zones, which is predicted in some dynamic models.

References

- Sun D.Y., Tan E., Helmberger D., and Gurnis M., (2007), Seismological support for the metastable superplume model, sharp features, and phase changes within the lower mantle, *PNAS* **10**.1073/pnas.0608160104.
- Sun D.Y., Helmberger D., Song X.D. and Grand S., (2007), Predicting Global Perovskite and Post-Perovskite Phase Boundary, AGU Monograph, *The Last phase Transition*, in press.