

AWARD NUMBER:  
DE-FG07-01ER63287

AWARDEE NAME:  
University of Oklahoma

PROJECT OR AWARDEE ACCOUNT NO.:  
EMSP 81908/Acct. 125-5275

PROJECT TITLE:  
Origins of Deviations from Transition-State Theory: Formulating a New  
Kinetic Rate Law for Dissolution of Silicates

PRINCIPAL INVESTIGATOR  
Dr. David London  
School of Geology & Geophysics  
University of Oklahoma  
100 East Boyd Street, Rm 810 SEC  
Norman, OK 73019

(405)-325-7626  
dlondon@ou.edu

Report name: EMSP final Report

Our charge in this research project was to synthesize single feldspar crystals large enough to conduct dissolution studies. We were instructed to employ conventional, small-volume hydrothermal reactors at elevated pressures and temperatures in this task.

We explored combinations of glasses, crystals, and oxide reagents as starting materials, added as solid glass cylinders or powders of glasses and other materials.

We added boron, phosphorus, and fluorine to act as fluxes to promote dissolution of all components (especially Al, which is highly soluble in the chloride solutions that are typically used) at elevated fluid pressure. After preliminary discussion with PI Icenhower, we decided that the boron flux was one we would utilize. We abandoned the phosphorus flux because P is too soluble in the feldspars that would be synthesized. We could not make fluorine-fluxed glasses at atmospheric conditions, because the fluorine was volatilized almost completely from the reactive mixtures via exchange with atmospheric oxygen.

As an additional consideration, we noted that the likely radionuclide containment medium, an alkali borosilicate glass, would impart B to the system, and hence feldspars synthesized in the presence of B would be most analogous to those of the containment scenario.

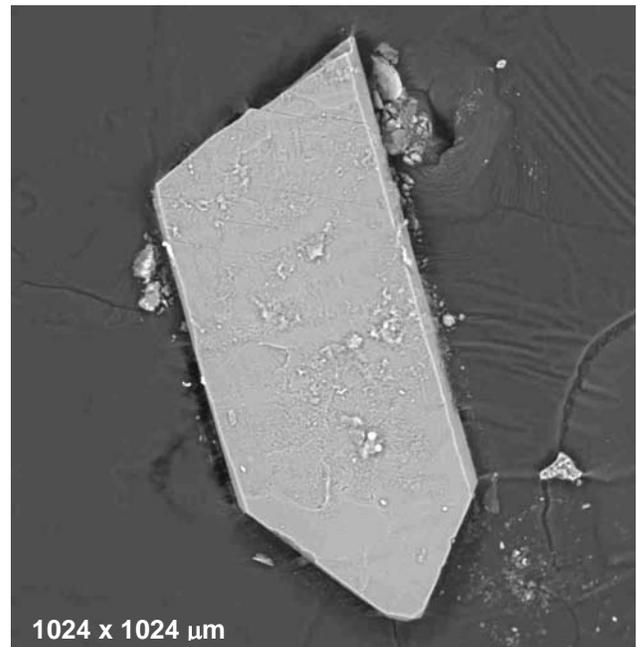
The following is the final procedure that provided the best results:

Oxide and carbonate reagent mixtures of alkali feldspar stoichiometry ( $\text{NaAlSi}_3\text{O}_8$  and  $\text{KAlSi}_3\text{O}_8$ ) were fired in air at 800C for 12 hr to decarbonate the mixture and then milled to powder. The  $\text{NaAlSi}_3\text{O}_8$  and  $\text{KAlSi}_3\text{O}_8$  powders were mixed with an equal weight fraction of nominally anhydrous  $\text{B}_2\text{O}_3$  glass (prepared by firing reagent  $\text{H}_3\text{BO}_3$  in Pt over a Bunsen burner). The alkali borosilicate mixtures were then fired in air in a Deltech furnace at 1600C for 24 hr to ensure complete melting of any crystalline components. The resultant glasses were entirely crystal-free and homogeneous.

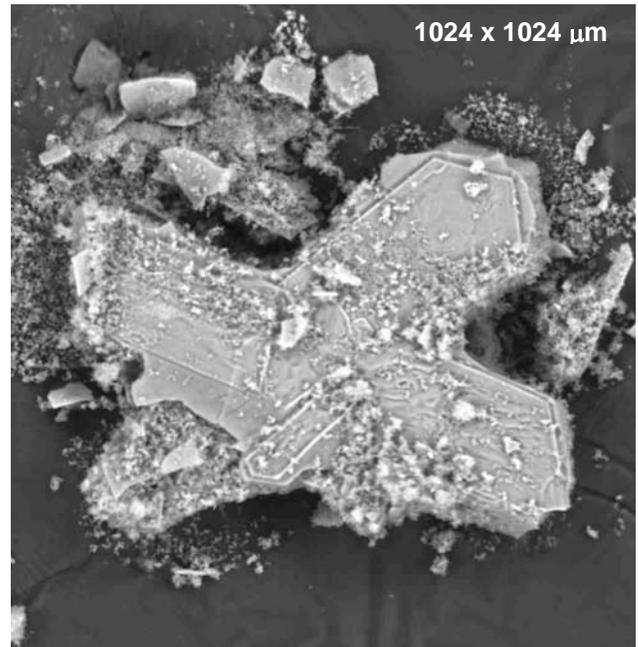
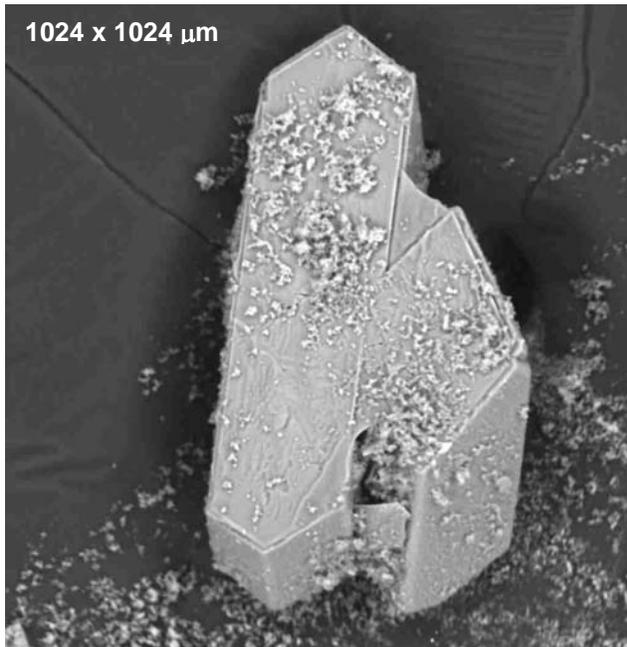
The glasses were cored with a diamond coring bit to a diameter of ~ 3 (W) x 5 (L) mm, the cores rounded, and sealed in Au foil capsules with an equal weight fraction of ultrafiltered deionized water. The capsules were loaded into cold-seal hydrothermal reaction vessels and run at 600C, 200 MPa, for periods of 150-500 hrs, then quenched.

Crystals of albite and of K-feldspar approaching 1 mm in maximum dimension were produced in the vapor space of capsules. Representative crystals are shown in Figures 1-4 below.

An Excel spreadsheet containing representative analyses of the phases shown in Figures 1-4 is attached as a supplementary document.



Figures 1 & 2: synthetic albite crystals; washed 1 hr in hot distilled water bath. Crystal in Figure 2 is ~ ½ its original length.



Figures 3 & 4: synthetic K-feldspar crystals, unwashed sample. Note glass phase adhering to reentrants in twinned crystals. Thin, smooth surface coatings on selective faces, however, appear to be pure K-feldspar.