

## YEARLY PROGRESS REPORT

Year 2

**Project Title:** Origins of Deviations from Transition-State Theory: Formulating a New Kinetic Rate Law for Dissolution of Silicates

**Covering Period:** June 1, 2002 – May 31, 2003

**Date of Report:** June 2, 2003

**Recipient:** Dr. David London (PI), University of Oklahoma

**Award Number:** DE-FG07-01ER63287

**Subcontractors:** None

**Other Partners:** Dr. G.B. Morgan (electron microprobe analyst, OU)

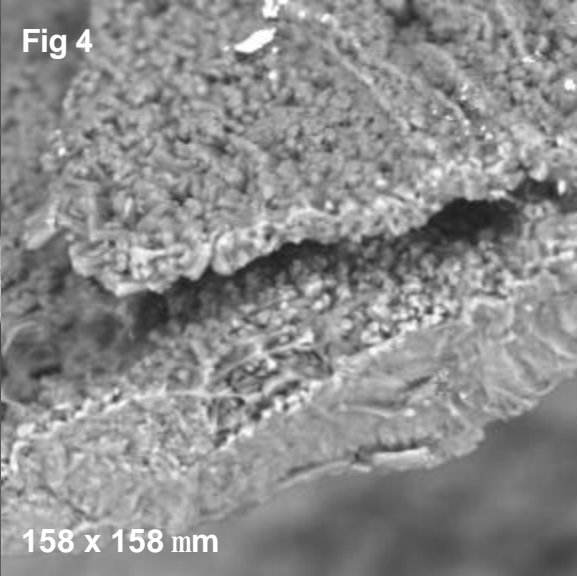
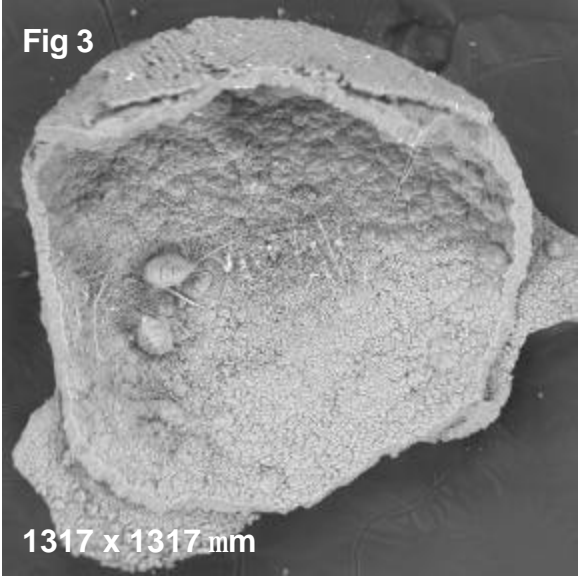
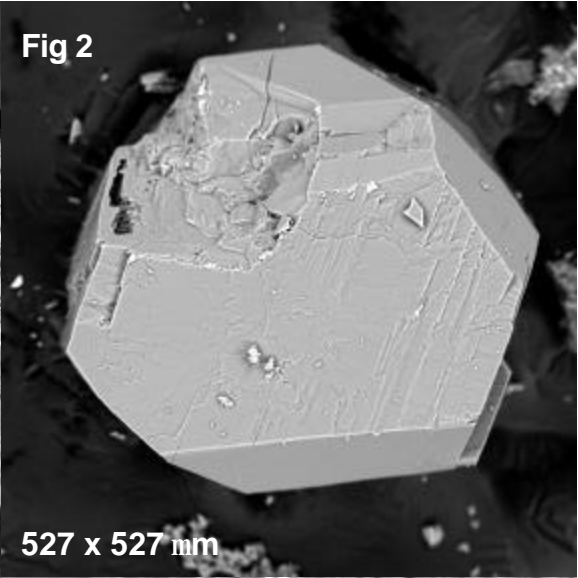
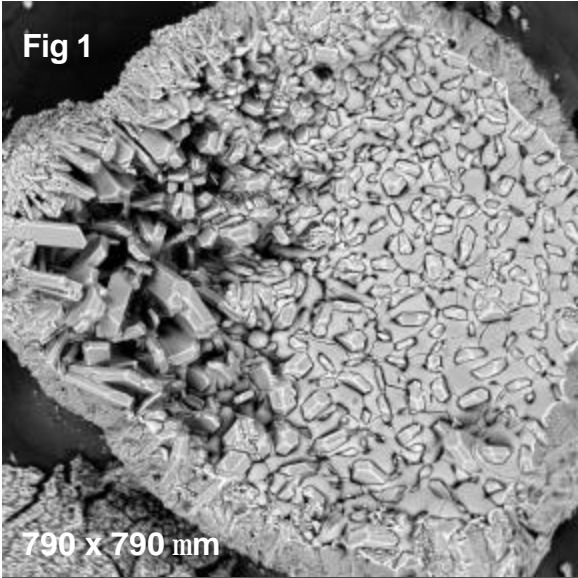
**Project Team:** J.P. Icenhower (PNNL), B.P. McGrail (PNNL), A. Lüttge (Rice University)

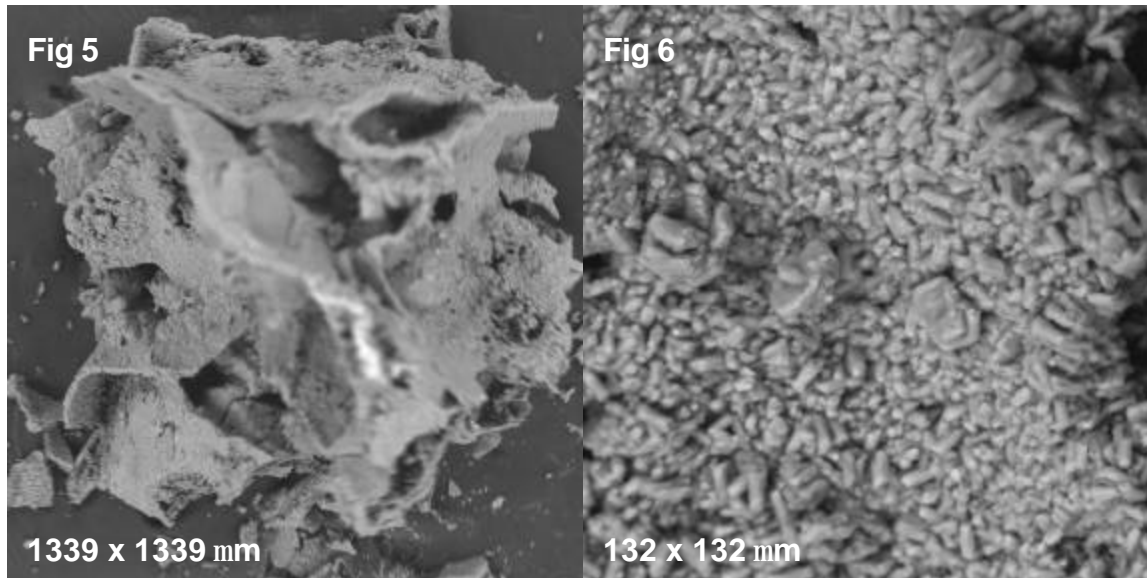
**Background:** The task assigned to PI David London, University of Oklahoma, was to devise hydrothermal methods of synthesis that optimize the size of synthetic monocrystals of alkali feldspars,  $\text{KAlSi}_3\text{O}_8$  (orthoclase) and  $\text{NaAlSi}_3\text{O}_8$  (albite). The synthesis method agreed upon will utilize convention cold-seal hydrothermal reactors. This equipment and synthesis method were chosen for two reasons: (1) the method best simulates hydrothermal reactions of silicate glass waste material with groundwater, and (2) the method employs small, sealed volumes of reagents, which minimizes potential hazards when and if radionuclides are added to the system. Note that the University of Oklahoma did not approve the award for acceptance until November 20, 2001.

**Status:** The reporting period above partly overlaps the reporting period for Year 1 (as stipulated by email from DOE-ID PSD on May 27, 2003, and May 28, 2003. As the report for Year 1 summarizes activity and expenditures through September 14, 2002, this report covers the period September 15, 2002 – May 31, 2003.

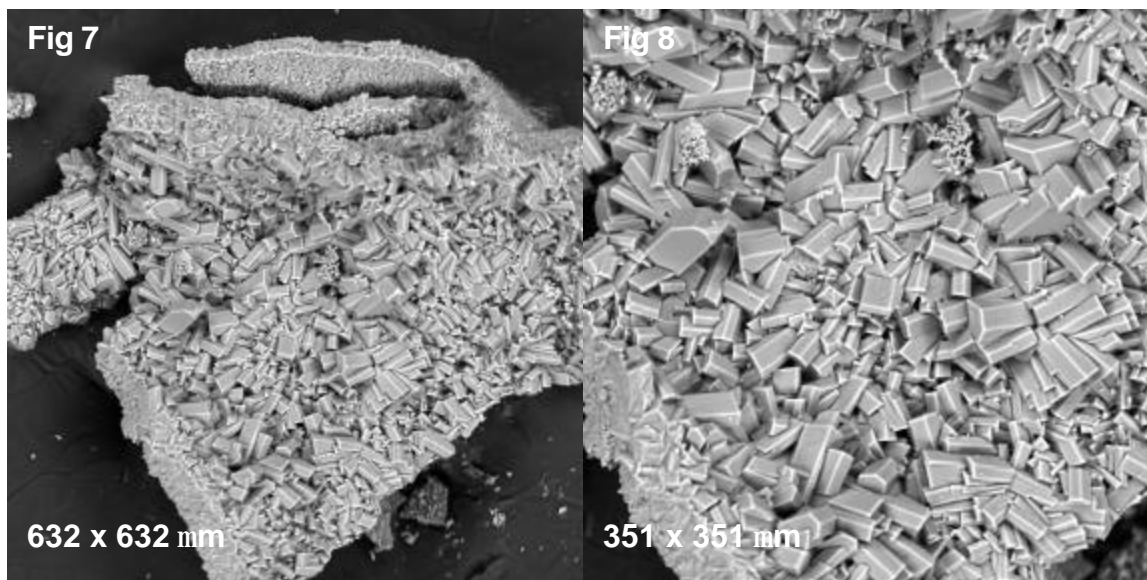
Hydrous borosilicate glasses produced by melting of the assemblages albite +  $\text{B}_2\text{O}_3$  +  $\text{H}_2\text{O}$  and orthoclase +  $\text{B}_2\text{O}_3$  +  $\text{H}_2\text{O}$  at 800C, 200 MPa, were reloaded into Au capsules with additional  $\text{H}_2\text{O}$  for crystal synthesis experiments (with normal temperature gradient of  $\pm 2\text{-}4\text{C}$  along the length of the capsule). Experiments involving albite were run at 650C (6 days), 550C (7 days), and 450C (14 days). The experiment at 650C produced fine-grained albite + some remnant borosilicate glass (Fig. 1), and some isolated monocrystals of albite measuring  $\sim 500 \mu\text{m}$  (Fig. 2). Experiments at 550C (Fig. 3,4) and 450C (Fig 5,6) produced frits of exceedingly fine-grained albite plus minor quench and

relict glass. As a result, subsequent experimentation was conducted at the nominal set point (vessel hot spot) of 650C.





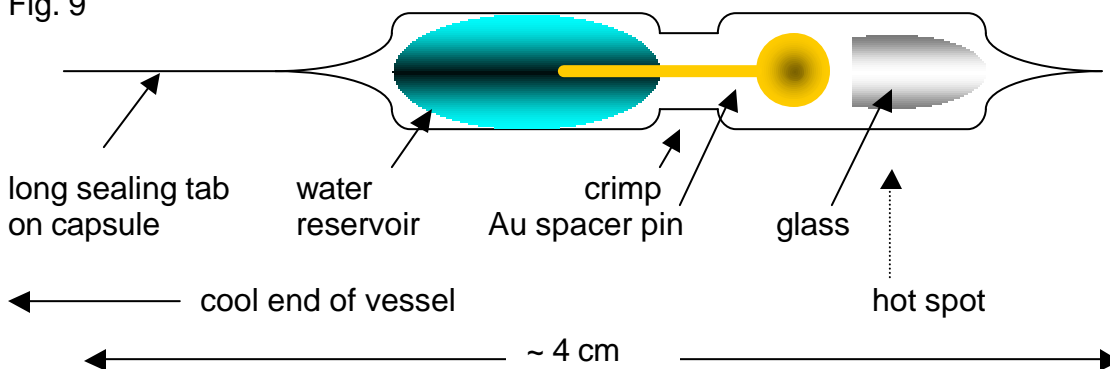
An analogous suite of experiments (650C, 550C, 450C, same durations) with the mostly vitreous product of melting orthoclase +  $B_2O_3$  +  $H_2O$  generated frits of fine-grained to exceedingly fine-grained orthoclase plus minor relict glasses. Even at 650C (Fig. 7,8), the crystalline products were finer-grained by an order of magnitude than in the albite experiments.



The synthesis of hydrous alkali borosilicate starting glasses begun in Sep 02 (see Year 1 report) continued through September and October of 02. The methodology was modified to facilitate the creation of a more uniform product. The effort began by milling together albite or orthoclase + the nominally anhydrous  $B_2O_3$  glass in equimolar proportions. These were fused to a white vesicular glass at 1000C, 1 atm (muffle furnace) for 1 hr at temperature. The glass-ceramic product was cored for loading.

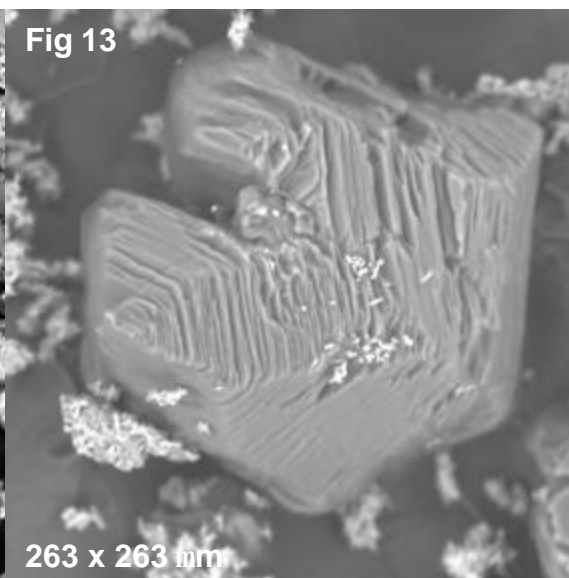
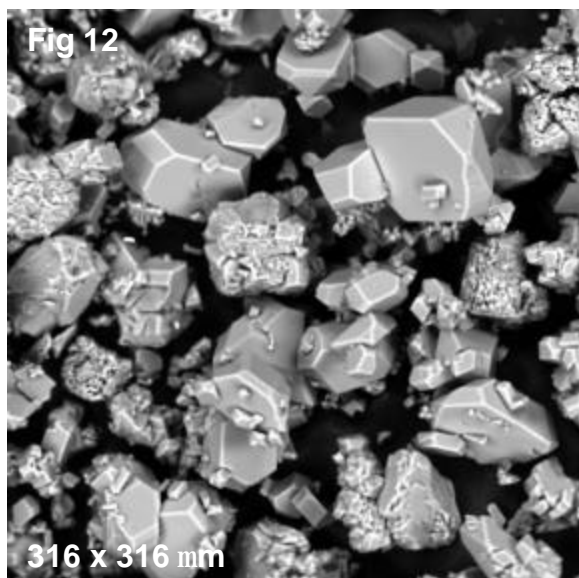
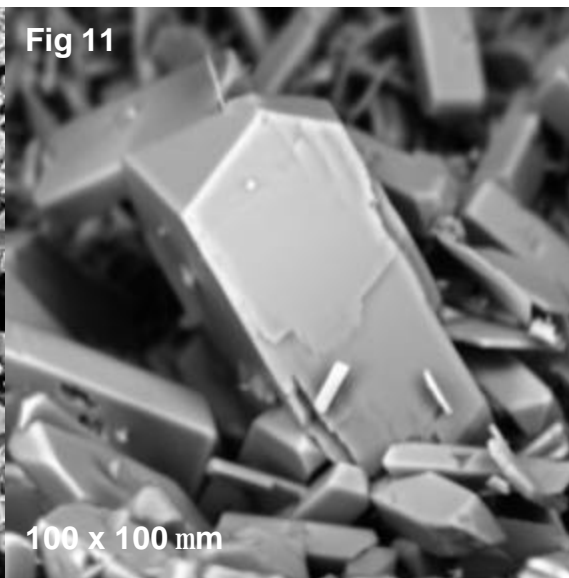
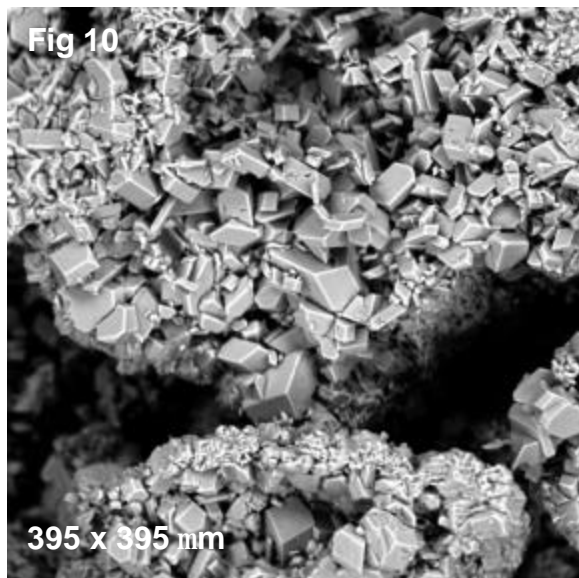
Reconnaissance experiments with this anhydrous glass-ceramic + 20 wt% added H<sub>2</sub>O were taken to 650C, 200 MPa, for 4 days, then dropped to 550C for an additional 7 days. Experiments were loaded with a weight ratio of water:glass near 3:1. The capsule configuration was modified to facilitate loading such large weight fractions of water (normally not possible to seal), and to span a temperature gradient of ~ \*C in the vessels. The capsule configuration is shown in Fig. 9.

Fig. 9



Use of an uncommonly long sealing tab (second weld) allowed capsules to be nearly filled with water (water reservoir) and successfully sealed. Filling the water reservoir completely is necessary to create the open space for crystal growth. A spacer pin was fabricated by creating a bead at the end of a length of Au wire. A crimp on the shaft of the spacer pin keeps it and the glass charge from moving during pressurization. The entire Au pin also keeps the capsule from sealing between the two reservoirs. The round end of the spacer pin is approximately the same diameter as the glass core material; thus, only one end of the core needs to be rounded (sharp edges of starting materials can cut the Au tubing during initial compression; the cores must be rounded or else abut closely against a round object – in this case, the head of the spacer pin).

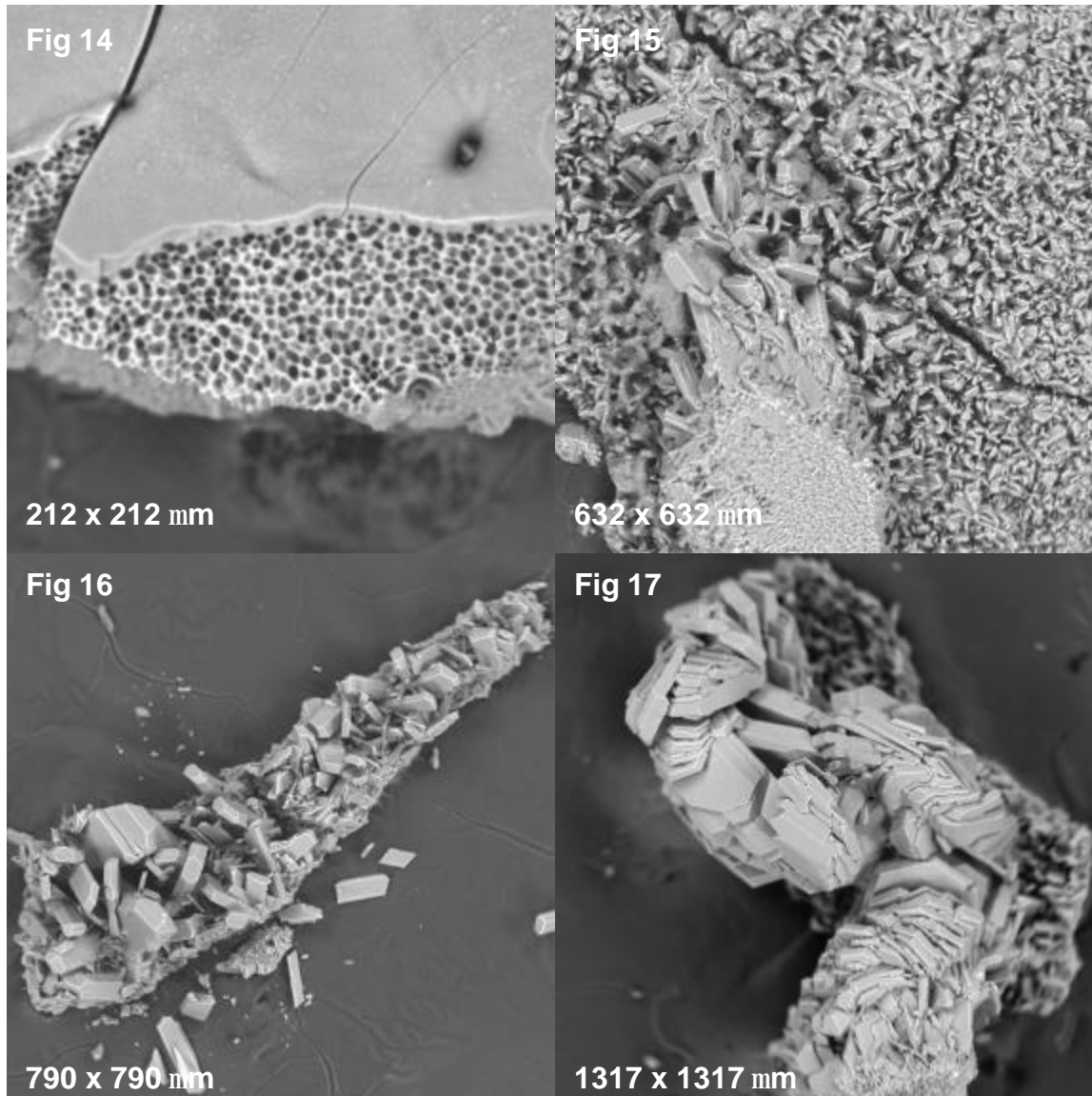
Experimental run products showed two feldspar crystal morphologies that probably reflect growth at the two run conditions (albite: Fig. 10,11; orthoclase: Fig. 12). From prior experiments, we suspect that the well-formed crystals grew at the higher temperature, which reinforces our plan to stick with a single run temperature of 650C. They are fine-grained, however, because of the large number of residual crystal fragments in the starting glass-ceramic; we infer that these many small fragments served as centers for continued crystal growth rather than the desired product of free nucleation from the aqueous vapor phase. We observed, however, that the run products consist wholly of alkali feldspar plus sassolite (H<sub>3</sub>BO<sub>3</sub>) plus low-solute water (Fig. 13). This is a very desirable result, because the method does not produce a vapor phase (at run conditions) with a large component of alkali aluminosilicate solute.



In a recent set of experiments, we took cores of the albite-borate and orthoclase-borate glass-ceramics to 800C, 200 MPa, with 20 wt% added water, for 3 days. The purpose of the preconditioning step is to obliterate crystal nuclei present in the starting 1-atm glass-ceramic, and hence to enhance the probability of growing fewer and large feldspar crystals. We hoped to produce a clear, crystal-free glass without an appreciable excess of vapor, and we succeeded in both regards. We loaded portions of these wholly vitreous products into capsules with the configuration shown in Fig. 9 for runs to 650C, 200 MPa, 10 days. We now know, however, that we can produce these crystal-free hydrous glasses as a preconditioning step in runs to a final temperature of 650C, i.e. we need to load only one experiment, not two.

The reaction products of an albite-borate glass experiment after 10 days still contained an appreciable fraction of glass, borate (sassolite) that crystallizes upon drying of the

punctured capsules, and some albite. The glass is highly vesicular (Fig. 14), and we do not know if the vesicularity represents a quench phenomenon or unmixing of borate and silicate melt components at temperature. The albite varies in size from fine-grained mats (Fig. 15) to medium-grained tabular crystals (Fig. 16) and relatively coarse-grained cocks-comb aggregates (Fig. 17).



**Plans for 2004:** We have not seen any enhanced crystal growth in the vapor space of the long capsules (Fig. 9), so we will try longer capsules (larger thermal gradients) and we will abandon the long capsules if there is no significant material transport along the thermal gradient. We have noted in most experiments that the albite and to a lesser degree orthoclase form crystals of widely varying size in the same capsule. We will attempt to promote Ostwald ripening of the crystals, therefore, by thermal cycling, in which experiments oscillate ~ 100C (e.g., between 750C and 650C) to promote

dissolution of small crystals and continued of larger ones. We will also explore this process as a means of obtaining a higher proportion of single monocrystals rather than aggregated mats.

**Patents:** None

**Milestone Status Table:**

Sep 02: begin synthesis of feldspar-boron glasses  
 Oct 02: synthesis experiments at 650C  
 Nov 02: synthesis experiments at 450C  
 Dec 02: synthesis experiments at 550C  
 May 03: synthesize feldspar-borate glass-ceramic, fuse glass-ceramic to hydrous glass  
 Jun 03: run synthesis experiments at 650C

**Budget Data:**

Phase/Budget Period			Approved Spending Plan			Actual Spent to Date		
			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	9/15/01	9/14/02	25,000		25,000	11,086.56		11,086.56
Year 2	9/15/02	5/31/03				10,824.48		10,824.48
Year 3								
Year 4								
Totals:			25,000		25,000	21,911.04		21,911.04

**Spending Plan for 2004:**

Month	Estimated Spending
June-03	Lab materials, EMPA: \$1500
July-03	EMPA: \$2500
August-03	\$0
September-03	\$0
October-03	\$0
November-03	\$0
December-03	\$0
January-04	\$0

February-04	\$0
March-04	\$0
April-04	Lab materials, EMPA: \$1000
May-04	PI sum sal 0.5 mo @ 1.00 FTE: \$7500