

**FINAL REPORT**  
**DEPARTMENT OF ENERGY GRANT DE-FG05-85ER13414**  
**"ACTIVITY COMPOSITION RELATIONSHIPS IN SILICATE MELTS"**

Below is a brief summary of work performed during this project. Relevant publications are listed in Appendix 1.

**1. Construction of furnace laboratory and calibration of instruments.** The laboratory that forms the nucleus of this project was constructed from scratch during the first 6 months of the project. It comprises a Deltech vertical-tube furnace with a high-precision, programmable controller; custom-designed, water-cooled, brass furnace-tube end closures; a gas-mixing apparatus with 3-stage regulation; a probe for monitoring oxygen fugacity in the chamber; and a polishing bench for sample preparation.

**2. Installation of electron microprobe.** During the grant period the MIT electron microprobe (a fully automated, 3-spectrometer MAC-5 with energy-dispersive capability) was purchased with department funds, moved to UNC, and significantly upgraded. Modifications include: (1) rebuilding of spectro-meters, (2) installation of new, larger diffusion pump, (3) installation of new cooling equipment in electronic racks, and (4) installation of new high-vacuum gauge. We also installed a new carbon coater. Current filament life is approximately twice that obtained at MIT. The precision of replicate analyses is approximately equal to that obtained by T.L. Grove at MIT.

**3. Determination of phase equilibria along a basalt-rhyolite mixing line.** This study comprises the bulk of work performed to date. We have completed approximately 100 experiments on the one-atmosphere phase equilibria of basalt-rhyolite mixtures. Starting materials were an alkali basalt from Pisgah Crater, California, and a high-silica rhyolite from the Bishop Tuff, Owens Valley, California. These materials were chosen because the compositional trend of the mixtures mimics many continental calc-alkaline suites. Some of the results of this study are illustrated in Figures 1-4. Significant results include:

1) Magnesian olivine ( $Fo_{86}$ ) is the stable liquidus phase in mixtures containing up to 63 wt%  $SiO_2$  (Fig. 1). This result suggests that olivine can crystallize directly from natural silicic andesites, and supports the conclusion reached by some investigators that olivine in silicic andesites is a phenocryst phase and not a xenocryst. Because olivine fractionation can have such a profound effect on the course of fractional crystallization, this observation has important implications for the genesis and evolution of intermediate rocks.

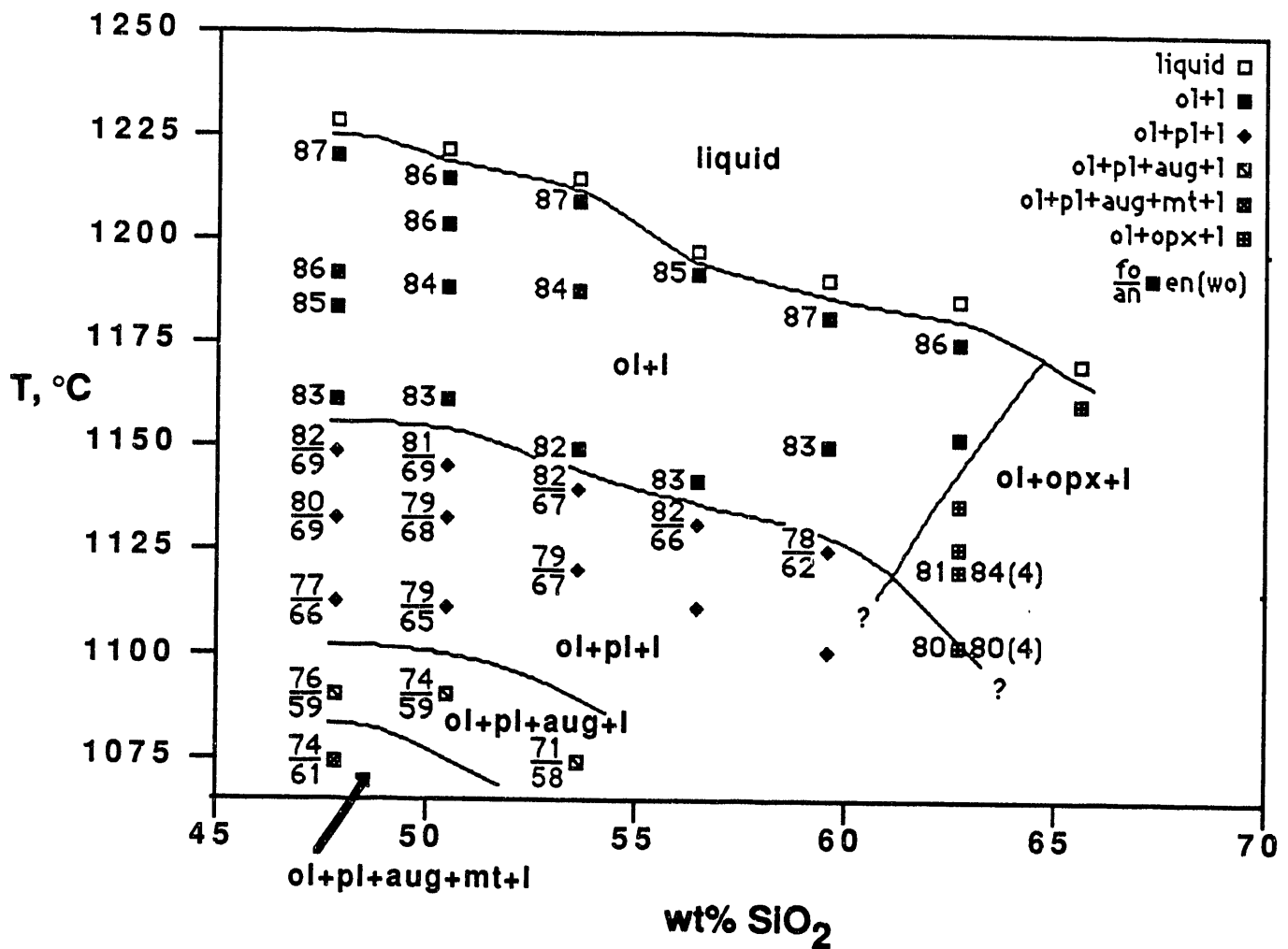
2) The coefficient for the distribution of Fe and Mg between olivine and liquid ( $K_D$ ) for the wide range of compositions studied is independent of temperature and composition (Fig. 2). The value obtained for these compositions ( $K_D = .30$ ) is the same as that obtained by Roeder and Emslie (1970) for a restricted range of basaltic compositions. This result indicates that fractional crystallization models using  $K_D = 0.30$  will be accurate, even in silicic andesites.

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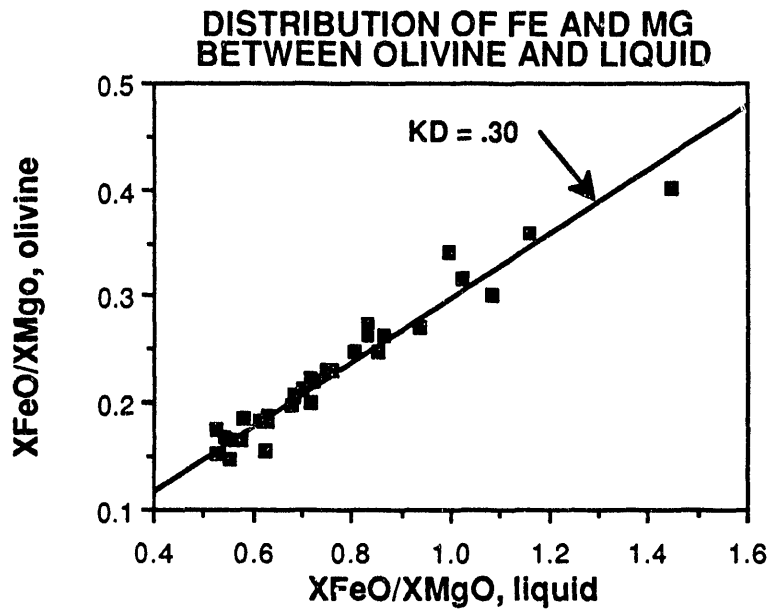
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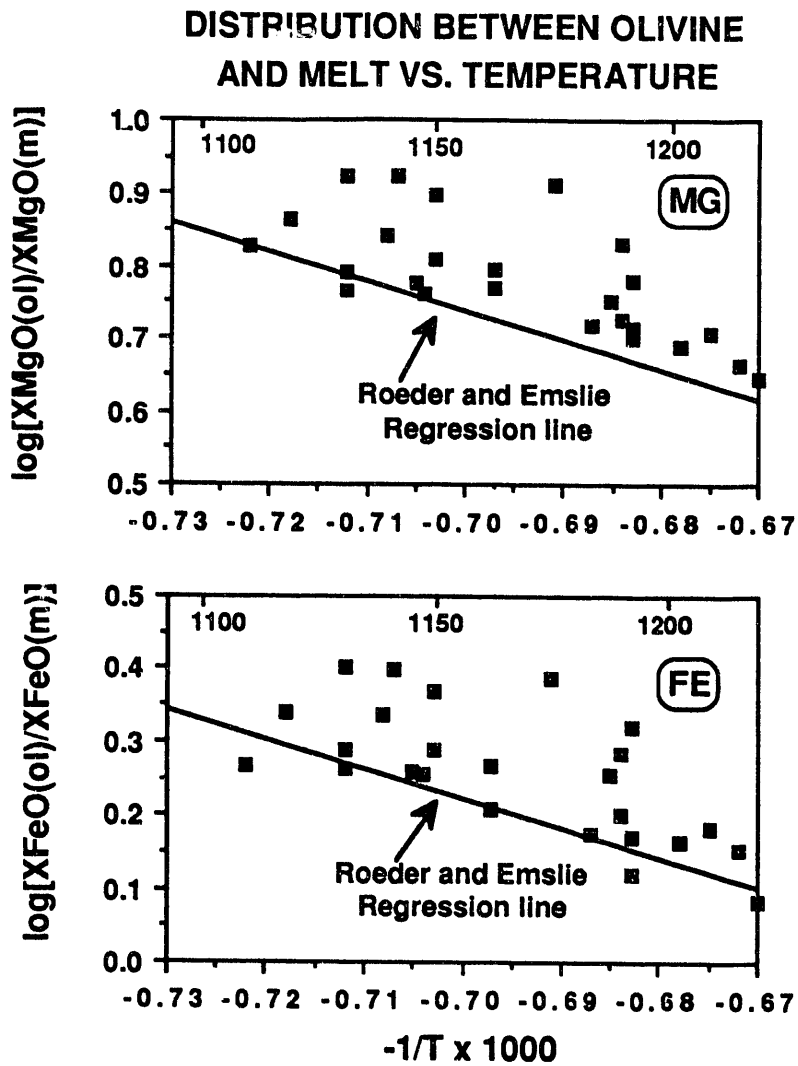
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**Figure 1.** Phase diagram for compositions along a mixing line between alkali basalt and rhyolite. Note the exceptionally large field over which magnesian olivine coexists alone with liquid. This accounts for the common observation that olivine is an apparent phenocryst in many silicic andesites and dacites. Numbers next to points give mol% forsterite in olivine, mol% anorthite in plagioclase, and mole% enstatite and wollastonite in orthopyroxene.

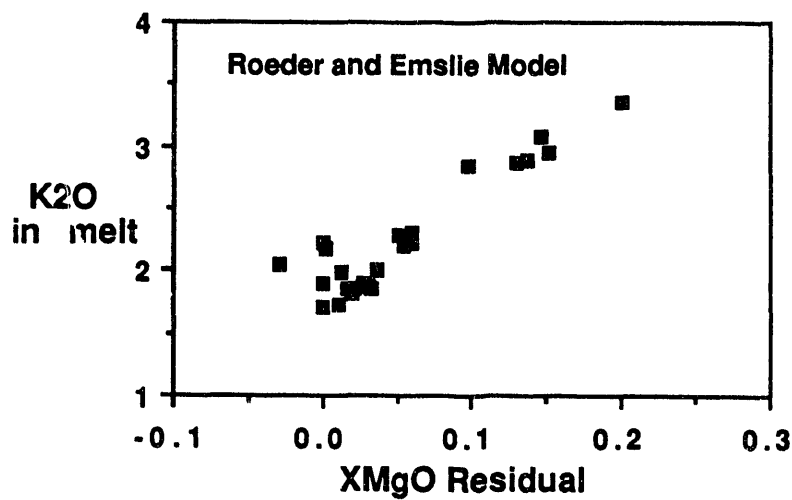


**Figure 2.**  $K_D$  plot of distribution of Mg and Fe between olivine and liquid. The distribution coefficient obtained here over the entire range of olivine crystallization in Figure 1 (0.30) is identical to that obtained by Roeder and Emslie (1970) for a restricted set of basaltic compositions. This indicates that  $K_D$  modeling of olivine crystallization is accurate.



**Figure 3.** Deviation of Mg and Fe partitioning between olivine and liquid from simple model of Roeder and Emslie (1970). Because the deviations for both Mg and Fe are nearly equal for a given experiment, the  $K_D$  values remain constant.

**K2O VS. RESIDUAL OF MG DISTRIBUTION  
BETWEEN OLIVINE AND MELT**



**Figure 4.** Plot of residual from MgO plot of Figure 3 vs.  $K_2O$  in the liquid. The strong positive correlation is consistent with the hypothesis that  $K_2O$  has a strong effect on the activity of forsterite in silicate liquids (see main body of proposal).

3) Even though our results corroborate and expand the applicability of olivine/liquid  $K_D$  calculations, the behavior of individual oxides in the silicate liquid deviates significantly from the simple activity-composition relationship assumed by Roeder and Emslie (1970). For many experiments the individual distributions of MgO and FeO between olivine and liquid deviate from the simple model of Roeder and Emslie by large but nearly equal amounts (Fig. 3). These deviations display a strong correlation with the  $\text{SiO}_2$  and  $\text{K}_2\text{O}$  contents of the residual liquid (Fig. 4), and give insight into the polymerization behavior of the liquids.

4) The distribution coefficients for Ca and Na between plagioclase and liquid are dependent on both temperature and composition. For the mixtures studied  $K_D$  varies between 1.43 and 2.27. These results, coupled other published values, suggest that correct selection of plagioclase-liquid distribution coefficients for crystallization modeling is not possible at the present time. A systematic study of the temperature and compositional dependence of this distribution coefficient is needed.

5) An extensive microprobe data set (110 average analyses of phenocrysts and coexisting glasses) for all the mixing experiments has been added to the experimental data base we have been compiling for the activity-compositional modeling part of this study. This data set fills an important gap in the data base and has improved the calibration of the silicate-liquid activity model which we are developing.

**4. Enthalpy-composition relationships in magmas.** We have developed a computer program (ENMAG) which allows the enthalpy of a magma, relative to an equivalent crystalline assemblage at 298°K, to be calculated. Knowledge of how this enthalpy difference ( $H^*$ ) varies with  $T$  is important for understanding the cooling history of magma bodies. A particularly important parameter of a magmatic system is the bulk heat capacity ( $C^*$ ), which is defined as the derivative of  $H^*$  with respect to  $T$ . From our experimental data on crystallization of alkali basalt, we calculate that  $C^*$  increases from 1.7 J/g°K for pure liquid to 3.8 J/g°K for olivine+liquid to 5.2 J/g°K for plagioclase+olivine+liquid (Fig. 5). This implies that the rate of cooling of the basalt will decrease greatly as new phases join the crystallizing assemblage, if heat is extracted from the system at a constant rate. Consideration of the variation of  $C^*$  with crystallization rate has led to a general model for the relationship between liquidus slope and cooling rate.

**5. Density model for magma ascent and contamination.** Using our experimental data, we have developed a general model for the role of contamination and mean crustal density in the buoyant rise of basaltic magmas in regions undergoing crustal extension. Comparison of the effects of crystal fractionation and magma mixing on calculated residual liquid densities shows that contamination of basaltic magmas is more efficient than crystal fractionation in reducing magma density. When applied to the Basin and Range province of the western United States, this model can explain (1) why the proportion of basalt erupted has increased with time, (2) why the amount of contamination suffered by basalts has decreased with time, and (3) why major silicic volcanic centers (e.g., Long Valley) are located in areas of low crustal density.

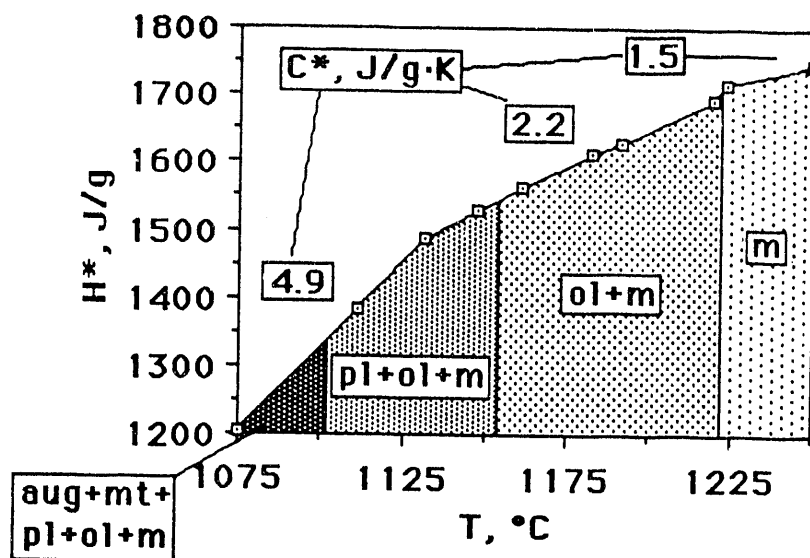


Figure 5. Variation in enthalpy ( $H^*$ ) with respect to temperature for an alkali basalt. The slope of the curve is  $C^*$ , the bulk heat capacity of the magma. Note the sharp increase in  $C^*$  as new phases join the crystallizing assemblage. This indicates that the cooling rate of the magma will decrease as new phases are added.

6. **Thermobarometry in igneous systems.** Compositional data gathered from the phase-equilibrium experiments has been added to the data base used for calibration of activity-composition relationships (see below). We have applied these new calibrations to the problem of determining the pressures and temperatures at which basalt phenocrysts equilibrate with their groundmasses. For example, the 1-atm. olivine-liquid and plagioclase-liquid geothermometers can be combined with high-pressure experimental data to produce an olivine-plagioclase-liquid thermobarometer. We have applied a preliminary calibration of this method to Quaternary basalts from Pisgah and Amboy Craters in the Mojave Desert. These results indicate that olivine and plagioclase phenocrysts in the basalts grew in upper-mantle magma chambers, at 30-35 km depth. One-atmosphere melting experiments on one of the basalts yield plagioclase crystals that are significantly more calcic than plagioclase phenocrysts in the rocks. This difference is consistent with the hypothesis that the phenocryst assemblage grew at high pressure. Neither of the volcanoes is associated with rhyolite. These results indicate that these basalt volcanoes lack associated rhyolite because they did not establish magma chambers in the crust. We have collected several basalt samples from bimodal basalt-rhyolite fields in California in order to see if these basalts predict crustal depths for olivine-plagioclase-liquid equilibration.

7. **High-pressure phase equilibria of an alkali basalt.** An initial study of the high-pressure phase equilibria of the alkali basalt used for the basalt-rhyolite mixing line study has been completed in collaboration with Dr. Art Boettcher at UCLA. The goal of this study is to obtain data on the compositions of coexisting plagioclase and

basaltic liquid at high pressures, in order to improve the calibration of the plagioclase-olivine-liquid thermobarometer. We have found only 3 published analyses of coexisting plagioclase and liquid in natural basalts at high pressure. Run products are currently being analyzed.

**8. Basalt-quartz mixing experiments.** Quartz crystals with augite coronas commonly occur in basalts and andesites. The origin of these coronas is not well understood. We have successfully duplicated this textural relationship by adding quartz grains to basalt-rhyolite mixtures. In addition, a series of basalt-SiO<sub>2</sub> doping experiments has been completed. A preliminary phase diagram for this pseudobinary system has been constructed and microprobe analysis of the run products is in progress. One important result is that orthopyroxene joins olivine as a liquidus phase as SiO<sub>2</sub> is added to basalt. This result suggests that the growth of augite rims on quartz is not an equilibrium process, but perhaps may be a diffusion-controlled process, as suggested by Sato (1975). The compositional data from these SiO<sub>2</sub> doping experiments will be used to improve the calibration of the olivine-liquid geothermometer.

**9. Phase equilibria of East African basalts.** We are currently determining the one-atmosphere phase equilibria of mafic volcanic rocks from the East African Rift (Lake Turkana) and from the East Pacific Rise. These studies complement our previous work on mixtures of alkali basalt and rhyolite from California and greatly extend the data base of compositions of coexisting crystals and silicate liquids. Doping experiments on alkali basalts from Lake Turkana indicate that addition of minor components such as TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> can greatly affect phase relations. We will extend these studies to other components (notably, K<sub>2</sub>O) in order to quantify these effects and, if possible, develop a projection scheme for basalts that is immune to bulk-composition variations. Studies of three basalts (alkalic, transitional, and tholeiitic) from the East Pacific Rise clarify the relationships between these three coexisting magma types and yield insight into the origin of high-alumina basalts. During this study we unexpectedly found extreme compositional zoning in a single pillow.

**10. Granitic minerals in mafic magma.** Additional experiments have been aimed at determining what happens when granitic minerals (quartz, alkali feldspar, and plagioclase) are immersed in basaltic liquid. Results indicate that alkali feldspar dissolves rapidly (thus accounting for the relative lack of sanidine xenocrysts in basalts), whereas quartz and plagioclase react with the liquid to form protective shells. Liquid halos around both plagioclase and quartz exhibit pronounced uphill diffusion of alkalis; this leads to abnormally high K<sub>2</sub>O contents in the cores of partially digested plagioclase crystals.



## PUBLICATIONS

### Refereed Papers

- Nielsen, R. L., Glazner, A. F., Baker, D. B., Nekvasil, H., and Russell, J. K., 1987, Developments in empirical and theoretical phase equilibria models for natural systems: EOS, v. 68, p. 121, 126-127.
- Glazner, A. F., and Ussler, W., III, 1988, Trapping of magma at midcrustal density discontinuities: Geophysical Research Letters, v. 15, p. 673-675.
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- Glazner, A. F., and Ussler, W., III, 1989, Crustal extension, crustal density, and the evolution of Cenozoic magmatism in the Basin and Range: Journal of Geophysical Research, v. 94, p. 7952-7960.
- Ussler, W. III, and Glazner, A. F., 1992, Enthalpy-composition relationships in mixed magmas: Journal of Volcanology and Geothermal Research, v. 51, p. 23-40.
- Mies, J. W., and Glazner, A. F., Origin of embayed quartz in volcanic rocks: Contributions to Mineralogy and Petrology, 24 ms. pages.

### Papers in Preparation

- Glazner, A. F., and Ussler, W. III, The bulk heat capacity of magmas: Applications to magma cooling rates and the origin of compositional gaps: to be submitted to Journal of Geophysical Research.
- Glazner, A. F., Ussler, W. III, and Mies, J. W., Fate of granitic minerals in mafic magmas: to be submitted to Contributions to Mineralogy and Petrology.
- Ussler, W. III, and Glazner, A. F., Origin of augite coronas around quartz xenocrysts in basalts and andesites: to be submitted to Contributions to Mineralogy and Petrology.

### Abstracts

- Glazner, A. F., Ussler, W. III, and Hughes, W. T., 1985, Crystal-melt thermobarometry: application to alkali basalt evolution, the depth of magma chambers, and basalt underplating of continental crust (abs.): EOS, v. 66, p. 1121-1122.
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- Mies, J. W., and Glazner, A. F., 1987, Quartz xenocrysts with rhyolite glass inclusions as evidence of assimilated granite (abs.): EOS, v. 68, p. 434-435.

- Ussler, W., III, and Glazner, A. F., 1987, Origin of augite coronas around quartz xenocrysts in basalts and andesites: Geological Society of America Abstracts with Programs, v. 19, p. 874.
- Glazner, A. F., and Ussler, W. III, 1987, Lithospheric extension and the change from intermediate to basaltic volcanism in the western United States (abs.): EOS, v. 68, p. 1529.
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- Glazner, A. F., and Ussler, W., III, 1988, Buoyant trapping of magma in the middle crust (abs.): EOS, v. 69, p. 493.
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- Glazner, A. F., Ussler, W. III, and Mathis, A. C., 1990, Interpretation of plagioclase texture in volcanic rocks: EOS, v. 71, p. 1678.

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