

Temperature and time marking of crystal growth during crystal-liquid partitioning experiments: a new technique and applications to anorthite-liquid partitioning.

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Introduction

All techniques for the experimental measurement of crystal-liquid partition coefficients (D) have inherent limitations, especially for incompatible elements with $D < 0.1$. Experiments in which a starting material is inserted either directly at subliquidus temperatures or heated briefly above the liquidus and then dropped to the temperature of interest, tend to yield very rapid crystal growth rates. To avoid high values (relative to equilibrium) for measured incompatible trace element partition coefficients, complete diffusive re-equilibration between crystals and glass must occur over the duration of the experiment. In addition, trace element analysis of the small crystals or the equilibrated rims of larger crystals produced in such runs is very difficult. Fractional crystallization experiments have the advantage of minimizing crystal growth rates (e.g. Benjamin *et al.*, 1980; Simon *et al.*, 1994). As long as interface equilibrium is maintained between the liquid and growing crystal, equilibrium partition coefficients can be reliably calculated from fractional crystallization experiments. The disadvantage of this approach is that the measured partition coefficients can only be associated with a range in temperatures, and it is difficult to make inferences about the temperature dependence of the partition coefficients. In this abstract we report improved 'temperature and time marking' fractional crystallization experiments which counter some of the limitations of the standard fractional crystallization approach and have wide general applicability.

Experimental

We have conducted fractional crystallization experiments using a CaO-MgO-Al₂O₃-SiO₂-TiO₂ bulk composition based on a meteoritic Ca, Al-rich inclusion liquid (Stolper and Paque, 1986) which has anorthite on its liquidus. The experi-

mental apparatus consists of a 3mm OD alumina tube inside a 7mm OD alumina tube with Pt hanging wires between them. The starting powder (~100 mg) was put in a Pt boat suspended directly under the inner tube, and the assembly was hung in the hot-spot of a Deltech 1 atm. furnace. Small (~1 mg) pellets of SrCO₃ and BaCO₃ were made with polyvinyl alcohol and dropped down the inner tube at different times during the cooling history to act as temperature and time markers during crystal growth. The thermal history used here consisted of an initial 2 hour hold 30°C above the liquidus then step cooling to 10°C below the liquidus where the charge was held for 24 hours. This was followed by cooling at 2°C/hour an additional 60°C below the liquidus in 20°C increments. The SrCO₃ and BaCO₃ pellets were dropped after the first and second cooling increments, respectively, and a 24 hour hold was placed on the sample immediately after the spikes were introduced to allow the sample to homogenize before the next stage of cooling and crystallization was begun. At the end of the cooling series, the sample was held for an additional 12 hours. Sr, Ba, Mg, and Ti abundances in anorthite and coexisting glass were determined by electron microprobe analysis using operating conditions optimized for acceptable counting statistics. A series of line scans were done on several anorthite crystals (e.g. Fig. 1a) in order to image the Sr and Ba variations in conjunction with Mg and Ti abundances.

Results and discussion

The approach of dropping pellets into the charge during the run seems to be sound and repeatable, since all charges, to this point, contain approximately 1 wt% of Sr and Ba. Ideally, the anorthite crystals grown in these experiments should contain Sr- and Ba-free cores, followed by a Sr-rich, Ba-free zone, and finally a Sr- and Ba-containing rim.

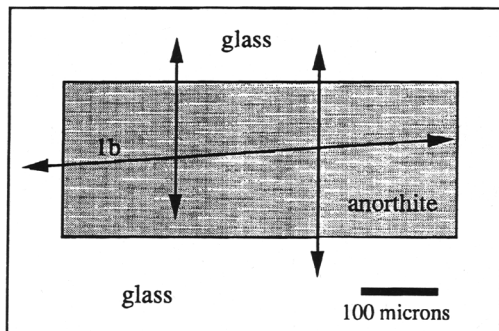


FIG. 1a.

The experimental procedure was successful in that Ba-rich rims are always present and clearly visible, both in trace element scans (Fig. 1b) and in backscattered electron images. Sr-free zones are not observed, and the low Sr points in Fig. 1b appear to coincide with a crack in the crystal. The lack of Sr-free cores in any anorthite crystal may be due to uncertainty in the estimation of the liquidus temperature for this composition, and experiments are underway to investigate this further. Nevertheless, the technique was successful in 'marking' the crystals at a specific time and temperature during fractional crystallization experiments. As indicated in Fig. 1b, the onset of the Ba-rich zones marks the 1300°C point in the crystal growth.

Our experimental method has a wide range of potential applications to the study of igneous processes, including evaluation of the temperature dependence of D 's, assessment of crystal growth rates and of changes in crystal morphology during crystallization, investigating the dependence of D 's on these factors, and observation of boundary-layer effects during trace element partitioning. An additional application is the ability to calculate D 's at the same temperature and time at a variety of points on different crystal faces. This in turn can lead to a better understanding of sector zoning (Shimizu, 1981). This has been done in the case of Mg, Sr and Ti for the crystal shown in Fig. 1a. Mg, Sr and Ti concentrations were measured on the Ba-free/Ba-rich surface delineated by the line scans, which coincides with 1300°C. The liquid

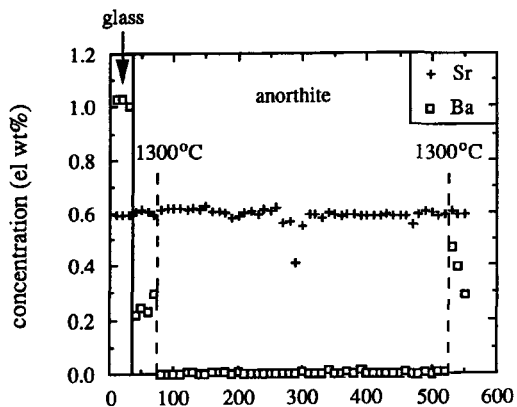


FIG. 1b.

concentrations were calculated using the Rayleigh equation assuming 10% crystallization. The resulting D 's are constant along the 1300°C surface, showing no correlation with growth direction. This indicates that the D 's for Mg and Ti are not seriously affected by interface disequilibrium phenomena, such as boundary layer formation. Adding 1 wt% Ba to the liquid composition did not produce measurable changes in the D 's for Mg, Ti, and Sr. At 1300°C, $D_{\text{Mg}}=0.034$, $D_{\text{Ti}}=0.035$, $D_{\text{Sr}}=1.07$, and are consistent with Simon *et al.* (1994); minor discrepancies may be related to temperature or compositional effects (Peters *et al.*, 1994). Further experiments are underway to assess the magnitude of the temperature dependence.

References

- Benjamin, T.M., Heuser, W.R., Burnett, D.S. and Seitz, M.G. (1980) *Geochim. Cosmochim. Acta*, **44**, 1251–64.
- Peters, M.T., Shaffer, E.E. and Burnett, D.S. (1994) *Lunar Planet. Sci. Conf. XXV*, 1075–6.
- Shimizu, N. (1981) *Nature*, **289**, 575–7.
- Simon, S.B., Kuehner, S.M., Davis, A.M., Grossman, L., Johnson, M.L. and Burnett, D.S. (1994) *Geochim. Cosmochim. Acta*, **58**, 1507–23.
- Stolper, E.M. and Paque, J.M. (1986) *Geochim. Cosmochim. Acta*, **50**, 1785–1806.