

# Effects of water content, temperature and pressure on actinide tracer diffusion in melts of haplogranitic composition

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## Introduction

An understanding of the rates and mechanisms of U and Th diffusion in silicate melts and glasses is necessary to fully understand such diverse phenomena as U-Th decay series disequilibria, melt-crystal partitioning, and leaching of actinides from nuclear waste glasses. Uranium diffusivities have been determined in anhydrous borosilicate nuclear waste glasses (Dunn, 1987), and numerous investigators have studied release rates of actinides during leaching of glass by hydrothermal solutions (e.g. Schreiber *et al.*, 1985). Dissolved water is known to enhance diffusion of other high field strength elements in silicate melts (e.g. Harrison and Watson, 1983). In light of the abundance of water in felsic silicate melts, and the prevalence of water-rich compositions in ancient weathered natural glasses (Mungall and Martin 1994), we have investigated the effects of water content and temperature on U and Th diffusion rates in a synthetic haplogranite composition at pressures ranging from one atmosphere to 10 kbars.

## Experiments

Two batches of bubble-free, homogeneous glass (one clean HPG-8 (see Holz *et al.*, 1992 for composition), the other doped with 0.1% each of U and Th) were prepared by fusing oxide and carbonate powders in a Pt crucible at 1600°C, stirring for several days with a Pt spindle, and cooling in air. For one-atmosphere anhydrous experiments, the glass was drilled and sliced into 8 mm-diameter discs 2 mm thick with polished ends. Diffusion couples were made by juxtaposing the two glasses in a Pt capsule. For high pressure experiments the clean glass was ground and tamped into Pt cylinders; in water-bearing runs double distilled water was added to give 4.5 wt. % water, after which doped glass powder was poured in, tamped, and the cylinder was welded shut. One atmosphere experiments were conducted in a box furnace; high pressure experiments were conducted in a 1/2" piston-cylinder apparatus with alumina pressure medium. One atmosphere

experiments were quenched by removing from the furnace, whereas high pressure experiments were quenched by turning off the furnace. Run products were sectioned and polished for analysis on a Cameca WDS microprobe at 25 kV accelerating voltage and 100 nA probe current, with a defocussed beam. Most traverses were 1 to 3 mm wide; if the flat extremes of the diffusion profile were not at least 500 µm wide the experiment was discarded. Because there is no variation in the matrix through the couple, data were collected and processed as raw X-ray counts at 1 to 7 (usually 5) micron point spacings.

## Results

Profiles were fit to an error function to minimize  $\chi^2$ ; all the products used had infinite couple geometry and to show no compositional dependence, i.e., the estimated diffusion coefficients are assumed to approximate tracer diffusion coefficients. Uncertainty was estimated by finding the range of values of D within which  $\chi^2$  gave 95% confidence of an insignificant residual. The variation of  $D_U$  and  $D_{Th}$  with temperature, water content and pressure is shown in Fig. 1 for all experiments. The logarithms of both U and Th diffusivities are linear against reciprocal temperature, and are given by the following Arrhenius relationships:

$$\begin{aligned} D_U &= 7.94 \times 10^{-3} \exp\{260 \text{ kJ mol}^{-1}/RT\} \text{ dry, 1 bar} \\ D_{Th} &= 1.92 \times 10^{-1} \exp\{318 \text{ kJ mol}^{-1}/RT\} \text{ dry, 1 bar} \\ D_U = D_{Th} &= 9.25 \times 10^{-1} \exp\{239 \text{ kJ mol}^{-1}/RT\} \\ &\quad 4.5 \text{ \% H}_2\text{O, 10 kbar (Eyring)} \end{aligned}$$

These lines are shown in Fig. 1; also shown are the diffusivities predicted by the Eyring equation  $D = kT/\zeta\lambda$  (using viscosity  $\zeta$  from Shaw (1972) at 10 kbar, measured viscosities from Dingwell *et al.* (1992) at 1 bar; jump distance  $\lambda = 2.3 \text{ \AA}$ ;  $k =$  Boltzmann's constant). The relation we have chosen for  $D_U$  and  $D_{Th}$  in hydrous melts at 10 kbar is that predicted by the Eyring equation, because regressed lines do not differ significantly

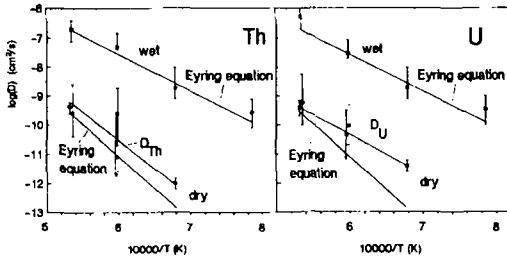


FIG. 1.

from it. This correspondence probably indicates that U and Th diffusion are controlled by the same thermally activated processes that control viscosity. Th is moderately well predicted by the Eyring equation in the anhydrous melts. However, the difference in activation energy of  $D_U$  from that of  $D_{Th}$  and viscous flow at 1 bar may indicate decoupling of  $D_U$  from melt viscosity (transition to intrinsic diffusivity). This observation suggests that U diffusivities at the low temperatures relevant to nuclear waste leaching could be very much higher than equations 2) and 4) suggest. The inference of decoupling hinges on only one measurement at 1200°C; further work will test this possibility with experiments at lower temperatures.

Oxygen fugacity was invoked by Dunn (1987) as a major control on the diffusivity of U in borosilicate glass. In our experiments, oxygen fugacity ranged from 0.21 in the 1 bar experiments to lower values presumed to lie near NNO in the 10 kbar experiments (unbuffered). Over this range in oxygen fugacities U is expected to change from a hexavalent state (uranyl ion  $UO_2^{2+}$ ) at high  $f_{O_2}$  to a mix of pentavalent and quadrivalent ions at lower  $f_{O_2}$ ; this change may be responsible for the apparent transition from extrinsic to intrinsic diffusion between 10 kbar and 1 bar, since uranyl ion has a much lower charge density than do  $U^{4+}$  and  $U^{5+}$ . An alternative explanation is that at low water contents (high viscosity) we are observing the intrinsic diffusivity of U whereas at high water contents (low viscosity) the increased mobility of network formers overtakes the intrinsic diffusivity, resulting in Eyring behaviour. An interesting consequence of this hypothesis is that as a magma cools and degasses the diffusivities of U and Th may progress from being

subequal to showing differences of several orders of magnitude.

The data show that isotopic decoupling of U and Th decay series by differences in diffusivity are not expected in hydrous silicic melts over a very wide range of temperatures, pressures and water contents, but that at magmatic temperatures in water-poor magmas transport of U may be significantly faster than that of Th, resulting in a potential for U–Th fractionation.

In a reconnaissance experiment at 1400°C, 10 kbar, dry, the estimated diffusivities of both U and Th are not significantly different from those calculated at the same temperature for the 1 bar experiment. The apparent slight offset to higher values may result from the diminished melt viscosity at higher pressure, but confirmation of this suggestion would require further work.

### Conclusion

Diffusion of U and Th in haplogranitic melt is Arrhenian over the temperature range 1000 to 1600°C, with diffusivities in water-rich melts predicted by the Eyring equation. At high oxygen fugacities and low water contents the diffusion of Th may remain coupled to melt viscosity, but U diffusion appears to be intrinsic, with diffusivity one to two orders of magnitude faster than the predicted Eyring diffusivity at 1200°C. U and Th may therefore become fractionated by transport processes under these conditions. Clarification of the effects of pressure and  $f_{O_2}$  over a wider range of temperatures is presently under way.

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