

**SELF DIFFUSION OF ALKALINE-EARTH IN Ca-Mg-ALUMINOSILICATE MELTS, EXPERIMENTAL IMPROVEMENTS ON THE DETERMINATION OF THE SELF-DIFFUSION COEFFICIENTS; O. Paillat and G. J. Wasserburg, Lunatic Asylum, Div. of Geological and Planetary Sciences, California Institute of Technology, Pasadena CA 91125.**

Experimental studies of self-diffusion isotopes in silicate melts often have quite large uncertainties when comparing one study to another. We designed an experiment in order to improve the precision of the results by simultaneously studying several elements (Mg, Ca, Sr, Ba), during the same experiment thereby greatly reducing the relative experimental uncertainties. Results show that the uncertainties on the diffusion coefficients can be reduced to 10%, allowing a more reliable comparison of differences of self-diffusion coefficients of the elements. This type of experiment permits us to study precisely and simultaneously several elements with no restriction on any element. We also designed an experiment to investigate the possible effects of multicomponent diffusion during Mg self diffusion experiments by comparing cases where the concentrations of the elements and the isotopic compositions are different. The results suggest that there are differences between the effective means of transport. This approach should allow us to investigate the importance of multicomponent diffusion in silicate melts.

As starting material we used a glass composed of 11.5 MgO, 12.5 CaO, 44 SiO<sub>2</sub> and 32 Al<sub>2</sub>O<sub>3</sub> by weight %, close to the compositions used by Sheng *et al.* (1992) [1]. This glass was powdered and half of the batch was mixed with weighted amounts of oxides or carbonates doped with <sup>25</sup>Mg, <sup>44</sup>Ca, <sup>84</sup>Sr and <sup>136</sup>Ba. The other half of the batch was mixed with the same amount of oxides or carbonates of normal isotopic composition. The two batches were thus chemically homogeneous and isotopically different. The final concentration of BaO was 0.3 wt% and of SrO was 0.2 wt%. Samples were put in a vertical furnace at 1763 K (above the liquidus) for fifteen minutes. This type of self-diffusion experiment is a continuation of the study of Sheng *et al.* (1992) [1] and consists of using a diffusion couple in chemical equilibrium but isotopic disequilibrium. This has been extended to a melt-melt couple instead of a spinel-melt couple. Analyses of the quenched glass were done with the PANURGE ion probe, and the electron probe. Two traverses along the sample were done: first for Ca and Mg isotopes, then for Sr and Ba isotopes at the same points but with a higher primary beam current. Results from two traverses along the sample are shown in Fig. 1, the two profiles are very similar and seem to follow very well an error function law; thus no evidence of convection has been found. Moreover the fit of these profiles with an inv(erf), Fig. 2, are very good, and an estimation of the precision of the value of the slope is 10%. The value of the diffusion coefficients obtained from these fits are:

D(cm <sup>2</sup> /s) x 10 <sup>6</sup>	<sup>25</sup> Mg	<sup>44</sup> Ca	<sup>84</sup> Sr	<sup>136</sup> Ba
traverse #1	1.50	1.28	0.86	0.55
traverse #2	1.38	1.23		0.44

The differences between the coefficients for the different elements are several times larger than the precision and can be exploited with more confidence than if we had done separate experiments. The self-diffusion coefficients seem to vary linearly with the ionic radii of the element while there is a suggested relationship with  $1/\sqrt{m}$  ( $m$ : atomic mass of the element) which is less clear. These interpretations will be investigated after we obtain the temperature dependence of the coefficients and the dependence on melt composition. In order to estimate the possible importance of multicomponent diffusion during self-diffusion experiments, we also designed an experiment in which only the <sup>25</sup>Mg concentration varies, but <sup>24</sup>Mg and <sup>26</sup>Mg concentrations are constant along the profile. This provides a small chemical gradient (10% of total Mg concentration variation compared to 100% variation of <sup>25</sup>Mg). The sample was held in the same furnace with the same time-temperature history as the previous experiment. We obtained a diffusion coefficient for <sup>25</sup>Mg of  $1.0 \times 10^{-6}$  cm<sup>2</sup>/s, which is about 30% lower than the previous one. Fig. 3a shows that the two lines clearly cross, and that the slopes are different; this difference is believed to be significant. Moreover, the <sup>24</sup>Mg/<sup>30</sup>Si<sup>+</sup> ratio recorded during the analysis showed a variation along the profile, (Fig. 3b), which shows a sinusoidal trend in the region of the interface. This can hardly be due to <sup>30</sup>Si concentration variation, which is constrained to be fairly constant. Therefore this observation is interpreted as a variation of the <sup>24</sup>Mg concentration. Since the <sup>24</sup>Mg/<sup>26</sup>Mg ratio is fairly constant along the profile, this suggests that <sup>26</sup>Mg should vary in the same way. These two independent observations can be consistently explained in terms of multicomponent diffusion between <sup>24</sup>Mg, <sup>25</sup>Mg and <sup>26</sup>Mg. Higher precision must be achieved on these observations to obtain a significant value for extra-diagonal term  $D_{ij}$  ( $i \neq j$ ). In summary, the approach used here appears to be applicable to essentially all chemical elements to determine their individual diffusion coefficients in a single experiment. We will attempt to carry these studies out below the liquidus and in the glass transition region if it is possible to eliminate

the problem of devitrification of the glasses at lower temperatures. Division Contribution 5240(803). References: [1]Sheng Y.J., Wasserburg G.J. and Hutcheon I.D. (1992) *GCA* 56, 2535.

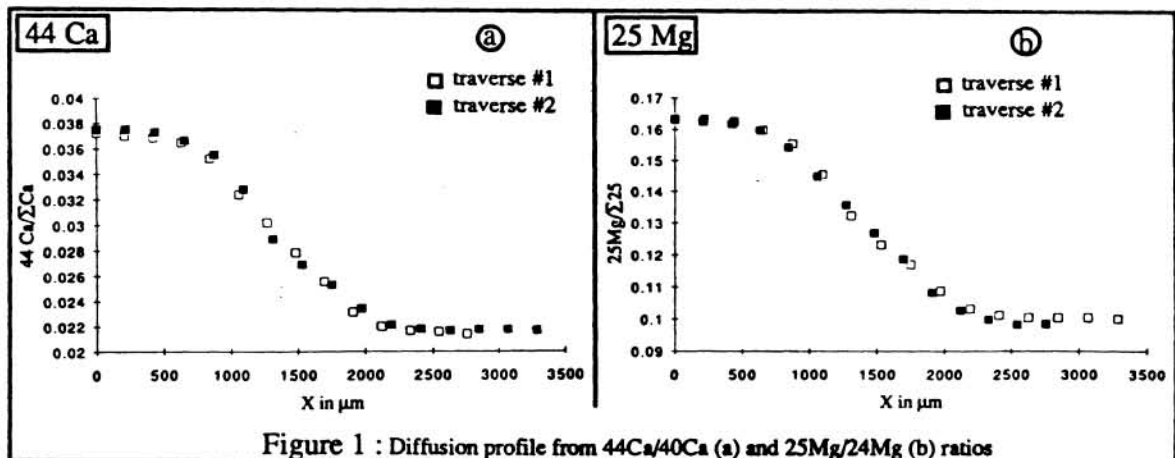


Figure 1 : Diffusion profile from  $^{44}\text{Ca}/^{40}\text{Ca}$  (a) and  $^{25}\text{Mg}/^{24}\text{Mg}$  (b) ratios

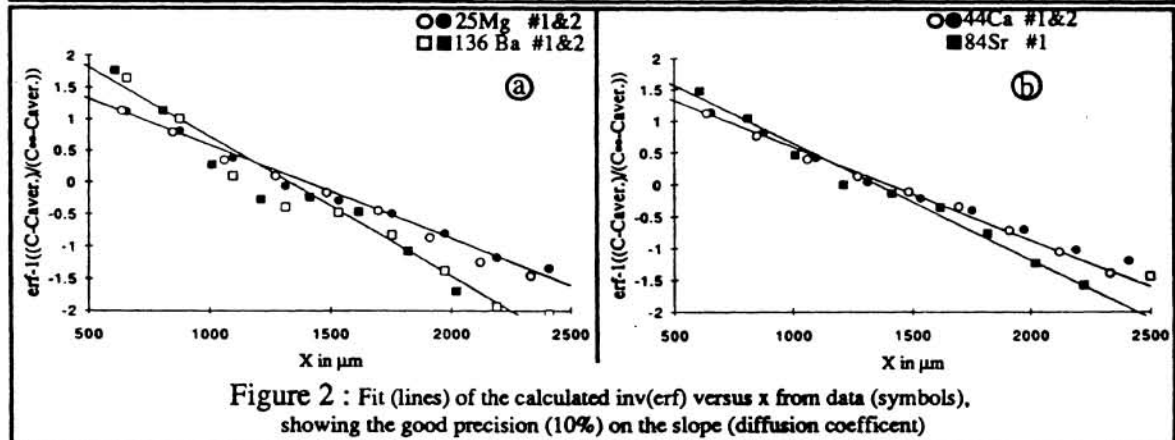


Figure 2 : Fit (lines) of the calculated  $\text{inv}(\text{erf})$  versus  $x$  from data (symbols), showing the good precision (10%) on the slope (diffusion coefficient)

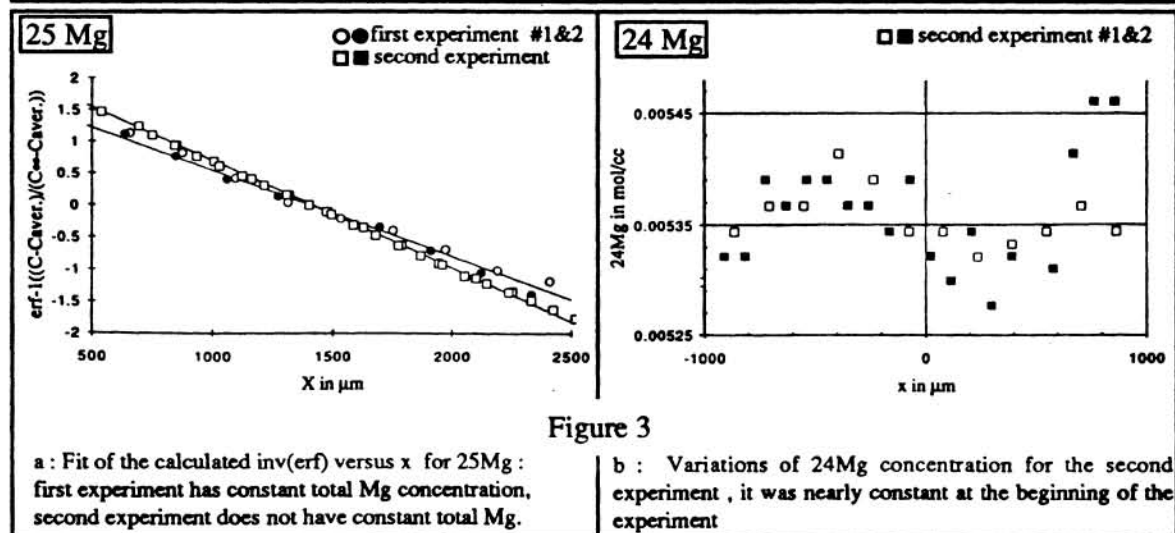


Figure 3

a : Fit of the calculated  $\text{inv}(\text{erf})$  versus  $x$  for  $^{25}\text{Mg}$ : first experiment has constant total Mg concentration, second experiment does not have constant total Mg.

b : Variations of  $^{24}\text{Mg}$  concentration for the second experiment, it was nearly constant at the beginning of the experiment