Geophysical Research Abstracts, Vol. 7, 07324, 2005
SRef-ID: 1607-7962/gra/EGU05-A-07324

The structure of potassium silicate glasses: ^{29}Si MAS NMR spectroscopy

W. Malfait, Y. Morizet, W. Halter, R. Verel, B. Meier
ETH Zürich, Switzerland
(malfait@erdw.ethz.ch / Fax: ++41 (0)1 632 1179 / Phone: ++41 (0)1 632 6137)

The speciation of potassium silicate glasses was determined and the abundance of ring structures was quantified for various compositions and fictive temperatures using NMR. We selected 9 compositions ranging from 14 to 50 mole percent K_2O and applied three different quench rates to obtain different fictive temperatures. The glass transition temperature of all samples was determined by calorimetry.

The spectra were deconvoluted to quantify the abundance of the different structural units and equilibrium (1) was used to interpret the data:

$$2\ Q^{n} = Q^{n-1} + Q^{n+1} \text{ with } k_{n} = [Q^{n-1}]\ .\ [Q^{n+1}]\ /\ [Q^{n}]^{2} \text{ and } (n=3, n=2)\ (1)$$

For the glasses with an intermediate quench rate, $k_3$equals 0.002 to 0.008 and k_2 equals 0.01 to 0.02. The results are in agreement with the data obtained by Maekawa et al. (1991), although the fictive temperature of their samples is not known.

In the potassium rich samples (NBO/T$\geq$1), two different Q^2 species were observed and assigned to chains ($Q^{2}_{(chain)}$) and 3-membered rings ($Q^{2,22}_{(ring)}$) respectively (Maekawa et al, 1991). The amount of $Q^{2,22}_{(total)}$ ($Q^{2,22}$ is a Q^2 connected to two Q^2 s) was calculated statistically from the total amount of Q^2 measured by NMR, assuming there is no clustering of the various Q^n species. The amount of $Q^{2,22}_{(ring)}$ was found to correlate linearly with the amount of $Q^{2,22}_{(total)}$ for the various compositions. We suggest that the following equilibrium reaction takes place in the melt structure:

$$Q^{2,22}_{(chain)} = Q^{2,22}_{(ring)} \text{ with } k = [Q^{2,22}_{(ring)}]\ /\ [Q^{2,22}_{(chain)}]\ (2)$$

The equilibrium constant was determined to be 1.5 for glasses with a glass transition temperature of 730 K.

We are investigating the possibility that the observed anomalous heat capacity of potassium silicate melts (e.g. Richet and Bottinga, 1985) is due to the presence of ring structures. The effect of the fictive temperature on equilibrium (1) and (2) is also studied.

Maekawa, H., Maekawa, T., Kawamura, K., and Yokokawa, T. (1991) J. Non-Cryst. Solids, 127, 53-64.

Richet, P., and Bottinga, Y. (1985) Geochim. Cosmochim Acta, 49(2), 471-486.