Abstract

The aim of this study is to demonstrate the effect of chlorine (Cl^-), fluorine (F^-), water (H_2O) and carbon dioxide (CO_2) on the viscosity of basaltic melts and a comparison to literature models. The basaltic composition is similar to a melt of flat-topped volcano from Mid-Atlantic Ridge (MAR). The iron content was decreased, to avoid crystallisation of the glass. The study is divided into three series with different oxygen fugacity adjusted by diverse synthesis conditions.

Series (I), (II) and (III) represents basaltic melts doped with Cl^-, F^- and (Cl^- + F^-), which were synthesised in a 1 atm furnace at 1473 K for 4 to 9 h in air. Afterwards, all series (II) glasses are redox equilibrated in a vertical gas mixing furnace at 1473 K for up to 20 h under a carbon dioxide and hydrogen gas atmosphere. Therefore, different oxygen fugacity can be generated and results in diverse Fe^{2+}/Fe_{total}. The hydrous glasses with 0.5, 1.5 and 3.5 wt% H_2O and CO_2-bearing glasses with 1000 to 3500 ppm CO_2 of Series (III) were synthesised in the internally heated pressure vessel (IHPV). The experiments were performed at 1550 K and 300 MPa for 24 h with a rapid quench device. In addition to H_2O and CO_2-bearing glasses, dry and CO_2-free glasses are synthesised in the IHPV.

The high viscosity is measured by the micropenetration technique in the range of $10^{8.5}$ to $10^{13.5}$ Pa s. The Raman spectroscopy and colorimetric micro-determination of Fe^{2+} content can be used for structural analysis. The volatiles (F^-, H_2O and CO_2) decrease the viscosity of basaltic melts, whereas the addition of F^- shows the smallest effect on the viscosity and CO_2 results in the strongest decrease in viscosity. The addition of 12.56 mol% H_2O in halogen-free basalt results in a decrease in viscosity by 5.2 log units, whereas the presence of 0.34 mol% CO_2 to a basaltic melt results in a strong decrease in viscosity by 0.7 log units. The addition of 7.73 mol% F^- to basaltic glass results in a decrease in viscosity by 2.5 log units. Amounts with up to 2.53 mol% Cl^- in basaltic melts result in an increase in viscosity, whereas further addition of chlorine results in a decrease in viscosity. The comparison of the experimental viscosity data of basaltic melts reflects that the current viscosity models do not consider all volatiles (Cl^-, F^- and CO_2) and the models are calibrated for diverse amounts of volatiles (Giordano et al. 2008; Duan 2014; Sehlke and Whittington 2016). Especially, the variable effect of chlorine on the viscosity of peralkaline and peraluminous silicate melts should be noted in future models.

Furthermore, the addition of volatiles to basaltic melts changes the Fe^{2+}/Fe_{total}. In peralkaline melts, the addition of fluorine results in a oxidation of Fe^{2+} to Fe^{3+}, which reflects an increase in polymerisation due to the increase in network formers. The addition of water results in a depolymerisation of the structure due to increasing Fe^{2+}/Fe_{total}. The addition of OH groups in halogen-free and –bearing basaltic glasses shows a linear decrease in Fe^{2+}/Fe_{total}, whereas the total water content shows an exponential trend. The OH groups describe the water species,

which is incorporated into the melt structure. A linear relation between the addition of chlorine and iron speciation cannot be confirmed. Also, no dependence between CO_2 content and Fe^{2+}/Fe_{total} is observed. Kress and Carmichael (1991) developed a model for the determination of Fe^{2+}/Fe_{total} by means of melting temperature, oxygen fugacity and melt composition. The model considers the amounts of Al_2O_3, FeO_{total}, CaO, Na_2O and K_2O. The results of the iron determination show that the volatiles (F^- and H_2O) have a strong effect on the Fe^{2+}/Fe_{total}. Thus, the volatiles have to be included by future models.

The falling sphere technique was used to extend the measurable viscosity range of CO_2-bearing basaltic melts to low viscosity ranges. This experiment was performed at 1223 K and 200 MPa for 5 h in a water cooled RQ-CSPV (rapid quench - cold seal pressure vessels). In this temperature range, the CO_2-bearing basaltic glass crystallises and the actual experiments cannot be realised with the present basaltic composition.