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## Dependence of glass transition temperature on the oxidation state of ferrosilicate melts and structural role of iron

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The oxidation state of iron is probably second only to water in its influence on the physical properties of natural silicic magma. This is shown by examining the effect of the oxidation state on the glass transition temperature.

The heat capacity of ferrosilicate melts has been measured using differential scanning calorimetry (DSC). Two different simple Fe-bearing systems have been studied: (i) anorthite-diopside eutectic composition (AnDi) with 10 wt% of Fe as a basalt analogue and (ii) sodium disilicate (NS2) with variable amount of Fe (up to 30 wt% Fe). Samples with different oxidation state of Fe have been prepared using the concentric cylinder method. This involves a continuous measurement of torque during stepwise reduction state under air, CO<sub>2</sub> and CO<sub>2</sub>-CO mixture at 1 atm and in a temperature range of 1573 to 1623 K. The melt was reduced by flowing  $CO_2$  and then successively reducing mixtures of CO<sub>2</sub>-CO through the alumina muffle tube. Gas flow rates were electronically controlled using the Tylan mass flow controllers and oxygen fugacity was directly measured using a ceramic oxygen sensor and calculated via the Nernst equation. The composition and oxidation state of the melt was monitored by obtaining a melt sample after each redox equilibrium step. The melts were sampled by dipping an alumina rod into the sample and drawing out a drop of liquid, which was then quenched in into water. The resulting glasses were analyzed by electron microprobe, and volumetric potassium dichromate titration was employed to determine FeO. In addition, high resolution XANES spectra have been collected in fluorescence mode at the BM08 beam line of ESRF. These provide information on the possible coordination

states of Fe and its structural role in the glasses. The data shown can be explained by a mixture of divalent Fe in [4] and [5] coordination (approximately in the same proportion) and trivalent Fe predominantly in [5] coordination. However, the data obtained cannot exclude that trivalent Fe is in a mixture of [4] and [6] -fold coordinations in equal proportions, or [4], [5] and [6] -fold coordinations in equal proportions.

Fragments of glass with mass about 55 mg were placed in a platinum crucible and heated through a range of temperatures from 298 to 1050 K, approximately 50 K above the glass transition. After initial heating at 5 K.min<sup>-1</sup>, the samples were cooled and heated at matched rates of 20, 15, 10 and 5 K.min<sup>-1</sup>. The calorimeter was calibrated using the heat capacity of single sapphire crystal, and the temperatures (*Tg*) have been defined as a peak of the heat capacity curve (*Cp*). In general, *Tg* peaks exhibit a non-linear dependence on the oxidation state of Fe. Tg decreases steadily with increasing Fe<sup>2+</sup> content, the strongest affect is during the initial reduction of Fe. Reducing Fe by about 66 % causes a drop in *Tg* of about 60 K. Moreover,  $\Delta Cp_{pk-onset}$  also decreases as Fe is reduced. These changes are independent of heating/cooling rate.

These effects are similar to those of water. Therefore, like with the addition of water, the reduction of Fe can strongly influence the magma's physical properties and thus magma behaviour during crystallization, degassing, foaming and fragmentation.