Auxiliary Materials:

Calculation of Optical Basicity (OB):

One approach to investigate the thermodynamic and structural properties of silicate melts is to consider them as arising from acid-base theory [e.g. *Duffy and Ingram, 1976; Moretti, 2005; Mathieu et al., 2011*]. Duffy and coworkers defined the concept of OB to express acid-base interactions in oxide systems (such as silicates), which are determined from Pauling electronegativity. OB is measured experimentally from the frequency shifts in the ultra-violet (UV) (s-p) spectra of probe ions (such as Pb^{2+}) and can be expressed on a numerical scale. In silicate melts, network modifying cations (e.g. Mg^{2+}, Ca^{2+}, Fe^{2+}, Na^{+}, K^{+} as well as H^{+}) are considered as bases (electron donors) and network forming cations (Si^{4+}, Al^{3+}) as acids (electron receivers).

For a given melt composition, the Optical Basicity is calculated as follows (equation from *Duffy and Ingram [1976]*, modified by *Zhang and Chou [2010]* to account for the charge compensation of Al^{3+} by Ca^{2+} and Mg^{2+}):

OB=A/B with:

-if $x_{CaO}+x_{MgO} \geq x_{Al2O3}$

$A= 2\gamma_{SiO2}x_{SiO2} + 3\gamma_{Al2O3}x_{Al2O3} + \gamma_{FeO}x_{FeO} + \gamma_{MnO}x_{MnO} + \gamma_{MgO}.(x_{MgO}+x_{CaO}-x_{Al2O3}) + 0.5\gamma_{Na2O}x_{Na2O} + 0.5\gamma_{K2O}x_{K2O} + \gamma_{H2O}x_{H2O}$

$B= 2x_{SiO2} + 3x_{Al2O3} + x_{FeO} + x_{MnO} + (x_{MgO}+x_{CaO}-x_{Al2O3}) + 0.5x_{Na2O} + 0.5x_{K2O} + x_{H2O}$

-if $x_{CaO}+x_{MgO} < x_{Al2O3}$

$A= 2\gamma_{SiO2}x_{SiO2} + 3\gamma_{Al2O3}x_{Al2O3} + \gamma_{FeO}x_{FeO} + \gamma_{MnO}x_{MnO} + \gamma_{MgO}x_{MgO} + \gamma_{CaO}x_{CaO} + 0.5\gamma_{Na2O}x_{Na2O} + 0.5\gamma_{K2O}x_{K2O} + \gamma_{H2O}x_{H2O}$

$B= 2x_{SiO2} + 3x_{Al2O3} + x_{FeO} + x_{MnO} + x_{MgO} + x_{CaO} + 0.5x_{Na2O} + 0.5x_{K2O} + x_{H2O}$

Where x_i is the molar fraction of an oxide i, and γ_i are the basicity moderating parameters [Table 1, *Duffy and Ingram, 1975]*.

As underlined by *Mathieu et al. [2011]*, OB is a more powerful tool than a bulk polymerization parameter (such as NBO/T), in the formulation of which Ca is equivalent to Mg, Si to Al and so on.