IMMISCIBLE LIQUIDS IN CaO – SiO_2 – TiO_2

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The computation of equilibrium phase diagrams of silicate systems requires a model of the Gibbs free energy of the melt. While in binary silicate systems non-ideal contributions to the free energy are often modelled by equations with few interaction parameters (e.g. BERMAN & BROWN, 1984), extrapolation in higher order systems remains unclear. The method of extrapolation strongly affects the shape of the excess free energy surface. Since compositions of coexisting liquids depend only on the topology of the free energy surface of the melt, they represent an excellent tool to test possible methods of extrapolation.

In order to determine miscibility gaps in silicate melts, a high temperature furnace has been constructed. Coexisting liquids in the silicate system CaO–SiO_2–TiO_2 at $T = 1600°C$, $p = 1bar$ have been quenched to glasses and their compositions have been determined by electron microprobe analysis. Measured compositions of the quenched liquid phases correspond more or less to the miscibility gap proposed by DEVRIES ET AL. (1955) at $T = 1600°C$. In contrast to their observations, the SiO_2-rich phase contains less than 1 wt% CaO.

Some extrapolation models from binaries into the ternary system (see HILLERT, 1980 and CHOU, 1987 for a review) have been tested with the observed miscibility gap using the Gibbs free energy minimizing algorithm »Theriak« (DECAPITANI, 1994). Formulations proposed by KOHLER, MUGGIANU, and COLINET permit extrapolation without fitting a specific ternary parameter. While the composition of the SiO_2-rich phase is correctly predicted, the calculated SiO_2 content of the TiO_2-rich liquid phase is in general too low. To reproduce the experimentally determined miscibility gap, we propose a generalization of an extrapolation formula of KOHLER (1960):

$$G^{xs} = \sum_{i,m} W_{(i1\ i2\ ...\ im)} \frac{x_{i1}\ x_{i2}\ ...\ x_{im}}{(S)^k}$$

where S = sum of the components x_i of the polynomial $x_{i1}\ x_{i2}\ ...x_{im}$, and W = W(p,T) are Margules interaction parameters indexed as by BERMAN & BROWN (1984). In KOHLER's original formula, the exponent k is fixed to the degree m of the binary Margules polynomial: k=m-2. k used as a variable parameter controls the expansion of non-ideal binary contributions to the Gibbs free energy of the ternary. To calculate the miscibility gap in CaO–SiO_2–TiO_2 we used KOHLER's formula for SiO_2-TiO_2 and CaO-SiO_2 binaries and k=1.62 for CaO-TiO_2 (see diagram). The proposed method represents a flexible extrapolation scheme for computing equilibrium phase diagrams of higher order silicate systems from the corresponding subsystems.
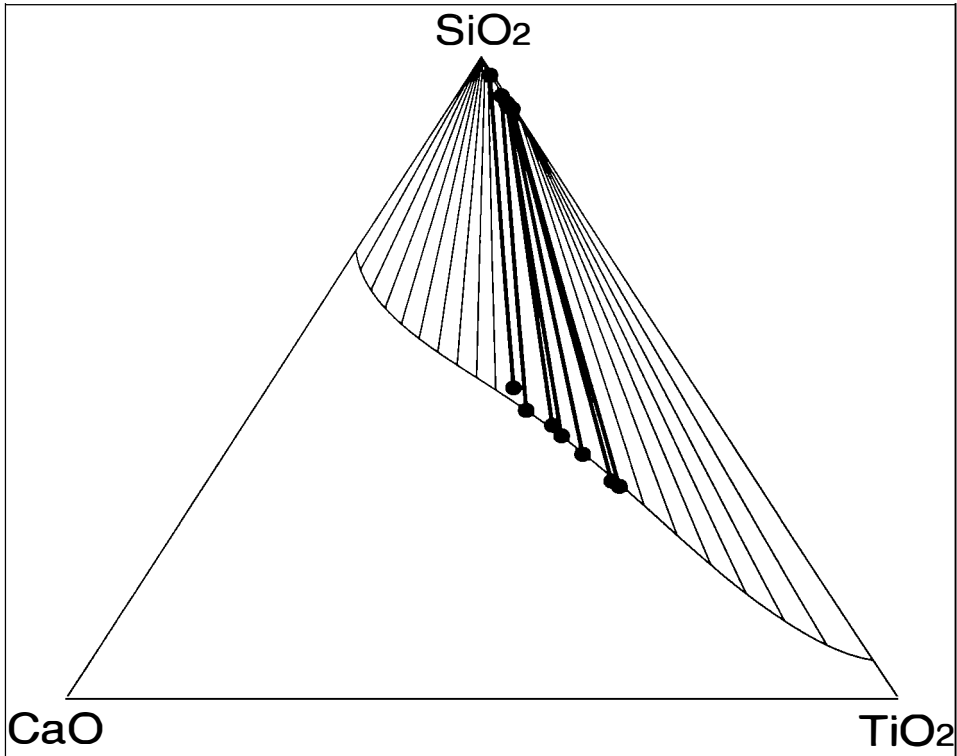
diagram:
experimentally determined (filled circles) and calculated tie-lines of coexisting
liquids in CaO-SiO$_2$-TiO$_2$ at T = 1600°C, p = 1bar.

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