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Immiscible silicate liquids in the CaO–SiO₂–TiO₂–Al₂O₃ system

by Marcus Kirschen¹ and Christian De Capitani¹

Abstract

Compositions of coexisting liquids in the CaO–SiO₂–TiO₂–Al₂O₃ system at 1600 °C have been determined. In the Al-free ternary system, the miscibility gap is modelled in detail with weighted extrapolation of binary excess Gibbs free energy terms. Addition of few wt% Al₂O₃ reduces dramatically the extent and consolute temperature of the solvus. Extrapolations of the CaO–SiO₂–TiO₂ model parameters to the Al-bearing system without additional corrections disagree with experiments. However, possible procedures for the expanded extrapolation in the four component system are discussed.

Keywords: multicomponent solution model, silicate melt, immiscibility, CAST system.

Introduction

Computation of phase diagrams in silicate systems at liquidus temperatures requires knowledge of non-ideal contributions to the Gibbs free energy of the melt. The excess Gibbs free energy G^{xs} may be estimated by evaluation of melting experiments that relate the energy of the melt to the free energy of the solid: $G^{melt}(T,p) = G^{solid}(T,p)$ at T_m . Assuming thermochemical values of the minerals as known (e.g. S^0 , H^0 , $C_p(T)$) from compiled databases (CHASE et al., 1985; BERMAN, 1988; HOLLAND and POWELL, 1990, or ERIKSSON and PELTON, 1993a and 1993b), thermochemical values for the pure liquids as well as non-ideal contributions for the multicomponent solutions are defined at the melting point. However, evaluation of experiments at liquidus temperatures often requires extrapolation of the specific heat capacity far beyond the range of experimental data. Thus, the high temperature value depends on the polynomial representation that is used to model C_p at lower temperatures, e.g. whether a linear T-term is included in the polynomial (ROBIE et al., 1978) or not (BERMAN and BROWN, 1985). In contrast, phase equilibrium data on coexisting liquids define direct constraints on non-ideal solution para-

meters through the equivalence of chemical potentials of component i : $\mu_i(\text{melt1}) = \mu_i(\text{melt2})$, $\mu_i = \mu_i^0 + RT \ln(a_i)$ because standard state chemical potentials for pure endmembers μ_i^0 cancel in the equations. Therefore the accurate determination of miscibility gaps is a step towards a comprehensive solution model for silicate liquids and offers an excellent tool to test solution models in multicomponent systems. As a model system we focus on CaO–SiO₂–TiO₂ that is characterized by a huge miscibility gap spanned from the SiO₂–TiO₂ binary to the silica rich part in CaO–SiO₂. The subregular solution model ($G^{xs} = x_1x_2[W_1x_1 + W_2x_2]$) is sufficient to model experimental solvus data in binary SiO₂–TiO₂ and CaO–SiO₂ systems using the BERMAN (1988) database. Fitted Margules parameters are given in table 1. Moreover, it allows to reproduce the liquidus line beyond the composition range of stable immiscibility. In the CaO–TiO₂ system no stable immiscibility of the liquid has been reported.

Immiscible silicate liquids in the CaO–SiO₂–TiO₂ system

In the CaO–SiO₂–TiO₂ system the two liquid field occurs stable above 1530 °C and over a broad

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Tab. 1 Margules parameters used in this study $W = W_H - TW_S, T$ in K.

	WH	WS	k
CaO-SiO ₂			
112	-719241.09800	-162.78172	0
122	119289.99150	99.23210	0
CaO-TiO ₂			
112	-404108.02430	-45.61255	1
122	-170426.41960	-4.81453	1
SiO ₂ -TiO ₂			
112	18844.22318	-9.08197	-4
122	67403.69615	8.44998	-4

Note: excess Gibbs free energy for CaO-SiO₂-TiO₂ liquid is calculated with $G^{xs} = \sum (W_{ij} x_i^2 x_j + W_{ij} x_i x_j^2) (x_i + x_j)^{-k}$

compositional range. The miscibility gap is bounded by the stability fields of rutile and cristobalite. Coexisting liquids have been synthesized from powder samples with a Rh/Pt resistance furnace at ~1600 °C, ambient pressure and quenched. Run durations have been varied from 0.5 to 3 h at high temperature. Cristobalite and rutile in equilibrium with one or two liquids appear as rounded grains and have been identified with microprobe and XRD analysis. The titania rich quench show traces of secondary exsolution due to the limited air quenching rate. The absence of exsolution blebs near the phase boundary to the silica rich liquid and in small inclusions indicate that diffusive processes alter the composition of the equilibrated liquids in a zone around the phase boundary when quenched. About 50 microprobe analyses per phase have been collected with a 5 to 30 μm defocused electron beam to account for secondary exsolution. Standard deviation of the measurements decreases with increasing run time of the samples, the mean is almost constant. This indicates that the molten samples were close to equilibrium. Measured compositions are shown in figure 1 as filled circles.

A well-known method to extrapolate binary interaction parameters in the ternary has been suggested by WOHL (1946). In this case, a ternary parameter is added to the sum of binary excess terms in order to approximate the ternary excess free energy: $G^{xs}(\text{tern.}) = \sum G^{xs}(\text{bin.}) + W_{123} x_1 x_2 x_3$, where W_{123} is computed from binary parameters W_{ij} ($i, j = 1, 2, 3$) with a possible ternary correction C_{123} : $W_{123} = \sum W_{ij}/2 + C_{123}$. The ternary term causes an asymmetrical contraction of the calculated ternary miscibility gap independent from C_{123} (= 0 or not). As a consequence the calculated invariant points either rutile + 2 liquids or cristo-

balite + 2 liquids are far from the measured compositions: the measured extend of the miscibility gap with respect to cristobalite and rutile stability fields is considerably larger than calculated. Calculations with geometrical extrapolation methods without ternary parameter proposed by Kohler, Muggianu and Colinet (see HILLERT [1980] for a review) yield similar results. Much better results were obtained by weighting the binary excess terms separately. The weights are expressed with $(x_1 + x_2)^{-k}$ that equals 1 when evaluated on the binary and control the decline of the excess term when extrapolated to higher order systems. This weighting scheme has been implemented in computer codes to determine the stable assemblages by minimizing the Gibbs free of the system (DE-CAPITANI, 1994). It includes and generalizes the KOHLER (1960) extrapolation (e.g. $k = 1$ for the binary subregular solution $G^{xs} = x_1 x_2 [W_1 x_1 + W_2 x_2]$). With $k = 1$ for the CaO-TiO₂, $k = 0$ for the CaO-SiO₂ and $k = -4$ for the SiO₂-TiO₂ excess terms, binary interaction parameters have been fitted with linear programming techniques to liquidus and solvus data. The coincidence of calculation and experiment is excellent. The calculated phase diagram is shown in figure 1 together with tie-lines of coexisting liquids and experimentally deter-

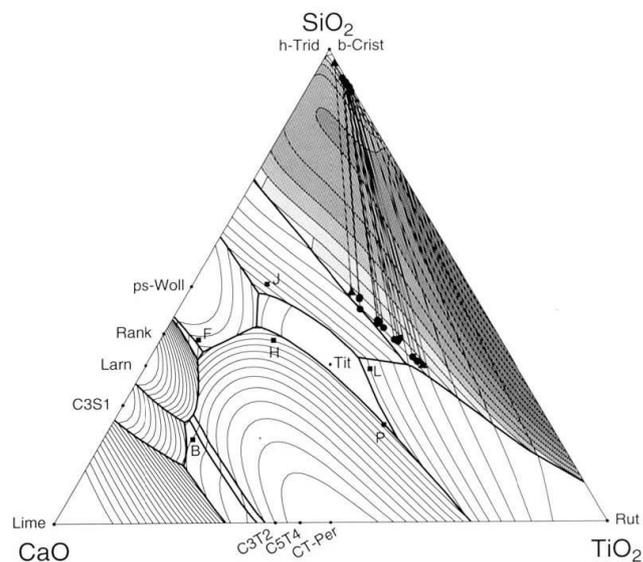


Fig. 1 Calculated phase diagram in the CaO-SiO₂-TiO₂ system.

Isotherms are shown from $T = 1300$ °C, to 2650 °C, with 50 °C steps. Experimentally determined compositions of coexisting liquids at 1600C are indicated with filled circles, triangles determine the two liquid + rutile and two liquid + cristobalite stability fields, respectively. Squares point reported ternary eutectics from DEVRIES et al. (1955) (their Tab. III: L: 1365C, K: 1365C, J: 1318C, H: 1348C, F: 1398C, B: 1650C). Region of stable liquid immiscibility is shaded.

mined eutectic invariant points from DEVRIES et al. (1955). Major discrepancies remain for the wolastonite stability field that may be due to negligence of possible TiO₂ solubility in this study.

Extrapolation to CaO–SiO₂–TiO₂–Al₂O₃ system

Addition of 3 wt% Al₂O₃ significantly reduces the extension, the consolute and the monotectic temperature of the ternary miscibility gap (see Fig. 2). Similar results have been obtained in Fe-bearing liquids (WOOD and HESS, 1980). Al is concentrated in the less polymerized liquid in the CAST system, in contrast to alkali bearing silicate liquids where Al is enriched in the silica rich liquid phase as a network forming cation. In bulk compositions containing 6 wt% Al₂O₃ phase separation is rendered metastable at 1600 °C: no phase boundary has been detected. However, the tarnished glasses and the characteristic scattering of microprobe analysis indicate spinodal decomposition on a sub-micron scale while quenching. In figure 2 experimental data at 1600 °C are projected on the 1.9 mol% Al₂O₃ plane in the CAST tetrahedron. Again, excess free energy of the melt in the Al₂O₃-bearing binary systems has been modelled with subregular solution parameters, no stable immiscibility has been reported. The calculated miscibility gap in figure 2 has been obtained with $k = 1.8$ for the extrapolation of all Al binaries. The observed contraction of the STC miscibility gap is in disagreement with the calculated solvus. The variation of k values for Al excess parameters is of minor importance and cannot reproduce the disappearance of phase separation at low Ti contents (at 1600 °C). In contrast, modifying k for the positive CaO–SiO₂ binary parameters has a considerable effect on the calculated STAC solvus at low Al and Ti contents. This is also improved by the decline of the SiO₂–TiO₂ solvus in the SiO₂–TiO₂–Al₂O₃ system, which is reproduced by varying k for the SiO₂–TiO₂ parameters to negative value rather than k for Al bearing binary excess terms. Consequently, it is suggested that either positive excess parameters of CaO–SiO₂ may be extrapolated with negative k values as for SiO₂–TiO₂ binary excess parameters or the fitted excess function in the STC system is weighted in a similar way with $(x_1+x_2+x_3)^k$ when extrapolated to the STAC system. More experimental data on immiscible liquids in multicomponent systems (e.g. MgO-bearing CMS and STMCA systems) need to be evaluated to enhance these suggestions.

Conclusion

Compositions of coexisting liquids in the quaternary CaO–SiO₂–TiO₂–Al₂O₃ system have been determined at 1600 °C. Experimental data in the CaO–SiO₂–TiO₂ system are modelled in detail with weighted extrapolation of binary excess parameters. The addition of few wt% Al₂O₃ reduces demixing of the liquid dramatically. Evaluation of

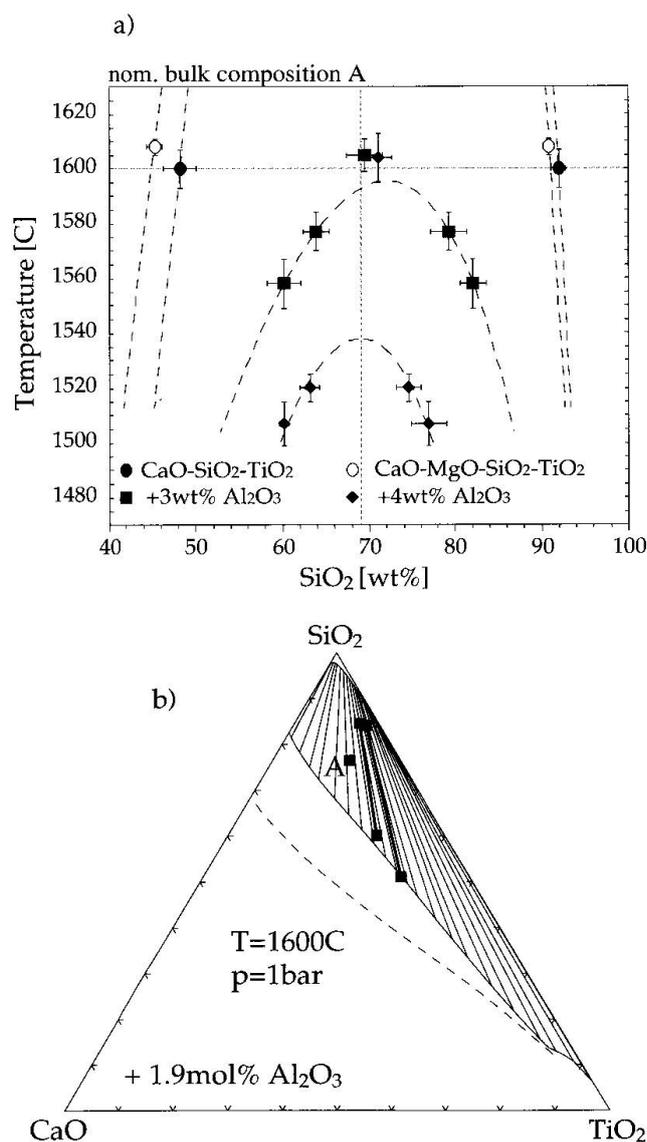


Fig. 2 Experimentally determined compositions in Al-bearing immiscible liquids. Addition of 3 wt% Al₂O₃ reduces dramatically the extension of the stable liquid miscibility gap. For bulk composition A, SiO₂ content (wt%) of coexisting liquids as function of temperature and Al content is shown in figure 2a. In figure 2b, dashed and solid lines indicate calculated miscibility gaps with $k = 1.5$ and $k = 1.9$ for the binary excess parameters in Al bearing systems, respectively. Filled squares indicate compositions of one or coexisting two liquids. Note the homogenous liquid A at low Ti in disagreement with calculation.

experimental data on the STAC solvus suggest that positive binary excess parameters contribute to a very minor degree to the free energy in Al-bearing silicate liquids even at low Al content.

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