

PREDICTION OF ACTIVITIES OF OXIDE COMPONENTS IN THE MULTICOMPONENT LIQUID SYSTEM $\text{FeO-MgO-CaO-Na}_2\text{O-AlO}_{1.5}\text{-SiO}_2$; A.Hashimoto, Harvard- Smithsonian Center for Astrophysics, Cambridge, MA 02138, USA

Calculation of chemical equilibria involving a liquid requires a full knowledge of chemical potentials (or activities) of all the oxide components present in the liquid phase. This is a rigorous requirement compared to that for solid compounds, where only total free energies need to be known in order to calculate their stabilities relative to other compounds; obviously the difference stems from the lack of a stoichiometric requirement for liquids.

The determination (or prediction) of activities of the components in oxide liquids is critical for understanding not only terrestrial and planetary igneous processes, but also chemical fractionations that occurred in the solar nebula. It is plausible that near the midplane of the accretionary disk proportions of rock-forming metallic elements and oxygen were enhanced relative to hydrogen. This would raise the condensation temperatures of oxides [1], possibly above the solidus temperature of oxide mixtures. Chondrules and once-molten Ca,Al-rich inclusions (CAIs) testify to the existence of liquid phases in the nebula (though of course these might be products formed under non-equilibrium conditions).

Activities of oxide components have been measured experimentally for many binary silicate solutions, but in most cases the compositional ranges studied are limited; experimental data are scarce for liquids containing more than two components, with the exception of a few ternary systems such as $\text{CaO-AlO}_{1.5}\text{-SiO}_2$ [2]. However, a recent experiment using a CAI-analog liquid [3] is promising. A fourth-degree Margules expansion has been used to predict the thermodynamic properties of mixing in a $\text{MgO-CaO-Al}_2\text{O}_3\text{-SiO}_2$ liquid [4]. This model, however, has a rather serious problem: it treats the thermodynamic quantities of simple oxide liquids (*i.e.* reference values for complex compounds) as adjustable parameters, and the adopted values for them are different from those in literature, beyond the 2σ uncertainty limits of the latter. A modified quasichemical model for binary silicate liquids has been developed, and expanded to include a third component [5]. In contrast to the model described above, which is basically mathematical, the latter scheme actually describes interactions between constituents by considering M "particles" (Mg, Ca, *etc.*) and Si particles to mix in a cationic quasi- lattice. This model, however, does not include aluminum oxide, which is an essential component of rocks and magmas.

I have developed a model for mixing the six oxide components in the liquid system $\text{FeO-MgO-CaO-Na}_2\text{O-AlO}_{1.5}\text{-SiO}_2$, which is described below. This system can be regarded as a mixture of subsystems that consist of binary solutions of a cationic oxide (MO or M_2O) with an anionic oxide (SiO_2 or $\text{AlO}_{1.5}$). There are two possible ways of assembling these subunits into the final six-component solution. One would be to produce the two quinary systems, $\text{FeO-MgO-CaO-Na}_2\text{O-SiO}_2$ and $\text{FeO-MgO-CaO-Na}_2\text{O-Al}_{1.5}$, by forming ideal mixtures of the four binary silicate liquids and the four binary aluminate liquids, respectively. Richardson [6] has shown that the free energy of mixing between the liquids $(\text{MnO})_x(\text{SiO}_2)_{1-x}$ and $(\text{FeO})_x(\text{SiO}_2)_{1-x}$ ($0 < x < 1$) is well approximated by ideal mixing between Mn and Fe sites. This indicates that the mixing effect is due to a configurational change in M sites; SiO_2 , being common to the two binaries, does not change configuration during mixing. The application of his method to mixing between CaO-SiO_2 and $\text{Na}_2\text{O-SiO}_2$ liquids [7] and between CaO-SiO_2 and MgO-SiO_2 also supports such mixing behavior. One could assume that ideal mixing also holds in cation exchange between binary aluminate liquids. In the next step the mixed silicates and aluminates would be brought into a single solution. In this step, however, ideal mixing is not a good approximation: it is known from existing activity data [2] that SiO_2 and $\text{AlO}_{1.5}$ mix nonideally when Ca-silicate and Ca-aluminate are combined, although mixing between Mg-silicate and Mg-aluminate occurs nearly ideally. Since it is difficult to deal with these different effects in the final mixing step, I have not used this procedure.

In the alternative method, which was eventually adopted, silicate and aluminate binaries that have a common M cation are first mixed. This enables the effects of different M species on the mixing of Si and Al to be dealt with separately. Ideal mixing was assumed when $\text{M} = \text{Fe}$ and Mg , while non-ideal mixing was used for $\text{M} = \text{Ca}$ and Na . The four alumino-silicate liquids thus produced were then mixed ideally: only cation exchange in the M sites needs to occur, since the four subsystems can be mixed so as to have the same Si/Al ratios from the outset.

The modified quasichemical model of [5] was adopted to provide activities of oxide components in the binary silicate solutions that are created at the start of mixing. In the case of binary aluminate solutions, for which the quasichemical model was not intended, I used the concept of "basicities" of cationic oxides proposed by [8]. *Basicity* is a measure of the degree of interaction between network-modifying cationic species (MO and M_2O) and network-forming anionic species (SiO_2 and $\text{AlO}_{1.5}$), and is approximately represented by an extremum (the top of a negative cusp) on the free energy surface of mixing of an M-silicate or M-aluminate solution. I assumed that the

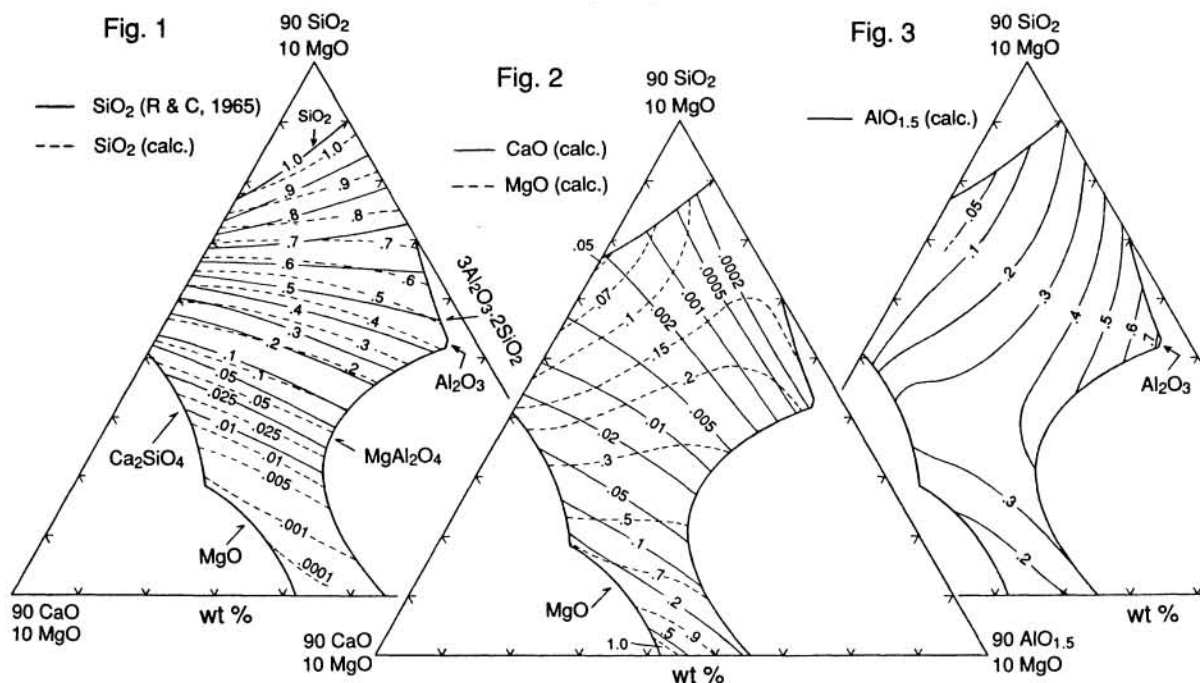
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ratio of basicities of one cationic oxide to the other is not affected by replacing SiO_2 by $\text{AlO}_{1.5}$ in the anionic sites. The free energy minimum in an M-aluminate system was calculated as the product of the basicity ratio of M to Ca in the silicates and the minimum energy in the Ca-aluminate (the only aluminate for which a relatively well-defined free energy curve is known). Since the free energy curve of the $\text{CaO-AlO}_{1.5}$ liquid has a nearly symmetric shape about $x = 0.5$, it is well approximated by the symmetric simple solution model; its only Margules parameter is easily calculable from the free energy minimum, yielding the activities of oxide components in the aluminate. The same procedure was applied to other M-aluminates.

A molecular formula was chosen for each oxide species to simplify mixing behavior. Sodium oxide behaves like the oxides of divalent cations on mixing if Na_2O is used as the unit formula [5]. $\text{AlO}_{1.5}$ (but not Al_2O_3) can be treated as a particle comparable to SiO_2 on mixing in a common cationic matrix.

A computer program was written to calculate activities of oxide components in the six-component liquid, given a temperature and the mole fractions. To check the validity of the method developed I have calculated the free energies of formation for various minerals at their congruent, incongruent, and eutectic melting points, where the activities of oxides in solids should equal those in the coexisting liquid (which are calculated by the program). The results agree with the literature data to within a fraction of 1 kcal/(oxide mol) for most of the minerals investigated. I have also calculated activities of oxide components in the $\text{MgO-CaO-AlO}_{1.5}\text{-SiO}_2$ system ($\text{MgO} = 10 \text{ wt}\%$), which approximately embraces the range of compositions of type B CAIs (except for Ti-oxides and minor components), as shown in Figs. 1-3. The activity of SiO_2 has been experimentally determined [2], and this agrees well with the calculated values. There are no data to compare with the calculated activities of MgO , CaO and $\text{AlO}_{1.5}$. However, the activity of the $\text{AlO}_{1.5}$ component at the corundum (\sim pure Al_2O_3) liquidus boundary, 0.72 (not unity), suggests that the model has to be improved if the phase diagram is correct. This is also apparent from the activity contours of MgO (0.7-1.0, differing from unity) at the periclase (\sim pure MgO) liquidus and the difference in their curvatures from the latter. Nevertheless, the present model provides 1st-order approximations to the real activities of oxide components which have not yet been measured.

REFERENCES: [1] Wood, J.A. & Hashimoto, A. (1988) *LPS XIX*, 1292. [2] Rein, R.H. & Chipman, J. (1965) *Trans. AIME* 233, 415. [3] Chamberlin, L. et al. (1990) *LPS XXI*, 177. [4] De Capitani, C. & Brown, T.H. (1987) *GCA* 51, 2639. [5] Pelton, A.D. & Blander, M. (1986) *Met. Trans. B* 17B, 805; Blander, M. & Pelton, A.D. (1987) *GCA* 51, 85. [6] Richardson, F.D. (1956) *Trans. Faraday Soc.* 52, 1312. [7] Neudorf, D.A. & Elliott, J.F. (1980) *Met. Trans. B* 11B, 607. [8] Yokokawa, T. & Niwa, K. (1969) *Trans. JIM* 10, 3.



Figs 1-3. Activity contours of oxides in the liquid system $\text{MgO-CaO-AlO}_{1.5}\text{-SiO}_2$ ($\text{MgO}=10 \text{ wt}\%$), at 1600°C . For SiO_2 , experimental data [2] are compared with calculated values (calc.). Solid lines separating contoured regions from blank areas are the solid/liquid boundaries (i.e., liquidus) at 1600°C ; also shown are solid phases that coexist with the liquid at these boundaries. Reference states of the activities are pure solid oxides.