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A Criterion for Predicting Liquid Immiscibility in Silicate Melts

Most petrologists hold that liquid immiscibility is not a significant process in the genesis of common igneous rocks. Recently, however, petrographic evidence of immiscibility has been discovered in a variety of igneous rocks¹⁻⁵ in the form of blebs (ocelli) of material which show physical evidence of formation as a separate liquid phase in equilibrium with the surrounding, predominant, liquid phase. In a number of cases, the immiscibility of the ocelli in their host has been demonstrated by melting experiments. Because droplets of immiscible liquid are both fragile and ephemeral, it seems probable that immiscibility may also have operated in some rocks which now show no physical evidence of such a process. In order to decide this question, a criterion must be developed to predict what types of silicate liquid may show immiscibility. From elementary thermodynamic reasoning, this criterion may be stated as follows: "An initially homogeneous silicate liquid will divide into immiscible fractions if the total free energy of the fractions is lower than that of the homogeneous liquid."

Lacey⁶ has shown that the free energy of some silicate liquids can be computed from thermodynamic data on the solids, using the fact that at the melting point the free energy of the liquid is equal to that of an equivalent amount of crystalline material. The results of Lacey's calculations, standardized to 1,250 K are shown in Fig. 1, where the data are plotted relative to the free energy of vitreous silica. This standard is chosen on the assumption that the melts are basically continuous networks of oxygens coordinated about silica and alumina. In that case, the free energy of melts containing varying numbers of silicon and aluminum atoms per fixed number of oxygen atoms should be calculated on the basis of a fixed number of oxygens. Using 100 oxygens as a base, an empirical analysis of the data of Fig. 1 yields the relation

$$-F = 83.3(100 - 3/2Al - 2Si) \sum_i (n_i r_i / E_i) \text{ kcal}$$

where F is the free energy per 100 oxygens, Al and Si the number of aluminum and silicon atoms per 100 oxygens, n_i the mol fraction of ion i relative to ions other than Si and Al , the ionic radius, and E_i the valence of i .

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This relation may be heuristically explained by supposing that the Si and Al are present as ions, surrounded by charge at a distance equal to the ionic radius. When one of these ions is replaced by another cation the ratio of the coulomb energies for the two ions is given by $(E_n/E_i)(r_i/r_n)$ where the subscript n denotes the network ion. The expression for the free energy

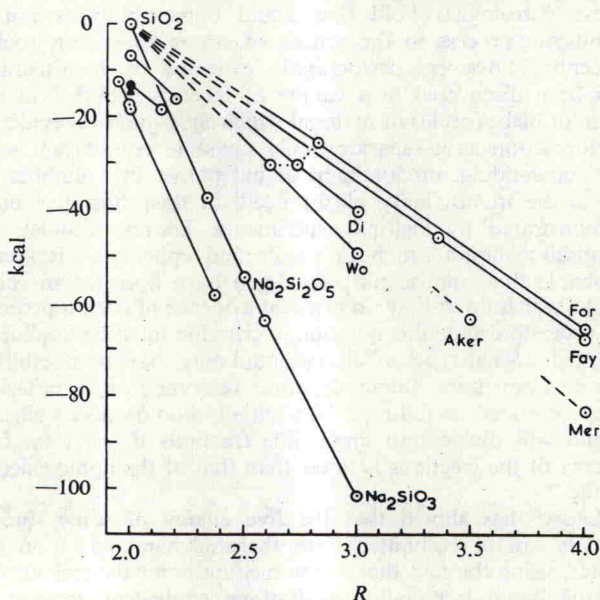


Fig. 1 Gibbs free energy of silicate melts relative to vitreous silica at 1,250 K (kcal per glassformer (Si+Al)). R gives the number of oxygens per glassformer. After Lacey⁶. ●, Anorthite melt; ▲, albite melt.

relative to vitreous silica is therefore a measure of the change in coulomb energy per ion of i introduced. The term $(100 - 3/2\text{Al} - 2\text{Si})$ expresses the total number of network ions replaced, and is zero for glasses containing no ions except aluminum and silicon. The term $(n_i r_i / E_i)$ expresses the number of ions i introduced per 100 oxygens, and gives the factor by which the coulomb energy per ion is changed by this introduction. The constant represents the coulomb energy per network ion. This term remains approximately constant because (E/r) is roughly the same for Si and Al in spite of the difference in charge. In the form quoted, the formula may be applied to any chemical analysis calculated into a standard cell of 100 oxygens.