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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 , r_i , 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

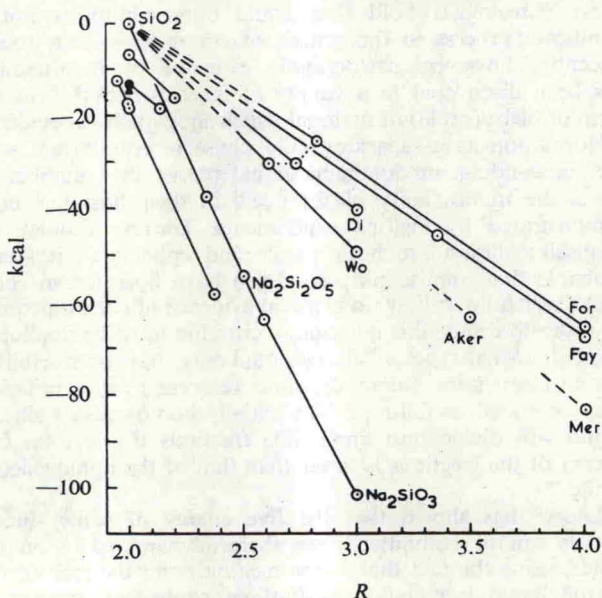


Fig. 1 Gibbs free energy of silicate melts relative to vitreous silica at 1,250 K (kcal per glassformer (Si + Al)). R gives the number of oxygens per glassformer. After Lacey⁶. ●, Anorthite melt; ▲, albite melt.

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.

No explicit account is taken of variations in temperature and pressure. At high pressures r_i decreases, commonly decreasing more for large ions. One would expect that differences between ions would be suppressed at elevated pressures, and that immiscibility would therefore tend to be suppressed. At high temperatures, the effects are reversed, the ionic radii expanding somewhat with temperature. All of these adjustments however are so small relative to the possible errors in the basic assumptions that it is not worthwhile to amend the model to attempt to take account of variations in pressure and temperature. As an empirical observation, immiscibility seems most common in silicate melts at low pressures (volcanic conditions), and temperatures at which abundant crystallization is occurring.

In order to test the model, the free energy of melts in the system fayalite-leucite-silica and related systems have been calculated (Table 1). The model correctly predicts the appearance of immiscibility in the system fayalite-kalsilite-silica, as discovered by Roedder⁷, and correctly denies the possibility of immiscibility in other related systems. Comparison of the calculations in the fayalite-kalsilite-silica system suggest that the criterion is somewhat conservative, since the calculated immiscibility field is smaller than that mapped by Roedder. The ionic radii utilized (from the *Handbook of Chemistry and Physics*, 47th ed., 1966, p. 3) may explain part of the difference.

The success of the model in this simplified experimental system suggests its application to more complex natural systems. When applied to the ocellar lamprophyre dikes at Callander Bay, Ontario, for which observational and experimental evidence of immiscibility have been presented², the formula predicts a large free energy advantage for splitting the homogeneous composition into immiscible fractions (Table 2). Indeed the advantage is the largest found thus far for any natural rock. Even here, experimental evidence suggests that immiscibility is suppressed by application of 3-4 kbar pressure².

The second group of data in Table 2 demonstrate a more speculative use of the criterion. Mont St Hilaire, roughly 20 miles east of Montreal, Quebec, is a circular pluton about 2 mile in diameter consisting of roughly 50% mildly alkaline gabbro, intruded by agpaitic syenite. Chemical analyses do not suggest any reasonable mechanism of normal differentiation which can produce either the compositions or the relative proportions of the two halves of the intrusion. Calculation of the relative free energies of the agpaitic syenite and of the latest differentiate on the gabbroic side of the mountain (nepheline diorite), suggests that they would form immiscible

Table 1 Calculated Gibbs Free Energy of Experimental

Fe ₂ SiO ₄ -SiO ₂		KAlSi ₂ O ₆ -Mg ₂ SiO ₄ -SiO ₂			NaAl
(1)	(2)	Homo	(1)	(2)	Homo
40.21	36.21	38.21	40.21	36.21	38.21
3.70	7.70	5.70	3.70	7.70	5.70
12.20	12.20				12.20
		12.20	12.20	12.20	
					5.70
3.70	7.70	5.70	3.70	7.70	
3.48	991.27	812.42	711.07	909.65	703.0
		812.42			703.0
842.37			810.36		

s per 100 oxygens. The composition in the field leucite and is compared with analogous compositions in related

Table 2 Calculated Gibbs Free Energy of Silicate Melts for Natural Rocks

Rock and mol fraction	Bulk rock		Callander Bay Ocellus (0.15)		Matrix (0.85)		Homogeneous		Mont St Hilaire Syenite (0.5)		Diorite (0.5)	
S ₁ O ₂	40.26	24.22	53.51	30.30	38.96	23.14	52.29	30.57	53.95	31.27	50.66	29.88
Al ₂ O ₃	15.48	11.12	21.62	14.41	14.76	10.33	20.03	13.81	19.03	13.00	21.01	14.61
TiO ₂	3.95	1.81	0.69	0.29	4.27	1.91	1.38	0.61	1.17	0.51	1.58	0.70
Fe ₂ O ₃	6.23	2.86	2.01	0.81	6.53	2.75	2.95	1.30	4.70	2.05	1.24	0.55
FeO	6.56	3.34	2.08	0.94	6.93	3.26	2.56	1.25	2.02	0.98	3.08	1.52
MgO	5.29	4.81	2.23	1.85	5.60	4.96	1.09	0.95	0.60	0.52	1.57	1.38
CaO	10.28	6.72	1.27	0.79	1.66	7.42	3.75	2.35	1.26	0.78	6.20	3.92
Na ₂ O	2.52	2.98	2.10	2.30	2.58	2.97	9.28	10.52	10.85	12.19	7.74	8.85
K ₂ O	3.69	2.87	10.22	7.38	3.05	2.31	3.27	2.44	3.67	2.72	2.73	2.16
H ₂ O	3.68	14.97	2.76	0.34	3.78	14.97	1.01	3.95	0.69	2.65	1.33	5.25
CO ₂	1.20	0.99	0.91	0.69	1.23	0.99	0.50	0.40	0.81	0.64	0.20	0.16
P ₂ O ₅	0.63	0.32	0.40	0.20	0.65	0.33	0.85	0.42	1.24	0.61	0.66	0.33
-F	974.43		792.20		1,032.68		989.81		1,077.30		905.06	
-F _{homo}	974.43						989.81					
-F _{immiscible}					996.36						991.18	

$$-F_{\text{homo}} = 80.3 (100 - 3/2\text{Al} - 2\text{Si}) \sum_i (n_i r_i) E_i$$

$$-F_{\text{immiscible}} = -(M_1 F_1 + M_2 F_2) \text{ where } M \text{ is the mol fraction of melt.}$$

liquids. An initially gabbroic pluton may have differentiated to a considerable degree, and then separated an immiscible agpaite fraction, which separated completely from its coexisting liquid, a process presumably requiring considerable periods at the appropriate temperature and pressure. This hypothetical process can readily be tested by experiment.

The tables of Nockolds⁸ were searched to find other immiscible pairs of rock compositions, but without success. The average nepheline and average nepheline syenite are close to being immiscible, as are the average gabbro and the average calc-alkaline syenite. The averaging process used to derive Nockold's values may obscure individual examples of possible immiscibility between these compositions. This question can be investigated by a variational procedure, in which the content of each ion is varied in turn and the effect on the free energy evaluated; such procedure would be aided by use of high speed computers. The search showed that there is a considerable range of generally gabbroic and generally syenitic compositions for which the formula predicts liquid immiscibility. All of these compositions are more or less peculiar by geological standards. Possible immiscible liquids must possess one or more of the following characteristics; unusually high potassium content (potassium is unique among major elements in having r/E greater than 1); low water content, because the small radius of H tends to inhibit immiscibility; low to moderate silica content, almost always less than 55%; and anomalous Si/Al ratios, especially in rocks rich in low valence cations.

The formula offers an easy test of the probability of liquid immiscibility between given chemical compositions. It correctly predicts the known examples of liquid immiscibility in silicate compositions, and in experimental systems seems to discriminate quite delicately between compositions showing immiscibility and those which do not. Only further experiments can show whether the formula is of general applicability, or whether the existing data happen fortuitously to fit a plausible, but incomplete, theoretical formulation.

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