SHORT COMMUNICATIONS

MINERALOGICAL MAGAZINE, DECEMBER 1979, VOL. 43, PP. 543–4

Immiscibility in tholeiites

MOST textural studies of alleged liquid immiscibility in natural rocks assume that the texture of two co-existing glasses, each as globules of one in the other, is the result of phase separation during cooling of a 'liquid'. Liquid is not defined but it is doubtful whether supercooled liquids and glasses are also included. In the case of the interstitial glasses of tholeiites the textural evidence is equally well interpreted as a phenomenon of the supercooled state, and the purpose of this note is to propose this case, pending further experiments at controlled cooling rates in metastable (supercooled) liquids and pending studies of the kinetics of phase separation and the subsequent coarsening of the structure (James, 1975).

A liquid on cooling may remain in equilibrium with its surrounding phases, and may split into two equilibrium liquids, as for example in the system K_2O-Al_2O_3-Fe-O_2-SiO_2 (Roedder, 1951) and Biggar (1978*a*) in which latter study globules of liquids were often as large as 50 to 80 μm. A liquid may undercool or supercool, continuously increasing in viscosity, and passing through a region called 'metastable zone of undercooling' (James 1975) in which homogeneous nucleation of another phase is unlikely. It then passes into a region where homogeneous nucleation is possible but rare, and growth of nucleii is rapid, leading, one supposes, to a few large globules of the second phase; then into regions where homogeneous nucleation is rapid, but growth is slow, at viscosities of about $10^{11.5}$ poise, leading to a large number of small patches of the second phase. Almost all of the examples of alleged liquid immiscibility in tholeiites produce globules of less than 10 μm. Roedder and Weiblen (1971) quote an average of 4.5 μm and a range from 2 to 10 μm. The photographs of Philpotts 1978 are similar.

A liquid or a supercooled liquid may nucleate a second phase heterogeneously and such a mechanism may be the origin of the glass globules attached to crystal growth surfaces (see example in Philpotts, 1978).

Finally a supercooled liquid may nucleate a second liquid spinodally (James 1975) which initially produces diffuse boundaries between the phases. If this texture were subsequently coarsened and exsolved to the homogeneous solvus, the product would not be detectably different from the homogeneous or heterogeneous cases. Because of the wave nature of the spinodal mechanism a regularity of spacing between the nucleii is common and may survive the coarsening process. Regularity is a feature possibly discernible in some of Philpotts' photographs.

At and below the glass transition temperature, growth and nucleation are virtually prevented by the increasing viscosity and the slow diffusion rate.

Experimental knowledge of phase separation in supercooled liquids is confined to technological rather than geological compositions, and to temperature regimes which commonly involve holding at a fixed temperature to promote nucleation followed by holding at another temperature to promote growth of crystals in the supercooled liquid (for glass ceramics) or of one supercooled liquid in the other (for opacified glasses). Thick tholeiite lavas probably cool continuously, but homogeneous nucleation, heterogeneous nucleation, and spinodal nucleation are all probable processes proceeding in the liquid and in the supercooled liquid.

The textural evidence of large numbers of small globules, which are abundant in the mesostasis of some tholeiites, suggests that coalescence was not easy, even although some samples have 44% of frozen liquid. Such a failure to coalesce would indicate a supercooled rather than a liquid state. Coalescence to form globules up to 50 to 80 μm was found in short (5 hour) experiments around 1170 °C in K_2O-Al_2O_3-FeO-SiO_2 and around 1060 °C for a composition representing Apollo 12 immiscible liquids. (Biggar, 1978*b*.)

Quench, or metastable growth of two liquids, leading in general to droplets smaller than 1 μm was discussed by Freestone and Hamilton (1977) and Visser and Koster van Groos (1977).

To summarize, there is an apparent anomaly of globule size between experiments and tholeiites. Experiments can easily achieve 50 μm diameter globules. Natural tholeiites commonly have globules of 2–10 μm. Some quenching techniques produce sub-micron globules. It would seem probable that some natural occurrences owe their origin to nucleation of a second liquid in the supercooled state, possibly with some subsequent coarsening of the texture. Criteria to distinguish stable immiscibility, which might lead to a petrologically important separation of two magma types, from metastable (supercooled) immiscibility can perhaps be found by a combination of experimental and petrographic techniques.

REFERENCES

Biggar (G. M.), 1978*a*. In *Prog. in Exptl. Petrol.*, 4th Rept. NERC London Series D No. 11, pp. 204-8.

—— 1978*b*. In *Prog. in Exptl. Petrol.*, 4th Rept. NERC London Series D No. 11, pp. 211-18.

Freestone (I. C.) and Hamilton (D. L.), 1977. *Nature*, **267**, 559.

James (P. F.), 1975. *J. Materials Sci.* **10**, 1802.

Philpotts (A. R.), 1978. *Mineral. Mag.* **42**, 417.

Roedder (E.), 1951. *Am. Mineralogist*, **36**, 282.

—— and Weiblen (P. W.), 1971. Apollo 12 Lunar Sci. Conf. Proc.: *Geochim. Cosmochim. Acta.* Suppl. 2, 1, 507.

Rutherford (M. J.), Hess (P. C.), and Daniel (G. H.), 1974. 5th Lunar Sci. Conf. Proc.: *Geochim. Cosmochim. Acta*, Suppl. 5, 1, 569.

Visser (W.) and Koster van Groos (A. F.), 1977. *Nature*, **267**, 560.

[*Manuscript received 24 January 1979;*
revised 30 May 1979]

Grant Institute of Geology
West Mains Road
Edinburgh, EH9 3JW

GORDON M. BIGGAR

MINERALOGICAL MAGAZINE, DECEMBER 1979, VOL. 43, PP. 544-6

Immiscibility in tholeiites

BIGGAR (1979) proposes that the two-liquid textures encountered in many lunar and terrestrial tholeiites may not have formed stably, but that the phase separation occurred in homogeneous liquids that had supercooled below their equilibrium crystallization temperatures. This possibility requires careful consideration, for if the immiscibility phenomena in the lavas, described by Roedder and Weiblen (1970, 1971, 1972) and Philpotts (1978), formed metastably, then any extrapolation to magmatic processes on a large scale is unwarranted. Certainly the mechanism proposed by Biggar (op. cit.) is technically feasible, for not only is metastable immiscibility commonly used in industry to develop special glasses and glass-ceramics (Charles 1973), but also metastable separation of supercooled liquids on the scale of the lunar glass-in-glass textures has been achieved in the closely related system K_2O-FeO-Al_2O_3-SiO_2 (Irvine 1976). However, in these instances, the liquids are commonly first superheated to remove any crystal nuclei, whereas the tholeiites contain abundant crystals. In support of his proposal, Biggar (op. cit.) cites a disparity in size between his experimentally-produced stable immiscible globules, up to 80 μm diameter, and the natural textures, in general 2-10 μm (Roedder and Weiblen, op. cit., Philpotts op. cit.). I wish to discuss this disparity with reference to my own experimental studies in parts of the system K_2O-CaO-MgO-Fe-O_2-Al_2O_3-SiO_2-TiO_2-P_2O_5 (Freestone 1978*a*, *b* and in progress).

Experimentally-produced textural features. The morphology and size of the two-liquid textures achieved in the experiments has been found to be extremely variable, depending on the relative proportions, viscosities and surface tensions of the immiscible melts and the presence and amount of crystalline phases. Above the liquidus, the formation of globules several hundreds of microns in diameter is readily achievable, and the separation of two layers in the charge may occur. However, the presence of a large proportion of crystalline phases inhibits the coarsening of the textures. In particular, where $\%$ crystals $>$ $\%$ Si-rich melt $>$ $\%$ Fe-rich melt, globules of Fe-rich melt in Si-rich melt are small, and range from 2 μm to 20 or 30 μm diameter. Globules greater than *c.* 10 μm are rare in these charges and, where they occur, often contain crystals (ore minerals, olivines, pyroxenes) which would nucleate further crystals on a slow quench, leading to their obliteration. Thus my own experiments suggest that the glassy globules in tholeiitic lavas which are 56-98$\%$ crystalline would in general be only 2-10 μm diameter if *stable* immiscibility had occurred. Furthermore, in their figures, Roedder and Weiblen show a few globules