American Mineralogist, Volume 64, pages 436–439, 1979

Silica activity and the classification of alkalic and tholeiitic basalts

RICHARD J. ARCULUS

Research School of Earth Sciences, Australian National University
Canberra, A.C.T. 2600, Australia

Abstract

The thermodynamic classification of basalts introduced by Carmichael *et al.* (1970) is based on ${}^{a}SiO_2$/melt *vs.* T°C data for the olivine/low-Ca pyroxene reaction. This classification is not consistent with geochemical classification schemes, and when ${}^{a}SiO_2$/melt data for a representative composition in the critical plane of silica undersaturation in the basalt tetrahedron are compared with the olivine/low-Ca pyroxene buffer curve, some rocks classified as alkali olivine basalts are shown to be tholeiitic basalts.

Introduction

A recent development in the classification of volcanic rocks is the application of the concept of reaction boundaries (*e.g.* Carmichael *et al.*, 1970) to the silica-saturation criteria of Shand (1943). The new concept is that the presence or absence of a particular crystalline phase can be used to define the activity of silica in the melt (${}^{a}SiO_2$/melt), and that appropriate buffer assemblages—for example olivine and orthopyroxene—can be used to define the boundary between tholeiitic and alkali olivine basalt compositions (Fig. 1). Calculated temperatures of rock crystallization together with ${}^{a}SiO_2$/melt data obtained from a variety of mineral assemblages have been employed to classify rocks of uncertain association, such as the basaltic lavas of the Snake River Plain (Stout and Nicholls, 1977).

The employment of ${}^{a}SiO_2$/melt data for the olivine–orthopyroxene (Ol–Opx) buffer curve to distinguish alkali olivine and tholeiitic basalts is not consistent with a substantial body of petrologic literature that uses a variety of discriminants related to critical plane (dividing nepheline- or hypersthene-normative compositions) criteria.

Although the reaction:

$$Mg_2SiO_4 \text{ (in olivine)} + SiO_2 \text{ (in melt)} \rightarrow 2MgSiO_3 \text{ (in orthopyroxene)}$$

is by definition characteristic of tholeiitic associations, it cannot always be observed petrographically in the more basic members of tholeiitic suites. In some samples, the reaction does not take place, perhaps due to premature quenching. For example, many ocean-floor tholeiites contain one or more of the following phases, in addition to groundmass glass: olivine, plagioclase, spinel (*sensu lato*), and clinopyroxene. However, low-Ca pyroxene is rarely found in these basalts, and the rocks cannot be classified as tholeiitic or alkali olivine basalt on the basis of petrography.

The merit of mineralogic as opposed to chemical classification schemes has been and will continue to be a vexing question in petrology given the complexity of the processes that may combine to perturb the degree of totally crystalline equilibrium approached by a given melt. A reasonable compromise, adopted by many petrologists and geochemists in their approach to olivine–hypersthene-normative basalts, is the employment of chemical discriminants in the first instance where the rock mode is not obviously disturbed by cumulate processes, qualified by mineralogical information where appropriate.

In a review of the problem of chemically distinguishing alkaline from tholeiitic basalts, Irvine and Baragar (1971) suggested that discriminants in the form of arbitrary boundaries in (1) alkalies–silica plots and (2) Ol–Ne–Q cation norm projections, together with (3) Chayes' (1965, 1966) Cpx–Ol–Opx discriminant functions, were the most reliable. Irvine and Baragar (1971) introduced a modification of the MacDonald (1968) dividing line for Hawaiian tholeiitic and alkaline rocks, and a line in the Ol–Ne–Q projection that mostly follows the critical plane of silica undersaturation (Yoder and Tilley, 1962), di-

0003–004X/79/0304–0436$02.00

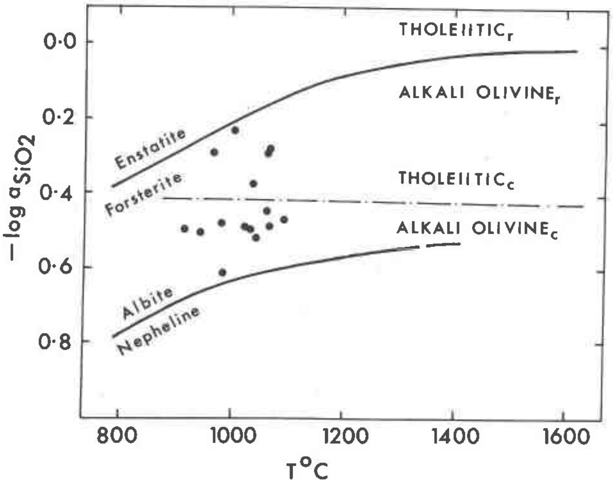

Fig. 1. *T vs.* $-\log {}^{a}SiO_2$/melt showing 2 buffer reactions, the extrapolated (dash-dot) curve for the critical plane eutectic composition, and the data for $-\log {}^{a}SiO_2$/melt at *T* for SRP lavas from Stout and Nicholls (1977). The subscripts *r* and *c* refer to buffer-reaction and critical-plane classification criteria respectively.

verging near the albite projection point to quartz-normative compositions.

The Hawaiian field boundary may be equivalent to the trace of the critical plane of silica undersaturation in the complex natural system, projected into an alkalies–silica plot (H. S. Yoder, Jr., quoted by MacDonald and Katsura, 1964). In this case, the chemical discriminants 1 and 2 listed above could be regarded as the results of different projections of the same crucial boundary, namely the critical plane. In detail, DeLong and Hoffman (1975) have shown that the effectiveness of the alkalies–silica discriminant derives from a more complex projection of the phase relationships (Ol–Cpx–Plag) of the 1 atm thermal divide of Yoder and Tilley (1962). The deviation of the natural 1 atm thermal divide from the critical plane of silica undersaturation is dependent on the extent to which the composition of the clinopyroxene differs from that of pure diopside. However, to a first approximation, a characterization by the presence of normative nepheline or hypersthene would be taken as separating basaltic melts that are capable of crystallizing either feldspathoid-bearing or quartz-bearing residues, and alkali olivine and tholeiitic basalts are named accordingly. In summary, the significance of the critical plane is stressed in most basalt classification schemes.

Problems do arise in the case of melts of Ol–Hyp-normative character, labelled olivine tholeiites by Yoder and Tilley (1962) and a variety of names including "transitional" by other workers (*e.g.* Bass, 1972). The problems are typically of both chemical and mineralogical nature. The melts may be enriched in large-ion lithophile (LIL) elements, and holocrystalline samples such as the Snake River Plain (SRP) olivine tholeiites [named as such in recent studies by Thompson (1975) and Leeman (1976)] sometimes show no evidence of orthopyroxene precipitation (Stout and Nicholls, 1977). Both of these features are suggestive of alkaline affinities for the basalts concerned.

The question then becomes whether, despite the normative character, the absence of low-Ca pyroxene together with thermodynamic evidence for the ${}^{a}SiO_2$/melt falling below the Ol–Opx buffer curve qualifies the rock as an alkali olivine rather than tholeiitic basalt, as suggested by Stout and Nicholls (1977) for some of the SRP lavas. A simple solution to this specific problem is not evident and a fuller understanding of the stable subsolidus and near-solidus assemblages of Ol–Hyp-normative basalts may be indicated. It is true that none of the experimental studies on SRP lavas (Thompson, 1975; Leeman and Vitaliano, 1976) have demonstrated a crystallization appearance for low-Ca pyroxene. However, it must be stressed that, under low-pressure (<5kbar) equilibrium crystallization conditions, it is possible for low-Ca pyroxene to be restricted to late-stage (low *T*) appearance in Ol–Hyp-normative melts, and none of the experimental studies have pursued the full sequence of crystallization from liquidus to solidus at low pressure.

Discussion

It may be desirable to examine the differences in a classification that adopts the ${}^{a}SiO_2$/melt prevailing along the Ol–Opx buffer curve from that using ${}^{a}SiO_2$/melt associated with the critical plane criteria for distinguishing tholeiitic and alkali olivine basalts. In other words, an attempt should be made to obtain ${}^{a}SiO_2$/melt data for compositions in the critical plane, as these values should more closely relate to the operational discriminants employed by petrologists and geochemists in distinguishing the two major basalt classes.

Unfortunately the data required to locate the critical plane in multicomponent space and define the ${}^{a}SiO_2$/melt prevailing in the equilibrium Ol–Cpx–Plag–melt are not available. If recourse to a simple approach is made, some information is available for a portion of the CaO–MgO–Al_2O_3–SiO_2 (CMAS) system that includes the end-member compositions of the critical plane. If we ignore for the present the deviation of the clinopyroxene from pure diopside, then any melt falling in this plane will reach the eutectic (actually piercing point) composition where crystallization of olivine, plagioclase, and diopside will occur in equilibrium with the melt (Osborn and Tait, 1952).

Thus the $^{a}SiO_2$/melt prevailing at the eutectic is of critical concern, as (to a first approximation) this value may be regarded as defining part of the limiting curve in $^{a}SiO_2$/melt–T space between melts of tholeiitic and alkalic character.

Due to the deviation of the clinopyroxene from the pure diopside composition, the eutectic is actually a piercing point where the assemblage Cpx(ss)–Ol–Plag is in equilibrium with a melt that with further crystallization will be driven towards either SiO_2-poor or SiO_2-rich melt compositions, depending on the nature of the clinopyroxene components.

The piercing-point composition in the critical plane between melt, forsterite, anorthite, and diopside is given by Osborn and Tait (1952) as (in weight percent) $SiO_2 = 49.18$, $Al_2O_3 = 15.94$, $CaO = 21.46$, and $MgO = 13.42$. Interpolation of the data of Rhein and Chipman (1965) gives $^{a}SiO_2$ melt at 1600°C (cristobalite as standard state at the same temperature) for the piercing point composition as 0.38 and $-\log$ $^{a}SiO_2$/melt as 0.42, but at a similar temperature the $-\log$ $^{a}SiO_2$/melt associated with the olivine low-Ca pyroxene reaction (cristobalite standard state) is 0.05. In other words, $^{a}SiO_2$/melt for the reaction is considerably higher at the same temperature than for the piercing-point composition. In the absence of partial molar enthalpy data for SiO_2 in silicate melts, extrapolation of the silica activity to lower temperatures is not possible. However, Rhein and Chipman (1965) showed that, for melts in the system $CaO–Al_2O_3–SiO_2$, a slight increase in $^{a}SiO_2$/melt with decrease in temperature takes place. In Figure 1, extrapolation of the datum at 1600°C to lower temperatures for the 4-component piercing-point composition is made assuming constant $^{a}SiO_2$/melt, so that the approximate location of this curve may be compared with that defined by the olivine–pyroxene buffer.

At 1270°C, the simultaneous appearance of the three crystalline phases will occur from the piercing-point melt composition, and $^{a}SiO_2$/melt will probably be different from the extrapolated value at this temperature. In the temperature range above 1270°C, compositions defined as alkali olivine by the Ol–Opx buffer curve criteria would be classified as tholeiitic by the critical plane criteria (Fig. 1).

In a natural system, the crystalline solid solutions involved in the Ol–Opx–melt buffer and the Ol–Cpx–Plag–melt assemblage would give rise to a band instead of a single line in a projected $^{a}SiO_2$/melt *vs.* T plot. The critical plane curve as drawn in Figure 1 would be projected as a band continuing to temperatures lower than 1270° where, in the simple system analyzed, the melt becomes metastable with respect to the solid assemblage. The data necessary to construct such a plot are unavailable. However, I suggest that the relative positions of the two curves or bands in $^{a}SiO_2$/melt–T space for natural systems are such that the Ol–Opx buffer curve would lie above the $^{a}SiO_2$/melt values associated with the equilibrium Ol–Plag–Cpx-melt. Thus all melts falling to the SiO_2-rich side of the critical plane up to the Ol–Opx buffer curve are classified as tholeiitic rather than alkali olivine as implied by the Carmichael *et al.* (1970) classification criteria.

This discussion does not deny that some features of olivine tholeiites such as the SRP lavas are closer to alkali olivine than tholeiitic basalts, but illustrates that for conformity with the geochemical operational criteria for classifying olivine–hyperthene-normative basalts, critical-plane information rather than the Ol–Opx reaction should be used.

Acknowledgments

Stimulating correspondence with Jim Nicholls is pleasurably acknowledged.

References

Bass, M. N. (1972) Occurrence of transitional abyssal basalt. *Lithos, 5,* 57–67.

Carmichael, I. S. E., J. Nicholls and A. L. Smith (1970) Silica activity in igneous rocks. *Am. Mineral., 55,* 246–263.

Chayes, F. (1965) Statistical petrography. *Carnegie Inst. Wash. Year Book, 64,* 153–165.

——— (1966) Alkaline and subalkaline basalts. *Am. J. Sci., 264,* 128–145.

DeLong, S. E. and M. A. Hoffman (1975) Alkali/silica distinction between Hawaiian tholeiites and alkali basalts. *Geol. Soc. Am. Bull., 86,* 1101–1108.

Irvine, T. N. and W. R. A. Baragar (1971) A guide to the chemical classification of the common volcanic rocks. *Can. J. Earth Sci., 8,* 523–548.

Leeman, W. P. (1976) Petrogenesis of McKinney (Snake River) olivine tholeiite in light of rare-earth element and Cr/Ni distributions. *Geol. Soc. Am. Bull., 87,* 1582–1586.

——— and C. J. Vitaliano (1976) Petrology of McKinney basalt, Snake River Plain, Idaho. *Geol. Soc. Am. Bull., 87,* 1777–1792.

MacDonald, G. A. (1968) Composition and origin of Hawaiian lavas. *Geol. Soc. Am. Mem., 116,* 477–522.

——— and T. Katsura (1964) Chemical composition of Hawaiian lavas. *J. Petrol., 5,* 82–133.

Osborn, E. F. and D. B. Tait (1952) The system diopside–forsterite–anorthite. *Am. J. Sci., Bowen Volume,* 413–433.

Rhein, R. H. and J. Chipman (1965) Activities in the liquid solution SiO_2–CaO–MgO–Al_2O_3 at 1600°C. *Trans. Met. Soc. AIME, 233,* 415–425.

Shand, S. J. (1943) *Eruptive Rocks, 2nd ed.* Wiley, New York.

Stout, M. Z. and J. Nicholls (1977) Mineralogy and petrology of Quaternary lavas from the Snake River Plain, Idaho. *Can. J. Earth Sci., 14,* 2140–2156.

Thompson, R. N. (1975) Primary basalts and magma genesis II. Snake River Plain, Idaho, U.S.A. *Contrib. Mineral. Petrol., 52,* 213–232.

Yoder, H. S., Jr. and C. E. Tilley (1962) Origin of basalt magmas: an experimental study of natural and synthetic rock systems. *J. Petrol., 3,* 342–532.

Manuscript received, February 23, 1978;
accepted for publication, September 26, 1978.