

# Use and Abuse of the Terms Calcalkaline and Calcalkalic

RICHARD J. ARCULUS\*

DEPARTMENT OF GEOLOGY, AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA, ACT 0200, AUSTRALIA

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*The terms calcalkaline and calcalkalic are currently defined and used in multiple and non-equivalent ways. Generally, the variation of total Fe as FeO/MgO within evolving subalkaline rock suites is regarded as the most distinctive character of calcalkaline compared with tholeiitic suites, reflecting the relative timing of phase saturation with Fe–Ti oxides, plagioclase, and ferromagnesian silicates. Other classification schemes are widely used, including a minority of adherents to the original formalized definition of ‘calcalkalic’ by Peacock (1931, Journal of Geology 39, 54–67). Given the prevailing contradictory and confusing usage of these terms, which leads to miscommunication, it is proposed that the spectrum of subalkaline rocks be divided into high-, medium-, and low-Fe suites, complementing divisions made on the basis of K contents. The terms calcalkaline and calcalkalic should be restricted to rock suites that conform to Peacock’s definition.*

KEY WORDS: *calcalkaline; calcalkalic; subalkaline; tholeiitic; rock classification*

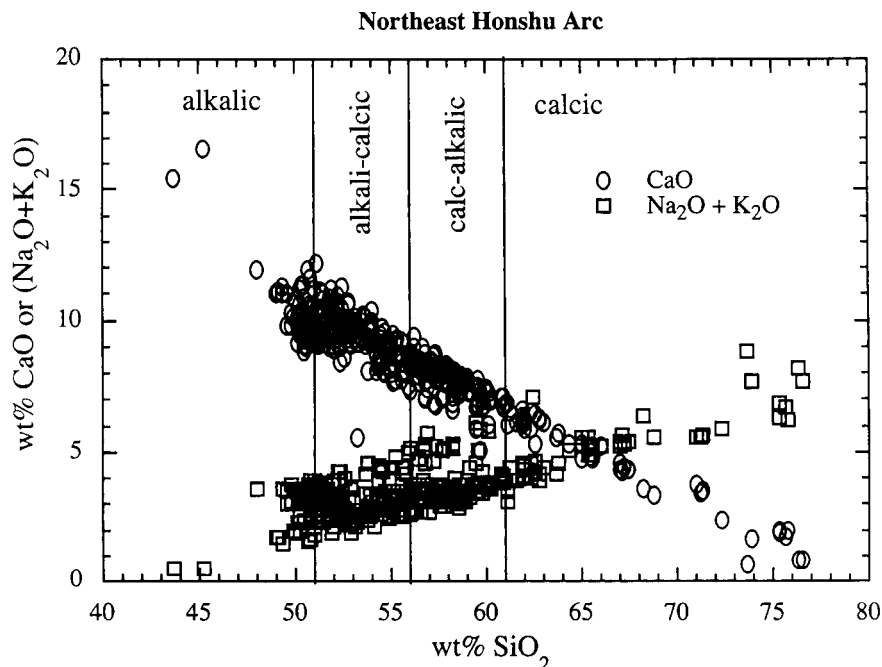
## INTRODUCTION

The etymology of the interchangeable (and variably hyphenated) terms calcalkaline and calcalkalic stems from the late 19th century (Harker, 1909, p. 90). A fundamental division between alkaline and subalkaline rocks had been recognized (e.g. Iddings, 1892), and a degree of competition prevailed between chemical and geographical distinctions, wherein Harker’s ‘Atlantic-branch’ corresponded to alkaline and ‘Pacific-branch’ to subalkaline. This fundamental distinction persists in the current International Union of Geological Sciences’ classification scheme involving the ‘total alkalis vs SiO<sub>2</sub>’ (TAS) diagram (Le Bas *et al.*, 1986),

in recognition of the linkage between a discriminant line in total alkalis vs SiO<sub>2</sub> space and the low-pressure thermal divide between critically SiO<sub>2</sub>-undersaturated and -saturated rock types (e.g. Yoder & Tilley, 1962). The subalkaline types were also recognized by early 20th-century petrologists as being richer in CaO (lime) at a given SiO<sub>2</sub> content than the alkaline types, so that the adjective ‘calcalkali’ was applied to some subalkaline series (e.g. Holmes, 1918).

Within the spectrum of volcanic rock series, Peacock (1931) formalized the term ‘calc-alkalic’ as one of several that can be applied to a specific group of rocks because he believed that the relations of total alkalis to lime (hence ‘alkali–lime index’) were fundamental in defining the feldspar compositions (readily determinable with a petrological microscope), and in themselves vital for rock classification. The terms used by Peacock (alkalic, alkali-calcic, calc-alkalic, and calcic) were applied to suites of rocks, not individual samples, and were based on arbitrary divisions drawn on a combined plot of total alkalis (wt % Na<sub>2</sub>O + K<sub>2</sub>O) and lime (wt % CaO) vs silica (SiO<sub>2</sub>). Relative to SiO<sub>2</sub>, CaO and (Na<sub>2</sub>O + K<sub>2</sub>O) show contrasting variation—CaO decreases with increasing SiO<sub>2</sub> and (Na<sub>2</sub>O + K<sub>2</sub>O) increases. Consequently, for any given suite, the lines of best fit through the lime and total alkali data arrays on a combined silica variation diagram intersect at a particular SiO<sub>2</sub> value, determined by how alkalic or calcic a particular suite happens to be (see Fig. 1). For calcalkaline rocks, the intersection between best-fit lines of lime and alkalis was defined to occur between 56 and 61 wt % SiO<sub>2</sub>. It is noteworthy that the only examples among individual volcanic suites that were accordingly classified as calcalkaline, and the immediate object of Peacock’s own research, were from Iceland, an area we currently

\*Telephone: 61 2 6125 2056. Fax: 61 2 6125 5544.  
E-mail: Richard.Arculus@anu.edu.au



**Fig. 1.** Variations of wt % CaO and Na<sub>2</sub>O + K<sub>2</sub>O vs wt % SiO<sub>2</sub> for bulk-rock compositions (major oxides, volatile-free, normalized to 100% totals) from the volcanic front of the NE Honshu (Japan) arc. Original named fields within wt % SiO<sub>2</sub> ranges are from Peacock (1931) and are applied to suites whose oxide variation trends intersect within a given field.

recognize as resulting from plume–ridge interaction. In contrast, volcanic suites from Katmai (Alaskan island arc) and Lassen Peak (southern Cascades arc) were classified as calcic. Similarly, Hatch *et al.* (1961, p. 337) commented: ‘Because they belong to the “alkali suite” the typical olivine basalts of Hawaii and elsewhere are now distinguished as “alkali olivine basalts,” although such rocks are among the most typically calcalkaline in composition.’ The important historical point is that within the spectrum of volcanic rock suites, application of Peacock’s ‘alkali–lime index’ resulted in the equating of calcic with most subalkaline.

The first half of the 20th century was also marked by a debate concerning variation of relative concentration of Fe oxides within the spectrum of subalkaline rock series [see Young (1998) for review]. The marked Fe enrichments in evolving subalkaline magmas advocated by Fenner (1929) and established by Wager & Deer (1939) for the Skaergaard intrusion brought into focus the possibility of differing trends of compositional evolution for subalkaline suites. E. F. Osborn and colleagues established experimentally the important role of oxygen fugacity ( $f_{O_2}$ ) in controlling the timing of appearance in a given crystallization sequence of Fe–Ti oxides (e.g. Osborn, 1959), which in turn determines the level of Fe enrichment in a particular suite. The important role of H<sub>2</sub>O in the relative retardation (and shift to more anorthitic compositions) of plagioclase saturation in subalkaline melts has also been

recognized as critical in the development of contrasted trends of Fe-enrichment (Grove & Kinzler, 1986). For many petrologists, variations in relative Fe concentration in evolving subalkaline suites, and the potential ultimate control of this characteristic by  $f_{O_2}$  and H<sub>2</sub>O variations, has become the most important initial classificatory parameter for distinguishing so-called tholeiitic from calcalkaline suites.

## THE PROBLEM

Petrologists and geochemists are collectively in trouble with the use of the term calcalkaline (or calcalkalic) because:

- (1) the continued use of Peacock’s formalized definition has only been retained to any extent by granite petrologists. Despite this usage pattern, many glossaries (such as those published by the American Geological Institute) retain the Peacock (1931) definition. Similarly, in the recently published *Oxford Companion to the Earth* (Hancock *et al.*, 2000, p. 557), it is asserted that ‘calcalkaline magmas... contain relatively large amounts of calcium (CaO) in relation to alkalis (Na<sub>2</sub>O and K<sub>2</sub>O)’. In a complementary way, a number of dictionaries (e.g. that published by Penguin) of geological terms state that calc-alkali is to be ‘applied to igneous rocks in which the dominant

feldspar is calcium-rich', and that 'the converse of calc-alkali is alkali', whereas others (published by Collins) use a combination of the Wilkinson (1968) and Irvine & Baragar (1971) definitions (see below).

- (2) Nevertheless, the majority of geochemists and petrologists currently engaged in studies of volcanic rocks having employed the discriminant in the TAS diagram to first distinguish between subalkaline and alkaline series, then employ either Miyashiro's (1974) arbitrary discriminant based on total Fe as FeO (i.e. FeO<sup>\*</sup>)/MgO vs wt % SiO<sub>2</sub>, or Kuno's (1968) discriminant boundaries in an (Na<sub>2</sub>O + K<sub>2</sub>O) vs FeO<sup>\*</sup> vs MgO (AFM) diagram, to distinguish between tholeiitic and calcalkaline rocks. Another less popular discriminant between tholeiitic and calcalkaline series is that proposed by Irvine & Baragar (1971) on the basis of wt % Al<sub>2</sub>O<sub>3</sub> vs normative plagioclase composition, wherein the tendency towards higher Al<sub>2</sub>O<sub>3</sub> contents of subalkaline magmas erupted in arc settings (as a consequence of delayed plagioclase saturation) is emphasized. It should be noted that 'lime' (or 'calc') does not feature directly in any of the TAS, FeO<sup>\*</sup>/MgO vs wt % SiO<sub>2</sub>, AFM diagrams, and Irvine & Baragar discriminant, and alkalis are not involved directly in the FeO<sup>\*</sup>/MgO vs wt % SiO<sub>2</sub> diagram.
- (3) Calcalkaline has also become synonymous in many geologists' minds variously with: (i) medium-K (as opposed to low-K = tholeiitic, or high-K = shoshonitic/alkalic) volcanic rock series (see Rollinson, 1993, p. 56); (ii) derivative from high-Al basalt rather than 'low-Al = tholeiitic' (see Wilkinson, 1968); (iii) 'hypersthene' as opposed to 'pigeonitic' rock series (associated with low-K tholeiitic parental basalts) (e.g. Kuno, 1968); or even (iv), light (L) rare earth element (REE)-enriched compared with heavy (H) REE, in contrast to tholeiitic series characterized by low LREE/HREE.
- (4) Rock series that are claimed to be calcalkaline by one of these discriminants cannot necessarily be classified as such using any of the other discriminants (e.g. Kersting & Arculus, 1994).
- (5) Wherever calcalkaline rocks are commonly identified by any one of the non-equivalent classification schemes in use, it is assumed that the rocks must have formed in an island or continental arc setting.
- (6) Whenever the same term is being used to describe objects that, in reality, differ from one another in definable, different, and interesting ways then we have a clear scientific problem, and communication between scientists inevitably will be at

cross-purposes. The problem is not quarantined within petrology and geochemistry, as workers in other fields such as tectonics and geophysics inherit the classificatory mess.

The purpose of igneous rock classification is to identify distinctive members of the compositional spectrum, and to establish bounding parameters that help focus genetic theories for particular rock types. The inevitable redundancy of classification schemes that are based on genetic models has persuaded most workers to persist with directly measurable parameters, even if the majority of the field boundaries are arbitrary and simply geometrically or mathematically convenient, as for example in the TAS classification diagram (e.g. Streckeisen, 1976; Le Bas *et al.*, 1986). It should be noted, however, that the discriminant between alkaline and subalkaline rocks in the TAS diagram has particular significance because many volcanic suites of distinctive geochemical and mineralogical composition clearly diverge from the discriminant boundary (rather than crossing or straddling it), and the position of the boundary in wt % (Na<sub>2</sub>O + K<sub>2</sub>O) vs SiO<sub>2</sub> space results from the projection in this compositional space of the relatively low-pressure (~10<sup>5</sup> Pa to 1 GPa) thermal divide corresponding to the stability of olivine-clinopyroxene-plagioclase that separates melts that fractionate to feldspathoid-normative from hypersthene- and ultimately quartz-normative compositions, respectively.

## A PROPOSAL

Within the realm of subalkaline rocks, it has proven particularly useful to distinguish suites characterized by two major compositional parameters: (1) the abundance of K (or its oxide) vs SiO<sub>2</sub> content, reflecting a combination of initial petrogeneses and evolutionary processes (Gill, 1981); (2) the degree of Fe-enrichment at equivalent SiO<sub>2</sub> contents or some other measure of magmatic evolution (e.g. Carmichael, 1964; Osborn, 1979). The key factors controlling this latter variability are the independent variables of H<sub>2</sub>O concentration, which controls the timing of phase appearance of plagioclase compared with ferromagnesian minerals, and oxidation state (controlling *inter alia* the appearance and persistence of a spinel phase in the compositional range Al-bearing chromite to magnetite, the solubility of S, and sulphide/sulphate stability; O'Neill & Mavrogenes, 2002).

It has not yet been established that any single physico-chemical equivalent of the olivine-clinopyroxene-plagioclase low-pressure thermal divide exists to separate high- from low-FeO<sup>\*</sup>/MgO rock suites. Although saturation with an Fe-Ti oxide phase leads

to marked changes in the individual trends of volcanic suites on an  $\text{FeO}^*/\text{MgO}$  vs wt %  $\text{SiO}_2$  type of diagram (Osborn, 1979), overall in many island and continental arcs, a scatter of data across the Miyashiro (1974) discriminant line exists (see Gill, 1981, p. 4). We should assume for the present that a continuum exists.

Granted the usefulness of distinguishing independently of the  $\text{K}_2\text{O}$  vs  $\text{SiO}_2$  character the variations of  $\text{FeO}^*/\text{MgO}$  (at specific fractionation variable), I propose, first, that we restrict the use of the term calcalkaline to only those suites that conform to Peacock's original criterion, and, second, that we adopt new terms such as 'low-, medium- and high- $\text{FeO}^*/\text{MgO}$ ' (possibly abbreviated to loFe, meFe and hiFe, respectively) for 'subalkaline' suites (established by the TAS discriminant), based on arbitrary divisions of the natural compositional spectrum (see below). I suspect that the term tholeiite is too deeply embedded within the reflexive terminology of petrologists to abandon [see Chayes (1965) for a critique of this word], but in essence, the hiFe suite of subalkaline rocks would be equivalent to tholeiitic suites. It is illogical and uninformative to continue to use the term calcalkaline for rock suites where the defining characteristics are based neither on 'calc' nor 'alkaline', and where the multiplicity of definitions in use hinders scientific exchange.

## SOME EXAMPLES AND COMMENTS

It is instructive to examine some examples of the correspondence of representative volcanic arc suites to existing criteria for distinguishing calcalkaline suites. In Fig. 1, the variations of wt % CaO and  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  vs  $\text{SiO}_2$  for samples collected along the volcanic front from the northern Izu arc through NE Honshu (Gust *et al.*, 1997) are shown relative to the Peacock (1931) discriminants. Although multiple suites are present [including the type 'pigeonitic' and hypersthenic' series described by Kuno (1950) for Hakone], very few of these suites could be classified as calcalkaline on the basis of the relevant discriminant boundary; the bulk of the suites are calcic in Peacock's terms. Compositional data for the same sample set are plotted in an AFM diagram in Fig. 2 and  $\text{FeO}^*/\text{MgO}$  vs wt %  $\text{SiO}_2$  in Fig. 3 (together with an example of a type tholeiitic suite from Thingmuli, Iceland); Kuno's (1968) and Miyashiro's (1974) discriminant boundaries between tholeiitic and calcalkalic rocks are shown in Figs 2 and 3, respectively. A clear bimodality can be seen in both Figs 2 and 3; fewer rocks are classified as tholeiitic by the AFM discriminant boundary compared with that in  $\text{FeO}^*/\text{MgO}$  vs wt %  $\text{SiO}_2$  space. In addition, the compositional gap between these NE Honshu suites

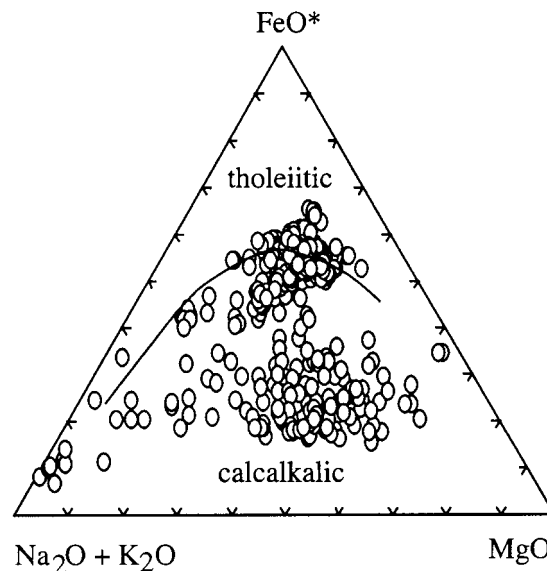
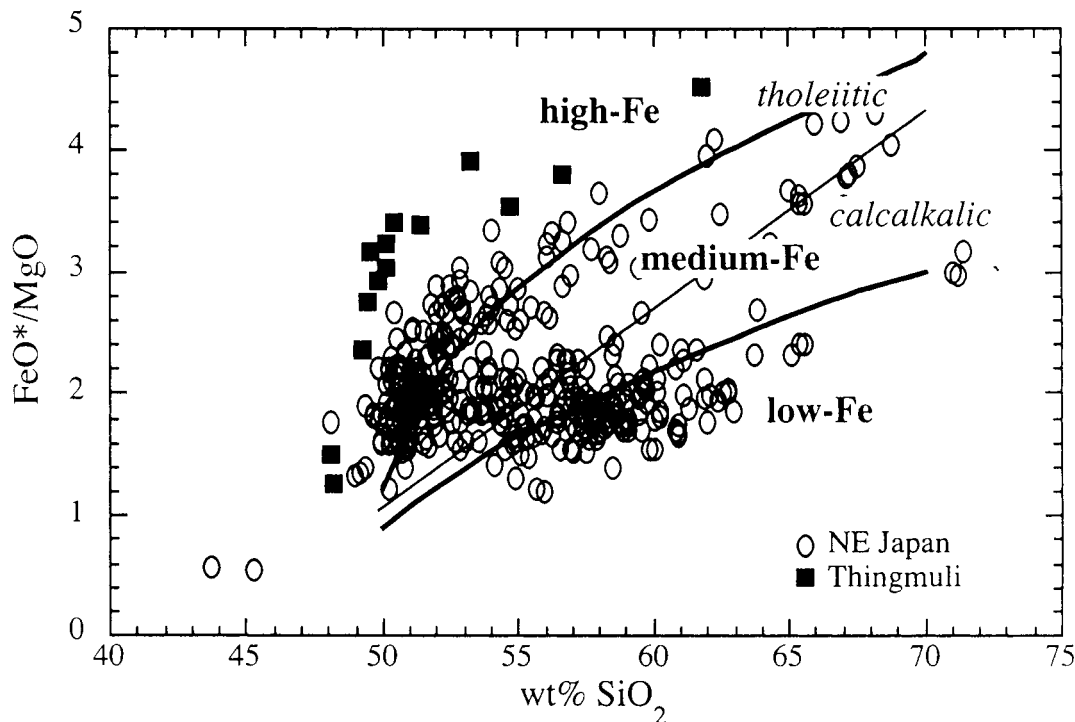


Fig. 2. Bulk-rock compositions from the volcanic front of the NE Honshu (Japan) arc projected in terms of wt % ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ) vs total Fe as wt %  $\text{FeO}$  ( $\text{FeO}^*$ ) vs wt %  $\text{MgO}$  (AFM). The discriminant boundary between tholeiitic and calcalkalic is from Kuno (1968).

does not correspond neatly to either of Kuno's or Miyashiro's discriminant boundaries.

I have placed arbitrary discriminant boundaries between the proposed low-, medium-, and high-Fe fields respectively in Fig. 3, superimposed on the NE Honshu data. Despite the convenience of straight lines, I suggest the discriminant boundaries should curve to parallel the decrease in rate of  $\text{FeO}^*$  increase as a function of  $\text{SiO}_2$  content, given the observed compositional effects in residual melts that saturation with, and fractional crystallization of, Fe–Ti oxides have in well-characterized rock suites. The values of  $\text{FeO}^*/\text{MgO}$  at specific wt %  $\text{SiO}_2$  contents for the proposed high–medium and medium–low  $\text{FeO}^*/\text{MgO}$  vs  $\text{SiO}_2$  boundaries are given in the figure caption.

These boundaries have been drawn as far as possible to ensure that various suites currently asserted to be dominantly formed by fractional crystallization remain within a given field. Thus, for example, the Thingmuli suite of Carmichael (1964) and the pigeonitic series of Kuno (1950) both fall within the high-Fe field, whereas Kuno's hypersthenic series falls within the medium-Fe field. Although it is not my purpose here to pursue petrogenetic aspects governing the diversity of these suites, it is worth noting that among possible interpretations of the clustering of some of the Honshu data in the medium-Fe field are that it results from phenocryst (plagioclase, clino- and orthopyroxene) accumulation and/or mixing processes, fractionation at higher pressures and/or  $\text{H}_2\text{O}$  contents (e.g. Grove *et al.*, 1982). Usage of the names pigeonitic and hypersthenic



**Fig. 3.** Bulk-rock compositions from the volcanic front of the NE Honshu (Japan) arc (○) and Thingmuli volcano in Iceland from Carmichael (1964) (■) projected in terms of  $\text{FeO}^*/\text{MgO}$  vs wt %  $\text{SiO}_2$  (major oxides, volatile-free, normalized to 100% totals). The discriminant boundary (fine line) between tholeiitic and calcalkalic (italicized) suites is from Miyashiro (1974). Coordinates for the proposed discriminant boundaries (bold lines) between low-, medium-, and high-Fe suites in  $\text{FeO}^*/\text{MgO}$  vs wt %  $\text{SiO}_2$  space are:

wt % $\text{SiO}_2$	50	52.5	55	57.5	60	62.5	65	67.5	70
$\text{FeO}^*/\text{MgO}_{\text{high-medium}}$	1.20	2.25	2.85	3.32	3.67	3.95	4.24	4.50	4.80
$\text{FeO}^*/\text{MgO}_{\text{medium-low}}$	0.90	1.30	1.65	1.90	2.20	2.40	2.65	2.85	3.00

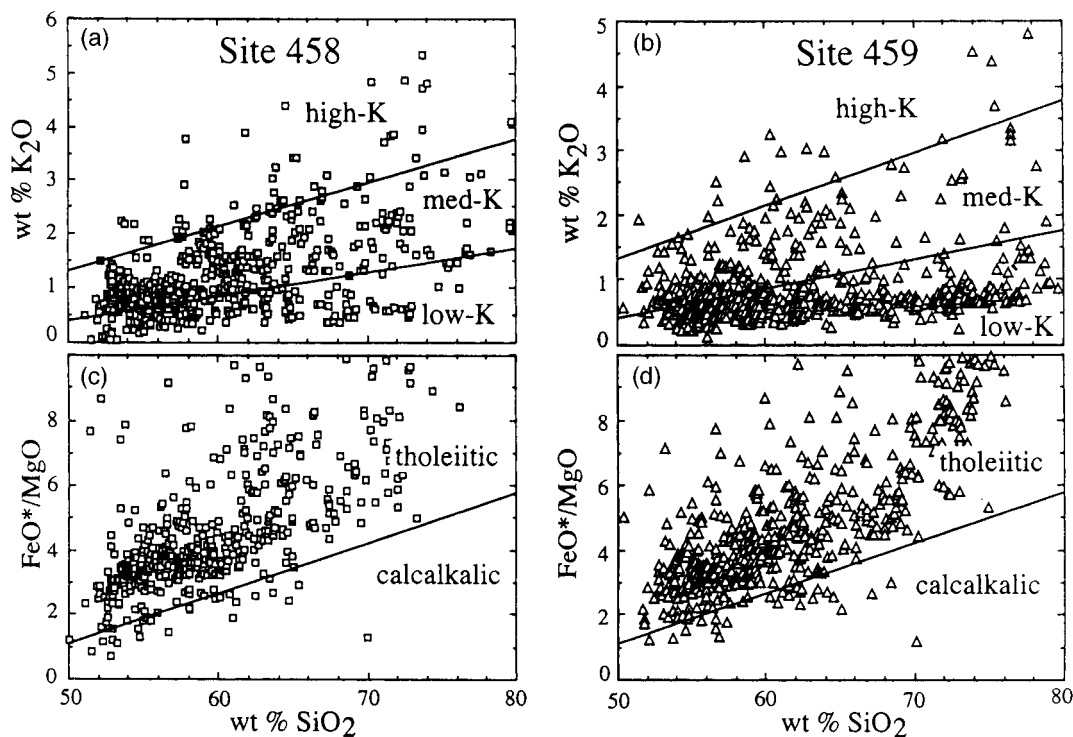
Third-order polynomial and logarithmic best-fit curves through these coordinates for the high-medium and medium-low discriminant boundaries, respectively, within the ranges of 50–70 wt %  $\text{SiO}_2$  ( $S$ ) are:  $\text{FeO}^*/\text{MgO} = -154.45 + 7.2672S - 0.11245S^2 + 0.000587S^3$ , and  $\text{FeO}^*/\text{MgO} = -23.255 + 14.277 \log S$ , with correlation coefficients of 0.99945 and 0.9966, respectively.

has not been globally useful because of the paucity or absence of the latter phase from many arc suites. In the case of Mt. Fuji [dominated by basaltic lavas erupted from a recharged-tapped-fractionated magma chamber (Arculus *et al.*, 1991)], Miyashiro's original boundary between calcalkalic and tholeiitic is transgressed, with the more evolved lavas being tholeiitic and the lower  $\text{FeO}^*/\text{MgO}$  (i.e. more primitive) lavas being classified as calcalkalic. The compositional spread of the basaltic lavas of Klyuchevskoy (the world's most active island arc volcano) is similar (Kersting & Arculus, 1994).

In fact, there is accumulating evidence for the importance of selective crystal accumulation in island arc lavas and deviation of the major element compositions of these rocks from genuine melts (Crawford *et al.*, 1987). One of the consequences of the delayed appearance of plagioclase in relatively  $\text{H}_2\text{O}$ -rich magmas is the consequent enrichment in alkalis and alumina in the residual melts, and the formation of genuinely high-Al liquids. However, the absolute degree of

alumina enrichment in hydrous arc suites may have been overestimated based on analyses of porphyritic rock samples, and we should be careful of equating high-Al with calcalkalic. For example, studies of glass shards in arc-derived ash layers (recovered by deep-sea drilling), which represent the genuine liquid line of descent, uncompromised by crystal accumulation (Arculus *et al.*, 1995), have demonstrated the following (Fig. 4) for the Mariana arc:

- (1) whereas the compositional spread of lavas erupted through the Tertiary-Quaternary from this arc system straddles the calcalkaline-tholeiitic boundary of Miyashiro (1974), the vast majority (excluding Eocene boninitic samples) of the glasses are tholeiitic in character;
- (2) most of the glass compositions span the range from low to medium K, with a few high-K glasses. The majority of the medium-K glasses are also tholeiitic, demonstrating the non-equivalence of 'medium-K = calcalkaline';



**Fig. 4.** Plots of wt %  $K_2O$  and  $FeO^*/MgO$  vs wt %  $SiO_2$  for individual glass shard compositions (determined by electron microprobe analysis; Arculus *et al.*, 1995) recovered in the Mariana forearc (Deep Sea Drilling Project Sites 458 and 459), sourced from Tertiary–Quaternary arc eruptions. Discriminant boundaries in (a) and (b) are from Gill (1981) and in (c) and (d) from Miyashiro (1974). It should be noted that for both Sites, there is no coupled relationship between the  $K_2O$  contents and the  $FeO^*/MgO$  as a function of wt %  $SiO_2$ , wherein med-K samples by the Gill (1981) criterion are automatically calcalkalic by the Miyashiro (1974) discriminant.

- (3) in the case of the Mariana arc (and in fact, also the Izu–Bonin and Kurile–Kamchatka systems), the overwhelming majority of glasses in the basalt to rhyolite compositional range have  $<17$  wt %  $Al_2O_3$ . In contrast, wt %  $Al_2O_3$  ranges up to 20% (or more) in the lavas, and many of these appear to be enriched in plagioclase phenocrysts (see also Crawford *et al.*, 1987).

## SUMMARY

The present application of the terms calcalkaline and calcalkalic is plagued with inconsistency, with the terms having different meanings for different users. Unfortunately, the terms are used for a variety of geochemical characteristics that are not necessarily correlated, and typically have no relationship with ‘calc’ or ‘alkaline’ character. Given the association in many geologists’ minds of calcalkaline rock suites with active or ancient subduction zones, we are also liable to erroneously assert the former existence of tectonic environments on the basis of mistaken rock suite labelling and classifications. Recognizing the importance of

the degree of  $FeO^*/MgO$  enrichment with  $SiO_2$  concentration in evolving subalkaline magma series, probably reflecting the critical effects of  $f_{O_2}$  variations and  $H_2O$  contents, I suggest we use labels that explicitly acknowledge the variability of  $FeO^*/MgO$  (in addition to the spread of  $K_2O$  contents) as a function of  $SiO_2$  content in our defining terminology. Furthermore, we should reserve the terms calcalkaline and calcalkalic solely for those suites that conform to Peacock’s (1931) discriminants.

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