

## Dry peralkaline felsic liquids and carbon dioxide flux through the Kenya rift zone

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**Preamble**—When Hat Yoder was in London to receive the Wollaston Medal of the Geological Society the chance arose for him to see the Michaelangelo Tondo in the Royal Academy. His reaction, naturally, was to marvel that such beauty could be wrought from stone. Along with other participants at the meeting we pay tribute to Hat, who in his own way has continually given petrologists new perceptions of rocks.

**Abstract**—Around Lake Naivasha, at the topographic culmination of the Kenya rift, a wide range of peralkaline felsic magmas erupted in the Holocene. Glassy samples are abundant. Volcanological and petrographic evidence indicates that these glasses reflect characteristically low concentrations of H<sub>2</sub>O in the melts, and this relationship is confirmed by experimental and chemical information.

Distinct magma types, trachytes, comendites and pantellerites, erupted almost exclusively from different centres, even though these are sufficiently close for intercalation of the erupted products from adjacent volcanoes. This individuality is maintained in chemical variation diagrams where the products from different centres form separate groups, with no gradational compositions. In some diagrams smaller clusters appear within the main groups. These distinctive patterns indicate that there is no continuous evolution of the melts below the rift, and that each centre represents the outpouring of a different melt. Batches within the same centre could also represent different episodes of melt generation.

Generation of these melts in a *regional* context can best be explained by melting of different sources during the influx of a CO<sub>2</sub>-rich fluid. Trachytes, pantellerites and comendites could then be the products of a flux/melting cycle as it climbs progressively through mantle, mafic deep crust, and sialic crust. The high concentrations of sodium and iron in the melts call for enhancement of these elements in the source rocks: this could be achieved by regional metasomatism resulting from prolonged activity through the rift segment over the past 23 Ma. Incompatible trace element variations cannot be attributed to solid-melt interactions but could be imparted by the fluid during melting.

### INTRODUCTION

FOR A VARIETY of reasons alkaline rocks have always held a fascination for igneous petrologists, but in recent years have assumed extra significance as it has emerged that their richness in incompatible elements and radio-isotopes are signalling special conditions of source, or melt-forming processes, or both. In most alkaline provinces peralkalinity has developed in varying degrees. Paradoxically, peralkalinity is strongest when magma penetrates continental lithosphere, where the crustal rocks are typically peraluminous. Such magmatism is especially evident in stable plate interiors where igneous activity of any kind must call for special explanation. Even where eruption is localised by an evident split in the lithosphere, there is still no ready explanation of why, for instance, continental fissuring may give vent to tholeiite floods in one region or epoch, and alkaline magmatism in another.

Aphyric volcanic glasses provide the closest samples to the composition of peralkaline melts, where it is clear that crystallisation, and indeed devitrification or hydration, leads notably to alkali and halogen losses (NOBLE *et al.*, 1967; MACDONALD and BAILEY, 1973). Glasses may also provide extra insight into the gases associated with strongly alkaline volcanism. This information is of value because the only direct, high temperature volcanic gas collection available is from the melilite nephelinite volcano of Mount Nyiragongo (CHAIGNEAU *et al.*, 1960): no direct, high temperature collections have been made of an oversaturated peralkaline volcano. The aim here is to examine and explore the potential information content of a range of oversaturated volcanic glasses from the central part of Kenya (Gregory) rift valley. All the samples are fresh, unaltered glasses; most are obsidians in which phenocrysts are absent or less than 2 percent in the mode; vesicles, if present, are widely sepa-

rated. Pumice samples are excluded because of their susceptibility to post-eruptive hydration and alteration.

#### INTRINSIC H<sub>2</sub>O CONTENTS OF PERALKALINE GLASSES

With one exception all peralkaline glass analyses in the compilation by MACDONALD and BAILEY (1973) have H<sub>2</sub>O<sup>+</sup> contents of 0.67 weight percent or less. Many more analyses (published and unpublished) have since been added (BAILEY, 1978; 1980) and it is clear that the vast bulk of the H<sub>2</sub>O<sup>+</sup> values are around the limit of detection (~0.1 weight percent): hence, most glasses are virtually anhydrous. These data are in complete accord with the case put forward earlier by NICHOLLS and CARMICHAEL (1969) that oversaturated peralkaline liquids are essentially dry. Other studies (see EWART, 1979) seem to indicate consistently low  $f_{O_2}$  and high temperatures in calc-alkaline rhyolites and dacites, which would be in keeping with the generally low H<sub>2</sub>O<sup>+</sup> values in the glasses. Recently, however, TAYLOR *et al.* (1983) have reported H<sub>2</sub>O contents up to 3.1 weight percent in fresh calc-alkaline rhyolite tephra, leading to the suggestion that these are the general levels in such melts, and that glasses with low H<sub>2</sub>O are degassed. They propose that the main degassing of the melt takes place during foaming within the vent, so that later flows and domes with low H<sub>2</sub>O represent extrusion of the collapsed foam. They report that there appear to be no differences in the compositions of the calc-alkaline glasses except for H<sub>2</sub>O<sup>+</sup> and deuterium contents. In view of the manifest compositional changes in peralkaline glasses during devitrification and hydration, and during high temperature fusion experiments (HAMPTON and BAILEY, 1985), any massive loss of several percent H<sub>2</sub>O from a high temperature peralkaline melt would render the consequent anhydrous glass suspect as a sample of the natural melt composition. It is essential, therefore, to examine the evidence with this in mind before considering the chemical variations among the glasses from the Kenya rift province.

#### *General relationships and field evidence*

The case presented here is part of a continuing study of alkaline glasses, encompassing the widest possible range of bulk compositions and samples from all regions and all different modes of eruption. The following list outlines the range and scope.

(1) Bulk compositions range from nephelinite through phonolite to comendite, *i.e.*, the maximum range of silica values.

(2) Samples are from all geographic and tectonic settings.

(3) Wide variations in vesicularity, and in phenocryst types and contents, are represented.

(4) Eruptive mode varies widely. Samples come from flow margins (top and bottom); flow interiors; angular blocks in agglomerate; angular fragments in pumice deposits; fiamme from welded ash flows; splatter; and agglutinated spatter.

Significantly, tephra fragments ranging from small chips in pumice deposits to large blocks in agglomerates are all low in H<sub>2</sub>O<sup>+</sup>; there is no evidence of high speed ejectamenta that could represent an H<sub>2</sub>O-rich melt.

#### *Experimental crystallisation and comparative petrography*

In marked contrast with calc-alkaline rhyolites, which fail to crystallise in the laboratory when dry, pantellerite glasses start to crystallise in as little as thirty minutes at appropriate temperatures without addition of water. Experimental study of the melting and crystallisation of peralkaline glasses under a range of conditions is, therefore, possible (COOPER, 1975; BAILEY and COOPER, 1978) with results as shown in Figure 1. Details of the experimental conditions and the phases developed were given in BAILEY and COOPER (1978), which also contains a discussion of the consequences of the contrasting behaviour of wet and dry pantellerite melts. Relevant points from this discussion are summarised below.

(1) The exsolution of vapour under near-liquidus conditions in the dry experiments (Figure 1) indicates that some natural volatiles were quenched in at partial pressures at least as high as 0.3 kbar. A synthetic rhyolite melt would contain 2.5 weight percent of H<sub>2</sub>O at an equivalent pressure (LUTH, 1976). Addition of H<sub>2</sub>O to the natural pantellerite profoundly changes the melting behaviour indicating that it is capable of dissolving a similar quantity of H<sub>2</sub>O at 0.3 kbar. As H<sub>2</sub>O is one of the most soluble gases in silicate melts it hardly seems credible that a pantellerite melt could lose 2–3 weight percent H<sub>2</sub>O whilst effectively retaining other gases at 0.3 kbar solubility levels. Hence, although there must have been some degassing from some samples (in decompression) this gas was not simply H<sub>2</sub>O.

(2) Crystallisation of an H<sub>2</sub>O-rich pantellerite results in acmitic pyroxenes and potassic feldspars quite different from those observed as natural phenocrysts, and in the wrong sequence.

(3) Kenyan obsidians with modal phenocryst

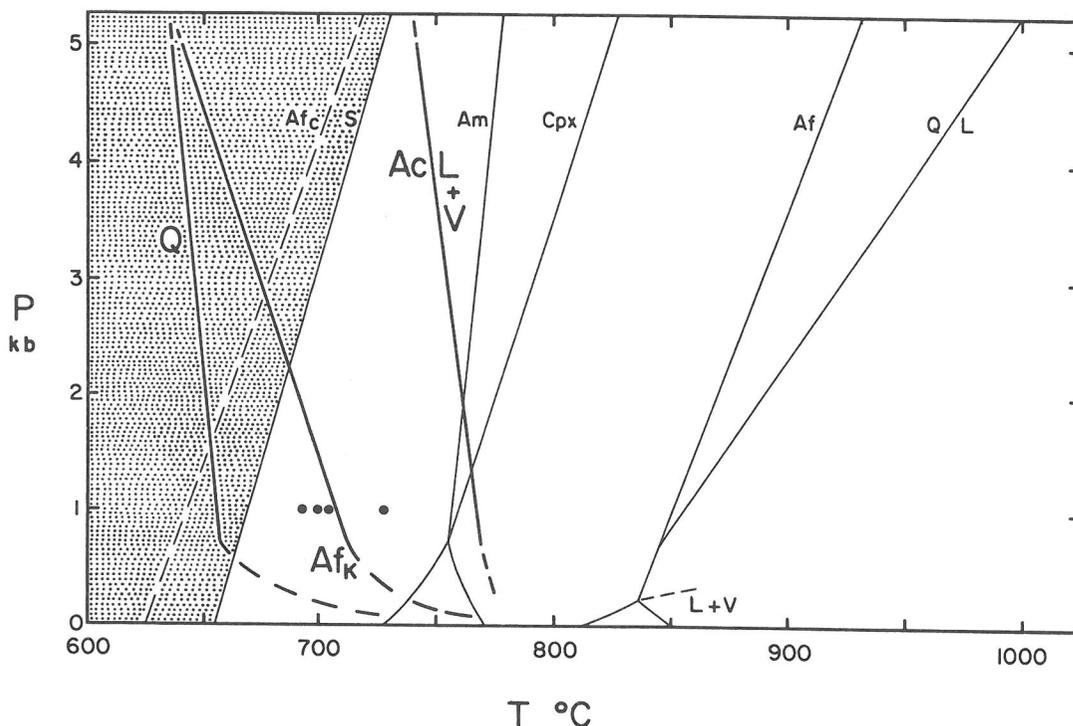


FIG. 1. Comparison of hydrous and anhydrous crystallisation of a pantellerite obsidian (sample KE12; Eburru, Kenya). Hydrous boundaries, heavy lines; anhydrous boundaries, light. The dry sub-solidus region is shaded. V = fluid, L = liquid; Q = quartz; Af = alkali feldspar; Af<sub>K</sub> = K-rich alkali feldspar; Af<sub>c</sub> = alkali feldspar critical line (LUTH, 1976); Cpx = sodic hedenbergite; Am = arfvedsonitic amphibole; Ac = acmitic pyroxene; S = dry solidus. The points shown at 1 kbar are the range of liquidus minima (quartz + feldspar + liquid) in related synthetic systems at  $P_{H_2O} = 1$  kbar (CARMICHAEL and MACKENZIE, 1963; THOMPSON and MACKENZIE, 1967). Taken from BAILEY and COOPER (1978).

contents greater than 5% are rare: most have less than 2% and, hence, have a near-liquidus aspect. This characteristic, combined with low  $H_2O^+$  contents, effectively rules out an origin from a magma at, or below, the  $H_2O$ -saturated liquidus in Figure 1. Firstly, the large differences in temperature between the wet and dry systems, require that sub-volcanic degassing of any wet pantellerite magma should have been accompanied by extensive crystallisation. Secondly, the negative slopes of the phase field boundaries in the wet system would imply that any wet pantellerite magma at depth could get to the surface only as a pyroclastic eruption composed of  $H_2O$ -saturated glass, or as degassed crystalline lava.

If pantelleritic melts ever were wet at depth then some special conditions of eruption would be called for to account for the dry, near-liquidus aspect of the glasses. Suppose the original melt had previously contained as much as 3 weight percent  $H_2O$  (e.g.,

approximately saturated at 2 km depth) and had somehow lost  $H_2O$  at a lower pressure. To achieve a dry near-liquidus condition its required starting temperature would be at least  $50^\circ C$  above the wet liquidus. Alternatively, it might have risen towards the surface from a point on a 3 weight percent  $H_2O$  liquidus, requiring a starting pressure of greater than 5 kbar. To make the transition from wet to dry melt therefore would seem to require an unusual eruption or thermal history. Non-systematic (various) variation within the sample population would be expected in  $H_2O$  contents, oxidation states, alkalis and halogens. Furthermore, when crystals are present, at least some should carry a record of this eruption history. In fact, they are remarkably consistent in composition (NICHOLLS and CARMICHAEL, 1969; SUTHERLAND, 1974) even to the extent of showing scarcely any sign of zoning in the feldspars, the dominant phenocryst phase.

Peralkaline glasses are still puzzling in the light of their laboratory behaviour. Dry pantellerite held

just above its solidus temperature for about an hour starts to crystallise; if taken to the liquidus temperature it bubbles. But both these states seem to have been largely missed out in the cooling of natural glass samples. In order to preserve such a glass it must somehow pass through the vesiculation and crystallisation temperature range (below about 700°C at low pressure) in a short time. Whereas this cooling history can be envisaged for particular instances such as flow margins, it is less easy in other cases. Glass clasts in pumice deposits are typically non-vesicular, non-porphyrific and *angular*. Hence, they were “through” this temperature range before incorporation in the pumice eruption. Our experiments with gas extraction indicate that foaming is a near-liquidus phenomenon (HAMPTON and BAILEY, 1984). It is difficult, therefore, to see how the obsidian clasts could have come from the part of the melt that was foaming. If they are chilled melt from the border zone of the foaming mass they should presumably record the highest H<sub>2</sub>O contents available for peralkaline liquids.

Glass fiamme in welded ash flows also pose problems if, as suggested by TAYLOR *et al.* (1983), they “remain at magmatic temperatures for weeks or months”. According to our experiments pantellerite fiamme could not survive as glass under such conditions. Almost wholly glassy flows and domes are also extruded from peralkaline silicic volcanoes and must pose similar problems. There is a need for some means of super-cooling peralkaline melts prior to eruption such that the viscosity is sufficiently high to inhibit crystallisation and bubbling, but flow is permitted.

#### *Chemical variations and H<sub>2</sub>O<sup>+</sup> levels*

If peralkaline magmas have previously contained several percent H<sub>2</sub>O, they must clearly have suffered massive vapour loss prior to glass formation. This must leave its mark on the melt composition, as other volatile species should be partitioned into the vapour. In high-temperature, gas extractions from glasses in the laboratory, H<sub>2</sub>O is always accompanied by other species, either in the form of gases, or precipitated as sublimates. Most typically, the high-temperature sublimates include alkali halides (HAMPTON and BAILEY, 1985). These products mirror those observed at high temperature fumaroles on volcanoes. Similarly UNNI and SCHILLING (1978) have recorded that concentrations of Cl and H<sub>2</sub>O in submarine basalts correlate with ocean depth, and are dependent on degree of vesiculation and loss of vapour on eruption at different pressures. In contrast to these observations, peralkaline silicic

obsidians show no correlation between H<sub>2</sub>O and Cl (Figure 2). In fact, no correlation between H<sub>2</sub>O and any other variable has been found in these rocks, certainly not with alkalis and halogens where it might be most expected. Present evidence offers no case for massive sub-volcanic loss of water-rich vapour from peralkaline melts. The low and variable H<sub>2</sub>O levels in the glasses may be essentially “accidental”, *i.e.*, unrelated to the melt generation process. On this basis it is appropriate to treat the glasses as melt samples, in an attempt to unravel their chemical relationships and try to discern their petrogenesis.

#### PERALKALINE VOLCANOES IN THE CENTRAL KENYA RIFT

Volcanism has been active along the Kenya rift for the past 23 Ma, ranging from carbonatites and nephelinites to rhyolites. Felsic rocks constitute about half the total erupted volume, about 150,000 km<sup>3</sup> (WILLIAMS, 1982). The bulk of the Tertiary-Recent felsic rocks are peralkaline making it the most voluminous and variegated peralkaline province in the world. Holocene activity in the central part of the rift, around its topographic culmination in the vicinity of Lake Naivasha, has been largely expressed by felsic central volcanoes on the rift floor. Figure 3 shows the largely monotonic magma compositions emitted from the main centres. Eruptives from adjacent centres may interfinger around the margins, but are always petrographically distinct. The general geology around Lake Naivasha has been described by THOMPSON and DODSON (1963), and there have been individual descriptions of Suswa (JOHNSON, 1969); Longonot (SCOTT, 1980); and

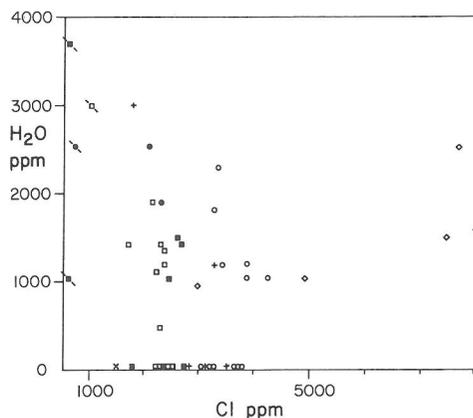


FIG. 2. Variation of Cl with H<sub>2</sub>O in oversaturated peralkaline glasses. Diamonds indicate samples from Pantelleria, all other samples from the Kenya rift (for details see Figure 4).

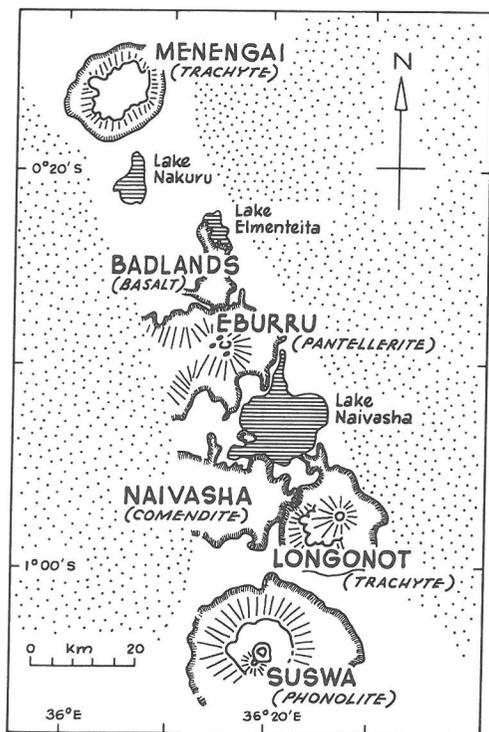


FIG. 3. Sketch map showing the chief Holocene volcanic centres in the Lake Naivasha section of the Kenya rift. Rift shoulders indicated by stipple.

south west Naivasha (MACDONALD *et al.*, 1986). In addition to the felsic volcanoes, there is a small basalt field forming the Badlands, north east of Eburru (MCCALL, 1957). Small basalt cones pepper the fringes of the comendite field of south west Naivasha, and mixed basalt/felsic lavas have been erupted from Longonot (SCOTT and BAILEY, 1984) and Eburru. North of the Badlands the next major central volcano is Menengai, erupting only trachyte (LEAT, 1984).

Lake Naivasha is located on the crest of the classic continental rift valley first described by GREGORY (1894) and its volcanism has a special place in igneous petrogenesis. Many of the lavas used by BOWEN (1937) to illustrate his concept of Petrogeny's Residua System (nepheline-kalsilite-silica) were from this region. The Holocene volcanism around Lake Naivasha is an almost perfect case for a petrographic province, fulfilling all the criteria laid down by WILCOX (1979).

The Lake Naivasha region has the added advantage that glassy samples, covering most of the range of oversaturated peralkaline compositions are abundant. The first pantelleritic trachyte glasses were recognised at Menengai and Longonot

(MCCALL, 1967; MACDONALD *et al.*, 1970), and the East African rift valley has so far provided the only samples of this melt. Trachyte glasses having clear chemical affinities with comendites are absent.

The extent and persistence of peralkaline activity through the East African lithosphere make it imperative to look for the causes, and the wide range of geology and sample compositions offer hope for eventual solutions to the questions of petrogenesis. It is appropriate first to look at chemical variations in the glasses with changing levels of peralkalinity.

#### *Major element variations with peralkalinity*

Some distinctions are seen immediately. For instance, the comendites from south west Naivasha separate from the pantellerites and the pantelleritic trachytes in terms of  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{FeO}$ ,  $\text{MnO}$  and total iron (Figures 4 and 6). They also appear as a distinct group on most other variation diagrams. Like all other continental comendites, they appear to fall close to the quartz-feldspar cotectic, as extended into the peralkaline region (BAILEY and MACDONALD, 1970, Figure 5; MACDONALD *et al.*, 1986, Figure 7), with the implication that the source contained free quartz. This characteristic, together with many other features of their major element composition would be most obviously satisfied by a crustal or sialic source (BAILEY and MACDONALD, 1970) and more detailed studies on trace elements and isotopes are consistent with this interpretation (MACDONALD *et al.*, 1986; DAVIES and MACDONALD, 1986).

Figure 4 also reveals separate clustering of trachytes and pantellerites, which persists in  $\text{Al}_2\text{O}_3$  (Figure 5). As might be anticipated, there is a general negative correlation between alumina and peralkalinity, but the comendites, pantellerites and trachytes form separate groups. This separation is emphasized when molecular  $\text{Al}_2\text{O}_3$  is plotted; the comendites and pantellerites appear to define one trend, while the trachytes form parallel trends at higher levels. This feature might be taken to reflect different series of liquids with various levels of silica, but it is noteworthy that trachyte liquids show no direct connection with rhyolites.

Just as it might be anticipated that  $\text{Al}_2\text{O}_3$  would correlate negatively with peralkalinity, so a positive correlation might be expected for the alkalis (Figure 5). In comendites and pantellerites,  $\text{K}_2\text{O}$  is almost constant around 4.4 weight percent, but there are signs of slight negative distributions, which are emphasised when the trachytes are taken into account. The general fall in  $\text{K}_2\text{O}$  levels with increasing peralkalinity may be linked in some way to the "or-

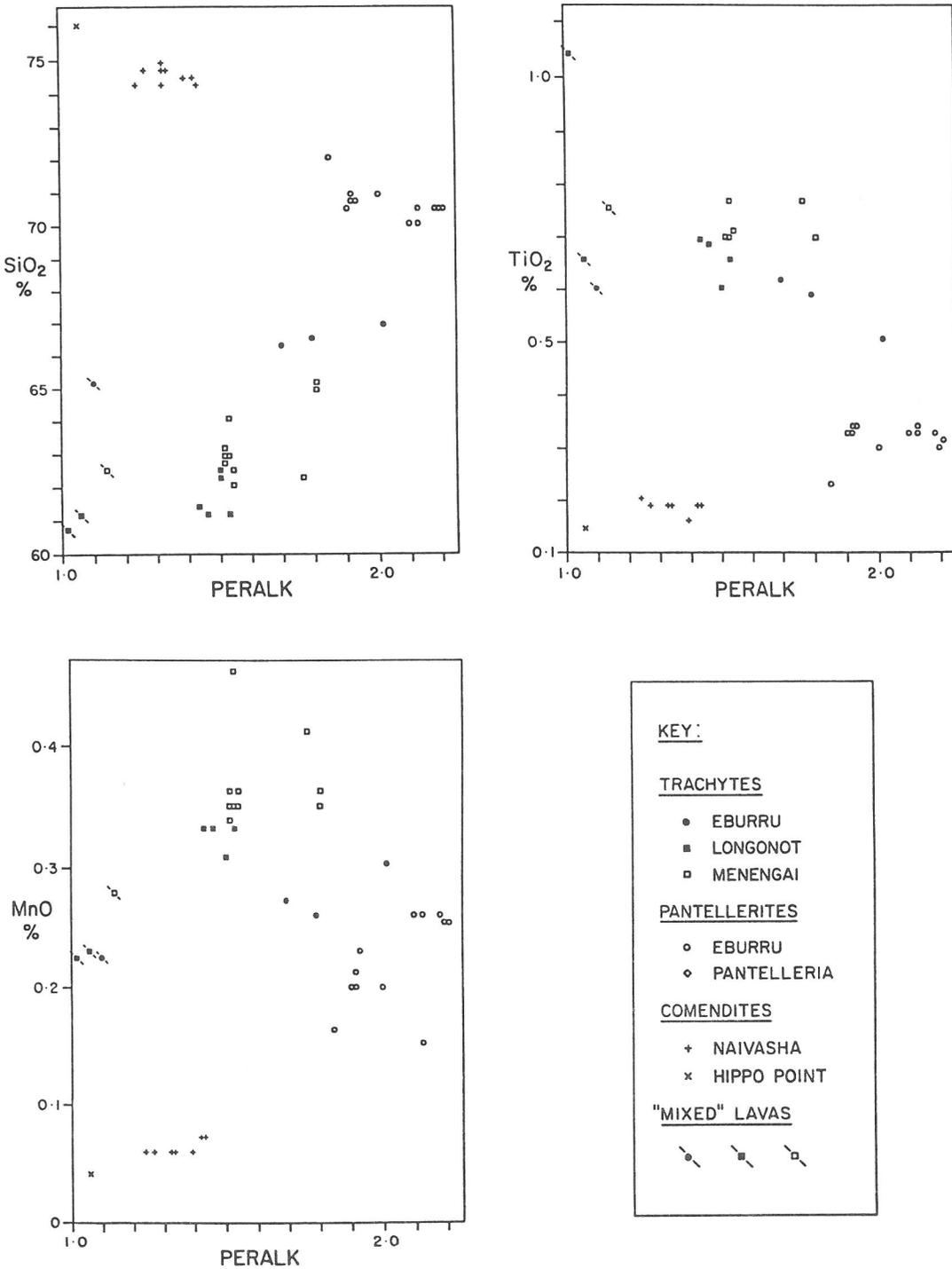


FIG. 4. Variations of SiO<sub>2</sub>, TiO<sub>2</sub>, and MnO with peralkalinity [Mol (Na<sub>2</sub>O + K<sub>2</sub>O)/Al<sub>2</sub>O<sub>3</sub>] in glassy samples from the Naivasha region. Plus signs, comendites from the main Naivasha field; cross, indicates tight group of comendites from the Hippo Point area on Lake Naivasha; open circles, pantellerites, closed circles, trachytic pantellerites from Eburru; filled squares, trachytes from Longonot; open squares, trachytes from Menengai; symbols with diagonal line indicate mixed lavas (possibly accumultic in the case of Menengai).

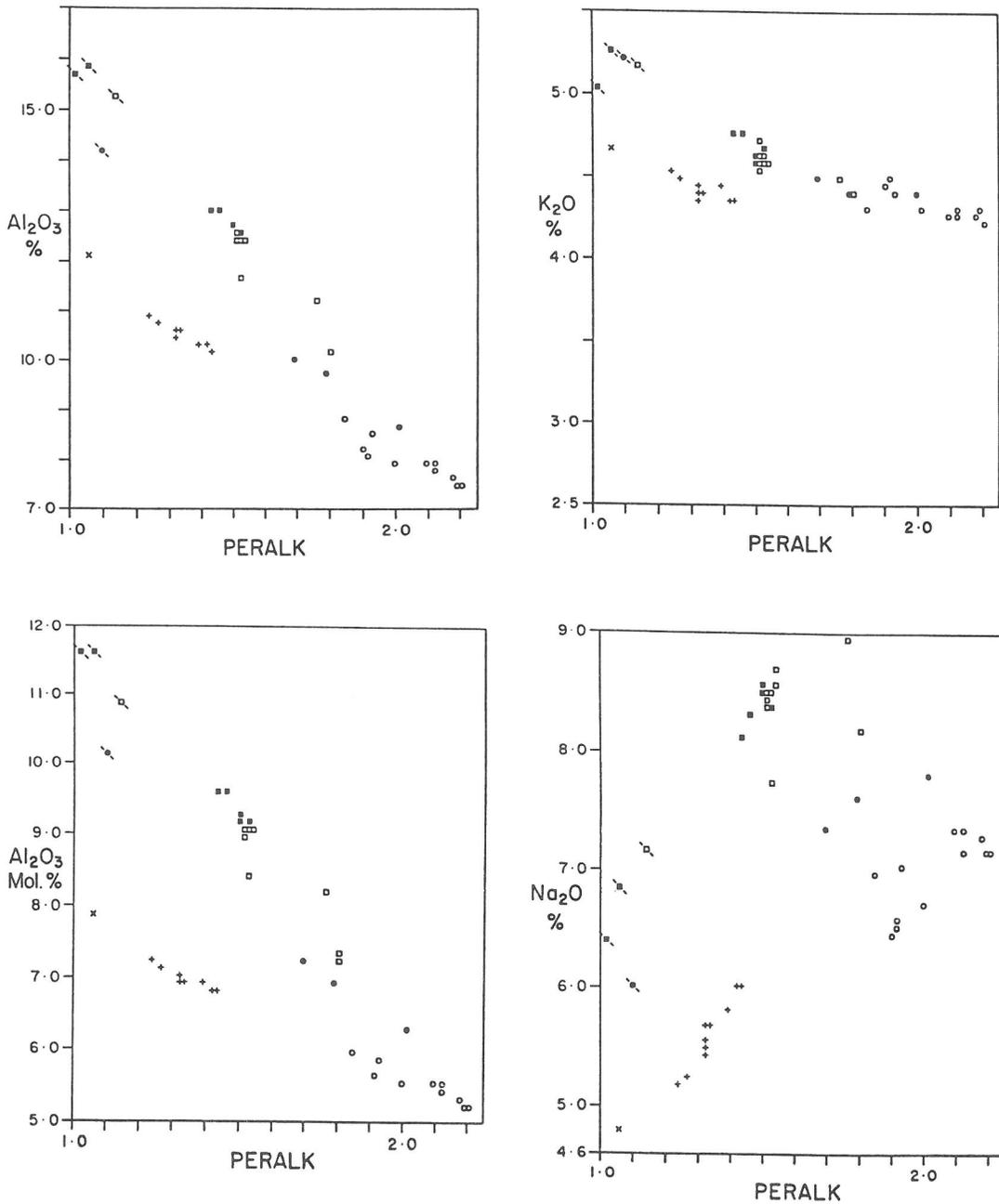


FIG. 5. Variations of  $\text{Al}_2\text{O}_3$  (weight percent and mol percent),  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  with peralkalinity. Mol percent  $\text{Al}_2\text{O}_3$  can be used as an indication of variation in potential feldspar in the samples. Symbols as in Figure 4.

thoclase effect" (BAILEY and SCHAIRER, 1964) whereby alkali feldspars tend to be richer in  $\text{K}_2\text{O}$  than their coexisting melts. It is not easy, however, to reconcile the relatively constant  $\text{K}_2\text{O}$  in the comendites and the pantellerites with this effect if indeed

they represent series of liquids controlled by closed-system fractionation.

An even more striking pattern emerges for  $\text{Na}_2\text{O}$  (Figure 5). Trachytes from Longonot and Eburru fall on quite separate positive trends, which them-

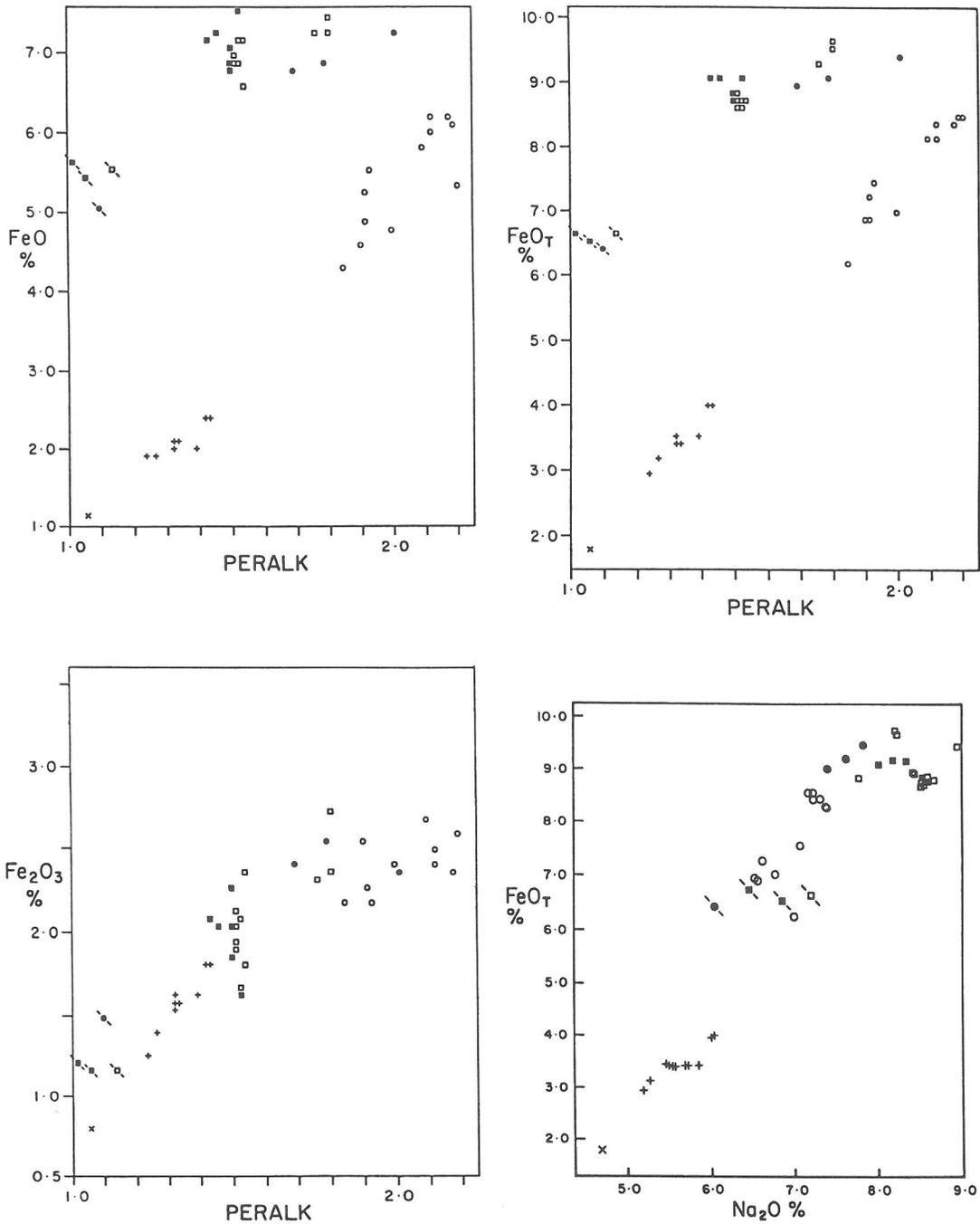


FIG. 6. Variations of soda and iron for Kenyan glasses. Symbols as in Figure 4.

selves are distinct from the distributions of pantellerites and comendites. This emphasizes the distinctions seen in  $\text{Al}_2\text{O}_3$  and is mirrored by variation in other major elements, particularly FeO and total iron (Figure 6). Discrete populations of liquids are

identified, some of which have been erupted even from the same volcano (Eburru). Within any series there is a general positive correlation between  $\text{Na}_2\text{O}$  and total iron, which may reflect some internal consistency in melt generation within that series,

but the separation of the series, especially trachytes from rhyolites, would seem to require generation at least in distinct batches. Increasing soda correlates with iron content, and *within* each group with peralkalinity. Between trachytes and pantellerites, however, there is a broad negative distribution which seems to defy explanation in terms of interactions between melts and their observed phenocryst phases.

Where these rocks are not aphyric, the ubiquitous phenocryst is alkali feldspar, and the bulk compositions of the melts require that this phase must dominate in any crystallisation sequence. Separation of potassic feldspar from the trachytic liquids must lead to increasing sodicity beyond that actually observed in the pantellerites (MACDONALD *et al.*, 1970). Therefore, *if* these liquids were linked in a crystallisation sequence, a sodic phase was removed from the magma system as crystallisation progressed: no appropriate composition appears as a phenocryst in the trachytes.

The distribution of soda and iron (Figures 5 and 6), confirm the earlier suspicion that there is no chemical continuum between trachytes and pantellerites, and that they developed under different conditions. Pantellerite may represent a quartz-feldspar cotectic composition for a specific range of source rock compositions and pressures. At higher pressures (and in different source compositions?) the cotectic melt is closer to trachyte, as with increasing pressure in the "granite system" (TUTTLE and BOWEN, 1958). The special requirement in the "pantellerite system" would be that there is a phase boundary (marking the appearance of a phase rich in soda and iron) imposing a limit on the peralkalinity of the liquid that can be reached at any given pressure (see BAILEY, 1974).

A plot of  $\text{Fe}_2\text{O}_3$  vs peralkalinity (Figure 6) reveals a steady progression through the comendites that could reflect an increasing contribution of acmite to the melts. There is no such regular variation of ferric iron and peralkalinity in the trachytes or pantellerites, and the latter appear to mark a "ceiling" in the possible levels of  $\text{Fe}_2\text{O}_3$  in peralkaline melts. As the trachytes also have more iron than comendites or pantellerites, it is not possible to appeal simply to an acmitic component to account for the  $\text{Fe}_2\text{O}_3$  variations in this part of the array. Melting of a source containing a combination of phases similar to the observed phenocrysts (feldspar, fayalite, sodic hedenbergite, aenigmatite, and oxide) could produce the trachytes. As discussed later, pantellerite melt generation may need to involve an arfvedsonitic amphibole in addition.

Formation of these peralkaline trachyte and

pantellerite liquids seems to require melting of appropriate source compositions. This is indicated by the marked composition gaps, which have persisted despite intensive sampling, and must depict a real distribution of natural melts. The gaps must militate also against generation of trachytes and pantellerites by progressive melting of a single source. The separation of the trachytes from Longonot, Menengai and Eburru in various diagrams also renders unlikely the possibility of fractional melting at separate trachyte and rhyolite invariant points, for which there is no experimental evidence in any case. The separation of trachytic and pantelleritic liquids is further emphasized by the fact that in many diagrams the variations within the groups run *across* any expected trend from trachyte to pantellerite (Figure 4, 5 and 6). Further discussion of the questions of melt generation is best deferred until trace element variations have been examined.

#### *Trace element versus major element functions*

When variation in incompatible trace element concentrations is compared with peralkalinity the patterns are different (Figure 7). The main Naivasha comendites show a positive variation, but no other simple relationship emerges between trace elements and peralkalinity. Patterns in the trachytes are not well defined but some signs of positive trends may be detected within groups. The pantellerites, however, are scattered, with the highest levels of incompatible elements near the lowest levels of peralkalinity. Essentially, the trachytes, pantellerites and comendites form separate populations (c.f., the major element data), but distributions within groups are hinting at further differences between them. One major difference becomes clear when traces are compared with soda and iron. For the comendites there is a positive correlation of trace elements with  $\text{Na}_2\text{O}$ , but in the pantellerites the broad distribution is negative (Figure 8). Because FeO and  $\text{FeO}_T$  correlate positively with  $\text{Na}_2\text{O}$ , their relationships with trace elements are similar. What also emerges in Figure 8 is distinct clustering of different parts of the pantellerite population.

#### *Variations between trace elements*

Trace element correlations are much stronger. The strong correlation of Zr with Rb and F that was first noted for Eburru pantellerites (BAILEY and MACDONALD, 1975) appears in all groups of liquids even though they may separate from each other in the diagrams (Figure 9). This relationship has been found also in sample suites from the Azores and from Pantelleria (BAILEY, unpubl.).

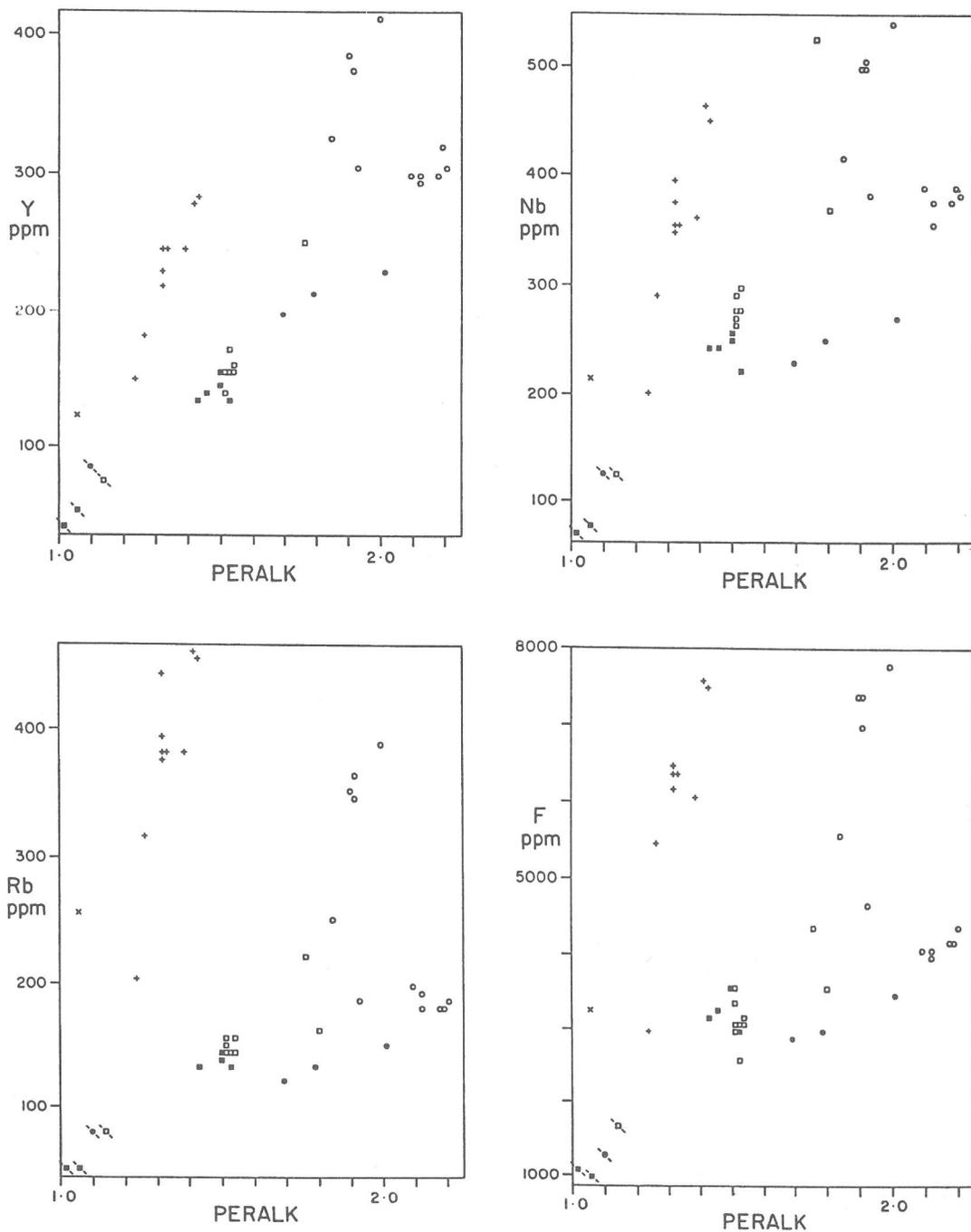


FIG. 7. Variations with peralkalinity for a selection of trace elements, Y, Nb, Rb and F, in Kenyan glasses. Symbols as in Figure 4.

Coherence also exists for Nb and Y through all the groups, and it had been noted previously (BAILEY and MACDONALD, 1975) that in the Eburru obsidians these two elements were more strongly correlated with Cl, as distinct from the strong co-

variance in F, Zr and Rb. When all groups of glasses are compared, the pattern of Cl distribution is less clear cut, and there is a strong suggestion in Figure 9 of decoupling of the Cl distribution from variations in the other trace elements in the higher con-

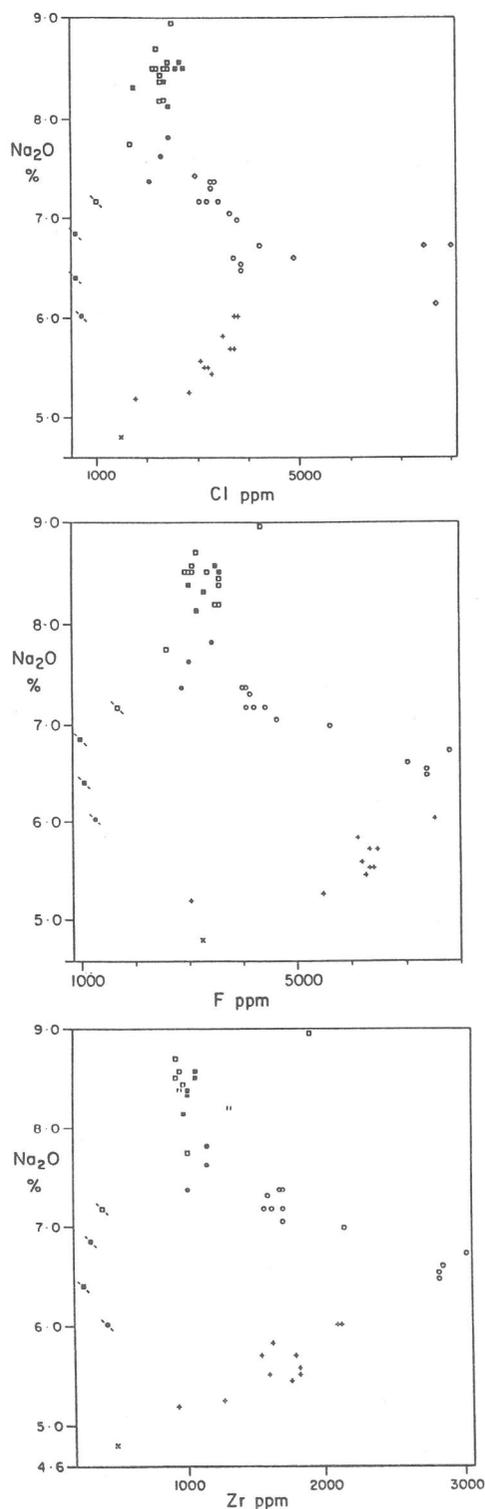


FIG. 8. Variations between different trace elements and  $\text{Na}_2\text{O}$  for peralkaline glasses from Kenya. Diamonds indicate samples from Pantelleria. Other symbols as in Figure 4.

centration ranges. There appears to be a "ceiling" for Cl in Kenyan glasses, which also shows up dramatically in the plot of  $\text{Na}_2\text{O}$  vs. Cl (Figure 8), where the negative distribution of the pantellerites and the positive distribution in the comendites appear to curve towards a common maximum. This contrasts with the  $\text{Na}_2\text{O}$  vs F diagram in which the more linear distributions might be pointing to a maximum outside the observed range. This limitation in the chlorine appears to be a regional effect because liquids from Pantelleria achieve much higher levels of Cl, describing a linear array with no obvious "ceiling" (Figures 8 and 9). The Kenyan rift liquids point to a limit in available Cl, but not F, in the source. The simple conclusion reached previously for the Eburru pantellerites that F, Zr and Rb formed one chemically coherent group, whilst Nb, Y and Cl formed another, therefore needs modification. A more reasonable conclusion would be that Zr and Rb cohere very strongly with F, whereas Nb and Y partly cohere with F, with part of their distribution connected with availability of Cl.

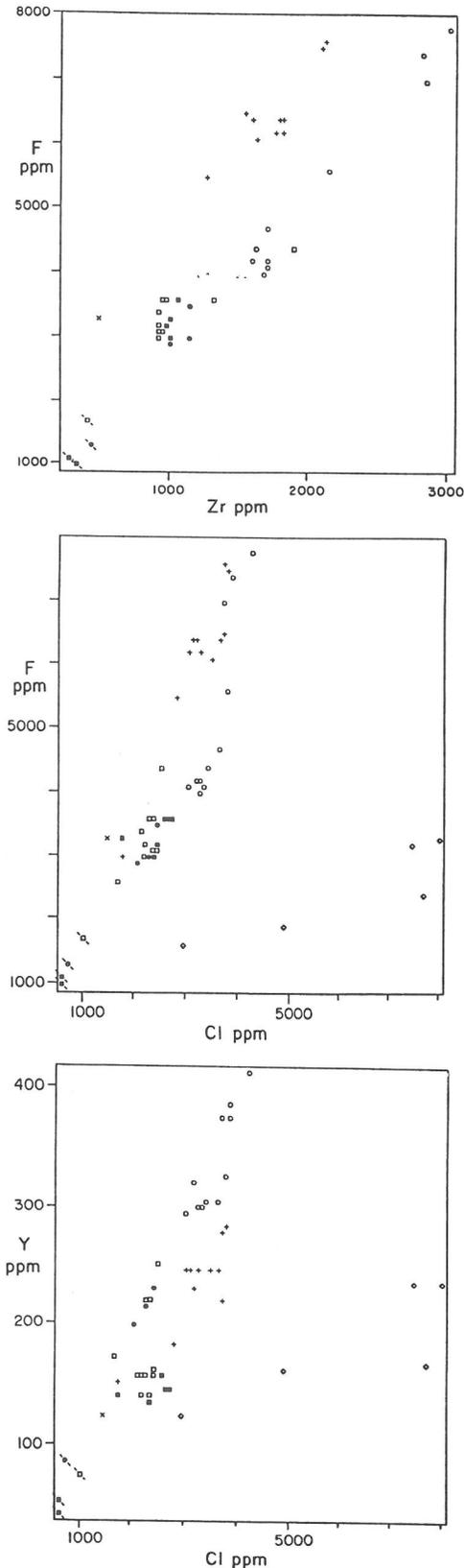
#### *Summary of the chemical distributions*

Comendites, pantellerites and trachytes form distinct populations, and for some elements, sub-groups of these populations emerge. Three recurring sub-groups in the trachytes relate directly to the source volcanoes, Menengai, Longonot and Eburru. Eburru trachytes are distinct from Eburru pantellerites in most plots. *Within* individual groups there is a general trend of increasing soda and iron with peralkalinity, with the pantellerite groups lying on the extension of the comendite trend (Figure 6). Superimposed on this, however, there is a broad negative distribution from trachyte to pantellerite. Furthermore, although incompatible elements show positive covariance *within* the groups, they correlate negatively with soda and iron in the pantellerites, in contrast with trachytes and comendites. Viewed as a whole, it is clear that more than one process has been at work in generating these liquids. Soda (and iron) and peralkalinity seemingly can vary independently of incompatible trace elements.

#### THE SIGNIFICANCE OF SEPARATE POPULATIONS OF FELSIC LIQUIDS

The chemical variation diagrams emphasise the individuality of different volcanic centres by showing that each has erupted distinct and separate felsic magmas. Furthermore, there are contemporaneous basalts and hawaiites, but no extruded rocks with silica percentages between 54 and 61 weight percent that are not mixed lavas.

Different volcanoes have, therefore, erupted products that are not only chemically distinct, but



between which there are no bridging compositions. These distinct felsic magmas are all products of a major igneous cycle working through this segment of lithosphere. They are coeval and share some distinctive chemical features, especially peralkalinity. What is their relationship? If a basaltic parent were to be invoked, then each felsic batch has to evolve quite separately to produce the batches under the different volcanoes. In all cases the parent and the process must lead to strong peralkalinity and great enrichment in incompatibles. But if each magma type represents merely a stage in a common evolutionary process why should any one stage be restricted to one volcano? The most ready alternative is that the different volcanoes do not represent various degrees of melt differentiation but *are different melts*.

Closed-system magma evolution can be discounted even for single complexes, such as Eburru, where Rb varies as if it were an incompatible element (BAILEY and MACDONALD, 1975). This relationship cannot be reconciled with generation of the liquids solely by crystal-liquid interactions because the distribution coefficient for Rb in alkali feldspar is greater than 0.3. The behaviour of Rb in a series of liquids in equilibrium with alkali feldspar, based on measured distribution coefficients for Rb and Zr and the Rayleigh fractionation law is shown for the Eburru sequence in Figure 10. Also shown are the actual and calculated distributions for the Naivasha comendites and pantellerite glasses from Pantelleria. In all three cases the predicted curves depart from the actual distributions, and it must be assumed that in each series some factor other than evolution by feldspar-liquid interaction is necessary to give the observed distribution pattern for rubidium. As halogen contents typically rise above one weight percent in the more siliceous liquids, no mineral seen in the rocks could provide the source for incompatible elements. One possibility is that a halogen-rich fluid was contributing to the source region from the onset of melting.

Alternatively the high levels of incompatible elements might perhaps be attributed to late-stage processes after the melt had filled a shallow magma chamber. Some limited variation is possible by crystal fractionation, as inferred for Longonot (SCOTT, 1980) but the Rb factor rules this process out for Eburru (BAILEY and MACDONALD, 1975) and for Naivasha comendites (MACDONALD *et al.*, 1986). Diffusion, or "liquid state" processes, may account for part of the variation, as suggested from

FIG. 9. Variations between trace elements for peralkaline glasses. Diamonds indicate samples from Pantelleria. Other symbols as in Figure 4.

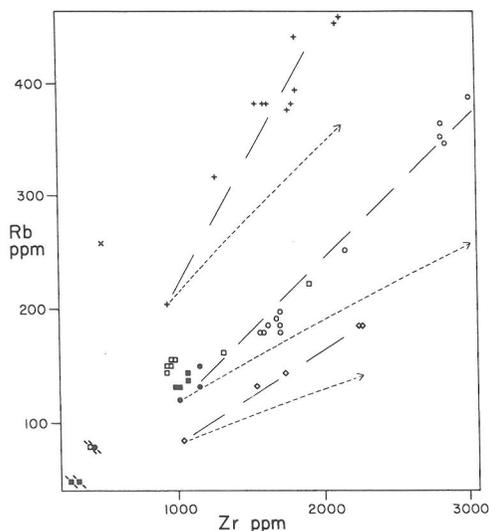


FIG. 10. Variation between Rb and Zr in peralkaline glasses. For three groups (comendites, and pantellerites from Eburru and from Pantelleria) the calculated alkali feldspar fractionation curves are shown by short dashed lines with arrows. The distribution coefficient for Rb ( $D = 0.3$ ) is a mean from values given in BAILEY and MACDONALD (1975) and additional determinations, in which the distribution of Zr ( $D = 0.046$ ) was also measured (using separated feldspars and glass matrices: Eburru samples; BAILEY, unpubl.). Symbols as in Figure 4.

the evidence of zoned ash flows on Menengai (LEAT *et al.*, 1984), but if such a process has given rise to zoned magma chambers, the products lie within the range for the magma type, which itself still remains tightly constrained in any one complex. Concentration of incompatible elements solely by diffusion also runs into difficulty with low and non-systematic variations of  $H_2O$ , and the apparent ceiling on Cl levels in the Kenya province. Difficulties are further compounded by the fact that the distribution pattern between Na, Fe, and incompatible elements is reversed in pantellerites compared with trachytes and comendites.

High level, magma chamber processes offer no solutions to the fundamental geological questions of how these distinct felsic magma types have been produced, how they have preserved their individuality, and what regional conditions have led to all the individual centres developing such striking richness in volatile and incompatible elements. An explanation that aims to encompass these factors must consider melt sources and the possible influence of fluids in magma generation.

#### CARBON DIOXIDE FLUX THROUGH THE RIFT

In previous papers attention has been drawn to the evidence for massive emission of  $CO_2$  through

the Kenya rift zone (BAILEY, 1978, 1980). The main points, with some additions, may be briefly summarised as follows.

(1) Igneous activity was initiated by nephelinite/carbonatite volcanism, which has continued intermittently for the past 23 Ma. An example of the early activity is the nephelinite volcano of Tinderet, with associated Miocene carbonatite ashes (DEANS and ROBERTS, 1984) 50 km to the west of the trachyte volcano of Menengai. The active carbonatite volcano of Oldonyo Lengai at the southern end of the rift is also part of regional igneous activity that includes felsic volcanism. In nephelinite volcanic gases,  $CO_2$  dominates over  $H_2O$ ; in nephelinite glasses from Nyiragongo,  $CO_2$  is about ten times as abundant as  $H_2O$ ; and carbonatite lavas from Oldonyo Lengai are anhydrous (but rich in F and Cl) (BAILEY, 1980).

(2) At the present time, all along the rift there is escape of  $CO_2$ , which is sufficiently abundant to be exploited in commercial wells at several places. This  $CO_2$  flux has led to the suggestion by Kenyan geologists that present day geothermal fields along the rift are the result of heating of the ground water by hot juvenile  $CO_2$  (WALSH, 1969).

(3) Due to the low solubility of  $CO_2$  in salic magmas, evidence of the former presence of  $CO_2$  in Kenyan peralkaline rocks is bound to be scarce, nevertheless, high-temperature carbonates are recorded in small pockets in some of the trachyte lavas on Longonot (SCOTT, 1982). A mixed carbonate/glass ash flow and carbonate lapillae tuffs have been discovered on Suswa (SKILLING and MACDONALD, personal communication, 1986). The main commercial  $CO_2$  well also happens to be on the edge of the rift just to the east of Suswa.

The Kenya rift is fizzing with  $CO_2$  and has been for at least the past 23 million years. This narrow gash in the lithosphere acts as a release channel for volatiles escaping from a large mantle volume below, analogous to the function of a pie funnel (BAILEY, 1980). The general thermal, chemical, and geodynamic consequences of such fluid focussing have been explored elsewhere (BAILEY, 1983).

#### SYNTHESIS

In the absence of any evidence for continuous melt evolution, the objective procedure would be to treat each magma batch as an entity, or the product of a separate event. Any links within or between the major groups, trachytes, pantellerites, and comendites, must then be attributable to common features in the melt generating regime. From this starting point, the following deductions are possible for the melting system:

(1) Comendites show regular increase in  $\text{Fe}_2\text{O}_3$  with peralkalinity, consistent with control by melting of an acmitic pyroxene in the source. A sodic pyroxene could exert some influence on the trachyte variations. Any such pyroxenes could be formed by metasomatism prior to melting.

(2) By contrast, pantellerites show no regular variation in  $\text{Fe}_2\text{O}_3$ , even though  $\text{Na}_2\text{O}$  and  $\text{FeO}_T$  rise steadily through the range. This relationship could describe an increasing contribution from a stable amphibole (fluor-*arfvedsonite*?) at increased melt levels. Such a melting pattern would give rise to higher sodium and iron with greater melt volumes, consistent with the negative correlation between  $\text{Na}_2\text{O}$  and incompatible elements in the pantellerites. It would imply also that any fluorine contribution from the amphibole was insufficient to produce a noticeable effect on the distribution pattern of F in the pantellerites as a whole.

(3) Halogens and other incompatible elements are mainly contributed from a fluid entering the melt zone. The anticipated general result would be higher concentrations in earlier, smaller melt volumes, but some variations in the melt samples could be due to varying amounts of fluid flux through the melt zone (see 4.d).

(4) Part of the fluid has very low solubility in siliceous liquids, with the effect that it is not wholly consumed in the initial melt. Consequently:

(a) Elements are partitioned between melt and fluid.

(b) Partitioning is dependent on melt composition, *e.g.*, trachyte or rhyolite.

(c) Partitioning is dependent on pressure-temperature conditions, and source mineralogy.

(d) Because part of the fluid is insoluble in the melt there can be fluid flux *through the melt region*.

Thus each melt may be buffered for incompatible elements by the fluid.

(5) The fluid is essentially anhydrous and  $\text{CO}_2$ -rich. It also carries other volatile elements such as alkalis (which can be contributed to the melt) but its most striking effect is on the incompatible element budget of the melt. Partitioning works both ways and the fluid scavenges alkaline earths (notably Ba and Sr) from the more siliceous melts. This would account for the extremely low Ba and Sr concentrations in these melts, which defy explanation by closed-system crystal fractionation or partial melting hypotheses.

(6) The three main magma types are determined by three types of metasomatised source rocks:

(a) comendite from metasomatised sialic rocks;

(b) pantellerite from metasomatised basic rocks;

(c) trachyte from metasomatised mantle containing felsic minerals (BAILEY, 1986).

(7) Different magma types show major differences in their chemical patterns. These might simply reflect fundamental differences in the fluid source, but there is a strong possibility that some of the differences may be a consequence of interaction between the fluid and rocks in its path before entering the melt zone. For instance, the higher Rb in comendites may be related to earlier scavenging of this element as the fluid moved through crustal rocks before entering the melt zone. On the other hand, the generally lower levels of incompatible elements in the trachytic melts may be more a function of variations in the partitioning between the  $\text{CO}_2$ -rich fluid and a less siliceous melt at higher pressures.

(8) Individual magma types erupt from distinct centres depending on the source level in the lithosphere. Trachyte centres tap a melt source in metasomatised mantle. As the trachyte source is exhausted, and the melting cycle climbs higher in the lithosphere, pantellerite can become the dominant eruptive. Comendite represents the ultimate stage of the rifting/melting process, when the melting cycle finally impinges on metasomatised sialic crust. Where an igneous cycle is well established, a range of sources, from mantle to crust, may be providing melts to a series of contemporaneous volcanoes. This scenario is consistent with the late development of the Lake Naivasha felsic magma centres, almost symmetrically disposed around the topographic culmination of the Gregory Rift.

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Tables of analysis are available from the first author.

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