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# Fluorine and chlorine in peralkaline liquids and the need for magma generation in an open system

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SUMMARY. Fluorine, chlorine, zinc, niobium, zirconium, yttrium, and rubidium have been determined on fifteen obsidians from Eburru volcano (Kenya Rift Valley), spanning the range from pantelleritic trachyte to pantellerite. All pairs of elements show positive correlation coefficients, ranging between 0·769 and 0·998, but with most values better than 0·900. In spite of some very high correlations, only two of the twenty-one best-fit lines pass near the origin of the Cartesian coordinates. Linear distributions are found *within* two separate groups of elements: F, Zr, Rb; and Cl, Nb, Yt. Zn behaves in general as a member of the second group but seems to be subject to an additional variation. When an element from the fluorine group is plotted against one from the chlorine group the resulting pattern is non-linear. Therefore, although the elements in both groups would generally be considered 'residual' (partition coefficients between crystals and liquid approaching zero) there are clearly detectable differences in their variation, and hence their behaviour.

Major-element variations in the obsidians are such that a vapour (fluid) phase would be needed to account for any magma evolution. The trace-element patterns are also impossible by closed-system crystal fractionation and suggest that this fluid may have been rich in halogens, with the metallic elements forming preferred 'complexes' with either F or Cl. The F–Zr–Rb 'complex' also varies quite independently of the important major oxides (e.g. $Al_2O_3$) in the rocks. In the case of Rb this is but one aspect of a more significant anomaly, in which there is no sign of any influence of alkali feldspar (which partitions Rb) in the variation. This is remarkable because trachytes and rhyolites have normative *ab*+*or* > 50 %, and any evolutionary process *controlled* by crystal ⇌ liquid interactions must be dominated by the melting or crystallization of alkali feldspar. The results on the Eburru obsidians show that *if they are an evolutionary series* then *either*, the process was not crystal ⇌ liquid controlled, *or* that any such process has been overriden (or buffered) by other processes that have superimposed the observed trace-element patterns. In the latter event, the buffering phase may have been a halogen-bearing vapour.

The same considerations must apply to other pantellerite provinces where Rb appears to have behaved as a 'residual' element.

IN recent years we have compiled all the available data on oversaturated peralkaline obsidians (Macdonald and Bailey, 1973) and set in train an analytical programme on all new samples that we have been able to obtain. Our own field sampling has been focused on the Nakuru–Naivasha region of Kenya, the topographic culmination of the East African rift, where there is an unparalleled development of Quaternary–Recent peralkaline volcanoes. In the trachyte to pantellerite composition range it had been demonstrated previously that the obsidians from different volcanoes showed systematic variations in major-element chemistry, but these variations were not consistent with a fractional-crystallization model involving the observed phenocryst phases (Macdonald *et al.*, 1970). The best development of pantellerite magmatism is found in the Eburru volcano (Sutherland, 1971) just north-west of Lake Naivasha. Trace-element analyses of some of Sutherland's samples by Weaver *et al.* (1972) were used (with data from five other volcanoes) to argue that the relationships between trachytes and pantellerites are most reasonably explained by fractional crystallization. Subsequent examination has revealed, however, that the 'Eburru' specimens used by Weaver *et al.* were a mixed population (Bailey *et al.*, 1975).

Since 1970 we have collected and analysed obsidians from Eburru, which span the composition range from quartz-trachyte to pantellerite, and the major-element variation within this one volcanic pile cannot be explained by fractional crystallization of the phenocryst phases. The major-element evidence on quenched liquids is thus in direct conflict with the conclusions reached through the trace elements by Weaver *et al.* (1972). Trace-element analyses of our own Eburru samples form part of the long-term study of peralkaline obsidians, and they are now sufficiently far advanced to demonstrate that fractional crystallization *cannot* explain the variations. This demonstration, however, is only a subsidiary aim of the present article—our chief concern is to describe some unexpected relationships (especially involving halogens) which may provide some real clues to the secrets of this magmatism.

We shall look at a small group of trace elements (F, Cl, Zn, Nb, Zr, Yt, and Rb), which includes the two (Nb and Zr) considered most significant by Weaver *et al.* (1972). Our population is fifteen obsidians from quartz-trachyte to rhyolite: we are unable to include any basalts because we are restricting our study to glasses (quenched liquids). Actually, there are no contemporaneous basalts in the Eburru pile, although there is a Recent basalt field in the lowlands just to the north. We believe it would be begging the question to include these basalts with the Eburru magmatism until we have evidence other than geographic proximity to indicate that the two may be cogenetic (this problem is currently being studied by A. W. H. Bowhill, University of Reading: see also Bailey *et al.*, 1975, fig. 1). Correlations among the selected trace elements are moderately to strongly positive, whereas their correlations with major elements are generally poor. Although the major element ranges in the population are small (e.g. $SiO_2$ range from 66·2 to 72·0 per cent) the trace element ranges are large (e.g. Zr range from 1038 to 3058 ppm). Samples with essentially identical major-element chemistry show widely different trace-element levels, and the impossibility of reconciling these facts with simple fractional crystallization has been noted elsewhere (Bailey, 1973).

*Trace-element relations.* The limits, means, and concentration factors are listed in Table I. Trace-element values, sample points, rock names, and age relations are given in the Appendix.

The absence of basic rocks, with very low levels of the selected trace elements, is not a serious drawback to correlation analysis because in the case of the strongly concentrated elements, F, Zr, and Rb, the obsidian values span two-thirds of the possible range from the maximum observed down to zero. The results of the correlation analysis are given in matrix form in Table II.

TABLE I. *Limits, means, and concentration factors in 15 obsidians from Eburru, Kenya. Values in ppm*

| | F | Cl | Zn | Nb | Zr | Yt | Rb |
|---|---|---|---|---|---|---|---|
| Minimum (m) | 2910 | 2090 | 333 | 230 | 1038 | 195 | 131 |
| Maximum (M) | 7800 | 4290 | 537 | 542 | 3058 | 410 | 417 |
| Mean | 4900 | 3300 | 457 | 388 | 1910 | 307 | 252 |
| Standard Deviation | 1660 | 630 | 58 | 96 | 671 | 63 | 98 |
| Maximum concentration factor (M/m) | 2·68 | 2·05 | 1·61 | 2·36 | 2·95 | 2·10 | 3·18 |

TABLE II. *Correlation matrix for trace elements in the Eburru obsidians (all coefficients are positive). Plus or minus indicates the sign of the intercept of the best-fit line (reduced major-axis equation: Till, 1973) on the axis of the second variable in those cases where the 95 % confidence limits do not include the origin. Zero indicates that the origin falls within the 95 % confidence limits*

| | F | Cl | Zn | Nb | Zr | Yt | Rb |
|---|---|---|---|---|---|---|---|
| F | 1·000 | | | | | | |
| Cl | 0·862(+) | 1·000 | | | | | |
| Zn | 0·769(+) | 0·879(+) | 1·000 | | | | |
| Nb | 0·955(+) | 0·943(−) | 0·909(−) | 1·000 | | | |
| Zr | 0·994(0) | 0·876(−) | 0·817(−) | 0·972(−) | 1·000 | | |
| Yt | 0·932(+) | 0·954(0) | 0·928(−) | 0·995(+) | 0·951(+) | 1·000 | |
| Rb | 0·996(−) | 0·853(−) | 0·790(−) | 0·959(−) | 0·998(−) | 0·937(−) | 1·000 |

### *Implications of the trace-element distributions*

The central tenet of the trace-element argument with respect to magma evolution, as propounded by Weaver *et al.* (1972), is that in a series of peralkaline liquids certain elements will be unable to enter the crystallizing phases, and will become progressively concentrated in the residual liquids. This assumes that the liquids are related by a process dominated by crystal $\rightleftharpoons$ liquid interactions: we would claim that this itself needs to be proven, but for the moment let us examine the rest of the case. Zr is chosen as the prime example of a residual element because of: its high solubility in peralkaline melts (and insolubility in the major crystalline phases); its impassiveness to late-stage 'volatile effects'; and its abundance and high-precision determination by XRF (Weaver *et al.*, 1972). Consequently Zr is claimed to be a more useful index of differentiation than the more commonly used major-element indices. More assumptions are, of course, compounded in this claim. In the case of the Eburru rocks we cannot reconcile the claim with the major-element patterns (Bailey, 1973) and, moreover, we now cannot find support for it in our trace-element data.

Weaver *et al.* (1972) state that in the six volcanic centres they have tested the graphical plots of each of the elements Ce, La, Nb, and Rb against Zr are linear, and project through the origin. They deduce from this (assuming that Zr is the archetype residual element) that the other four elements also have bulk distribution-coefficients (element concentration in combined crystal phases/concentration in liquid) close to zero. Compared with their data on Eburru (kindly provided by S. D. Weaver) our obsidian analyses show far less 'noise', more systematic variations, and higher correlation coefficients throughout. Our distribution patterns are quite different. Many are not linear, and most do not project through the origin. The latter are shown in Table II by plus and minus signs, to indicate the sign of the intercept on the axis of the second variable when the first variable reaches zero. Only those pairs of variables with a correlation coefficient better than 0·990 appear to be convincingly linear; these four are examined first.

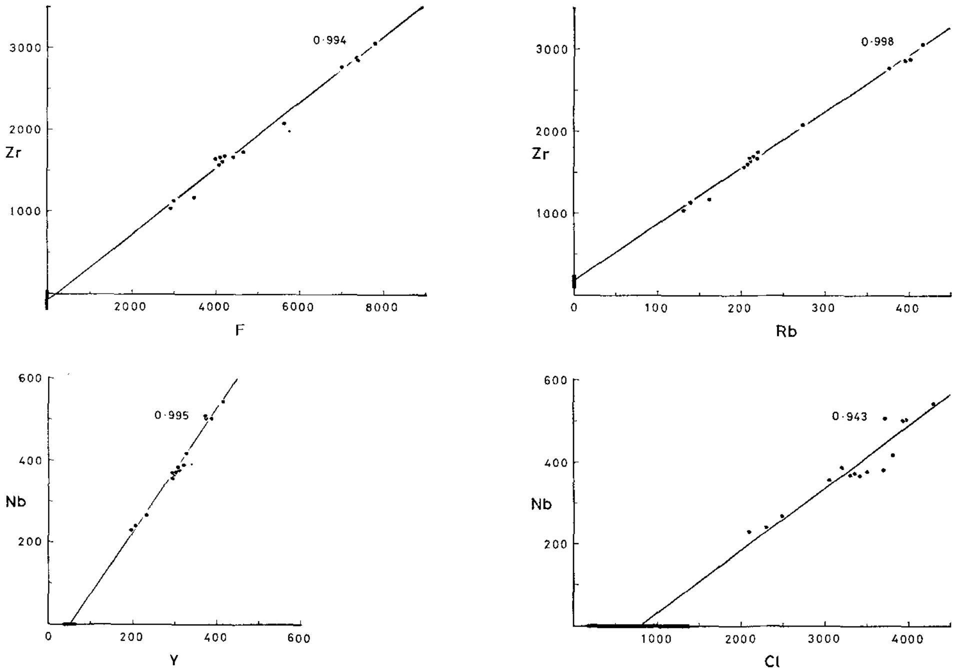

FIG. 1. Four examples of linear correlations of element pairs in the Eburru obsidians (solid circles). In every case the line is the computed reduced major-axis line and the heavy bar on the axis shows the 95 % confidence limits on the intercept. All values in ppm.

*Fluorine, zirconium, and rubidium.* These three elements are the most strongly correlated, each pair providing a linear plot, two of which are shown in fig. 1.

In the case of F and Zr the calculated best-fit line passes close to the origin, which falls within the 95 % confidence limits. Assuming that Zr is the archetype residual element, then F too would have a bulk distribution coefficient close to zero, and constant throughout the series. The consistent behaviour of F would also indicate that the population of obsidians is free of vagarious late-stage volatile losses, because our tests confirm the findings of Noble *et al.* (1967) that fluorine-loss is one of the most conspicuous effects of devitrification in this sort of lava.

The correlation of Rb with Zr, however, destroys the primacy of Zr as a residual element. The line misses the origin, making a positive intercept on Zr when Rb runs to zero. If this distribution is generated by crystal $\rightleftharpoons$ liquid relations in a closed system then Zr must be fractionated (at a constant distribution coefficient) in the solid phases throughout the lava series. If Zr is held to have a distribution coefficient close to zero then the *system must be open to Rb.* Because, if the data are fitted to a fractional-crystallization model, then Rb increases in the residual liquids at a greater rate than Zr: if a fractional-melting model is adopted then the level of Rb must fall faster than Zr as the liquid volume increases. Either way, Rb has to move in or out of the system if Zr is behaving as a residual element. The same deduction, but without the precision, could have been made from the concentration factors in Table I.

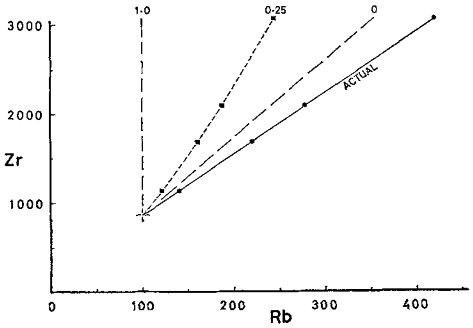

FIG. 2. Showing the difference between the actual array line for Rb *v.* Zr and that expected by fractional crystallization if the bulk distribution coefficient for Rb is finite whilst that for Zr is zero. In the latter case, taking a starting concentration of 100 ppm Rb, the points should lie between the broken lines 0 and 1·0 (if there is to be any concentration of Rb). The line 0·25 represents a reasonable case calculated on the basis of four-stage fractionation (solid squares) at intervals defined by Zr concentrations (solid circles) in the actual array.

In fact, the covariance of Rb and Zr shown in this range of obsidians is even more dramatic, because if the liquids were generated by fractional crystallization about two-thirds of the separating crystals would have to be alkali feldspar (based on normative *ab*+*or* in the trachytes) and the partition coefficient for Rb between alkali feldspar and liquid must be greater than zero. Relevant partition coefficients are available from Noble and Hedge (1970) for alkali feldspar phenocrysts and glassy matrices from peralkaline volcanics. They give values for the Rb partition coefficients in eleven peralkaline rocks, ranging from 0·25 to 0·45. Two of these determinations were made directly on separated phenocrysts and glass, giving values of 0·32 and 0·38 (1970, p. 235, Table, Samples 4 and 11*b*). Determinations of Rb have also been made on separated feldspars and glass from two Eburru rocks (PCO 134 and 135) giving partition coefficients of 0·41 and 0·31, respectively (Geochemistry Unit, Reading: analysts S. A. Malik and D. A. Bungard). Taking the average partition coefficient for Rb of 0·35 for alkali-feldspars/peralkaline-liquids, fractional crystallization (from a trachytic parent) in which 70 % of the separating crystals were alkali feldspar would result in a *bulk distribution coefficient* for Rb of 0·25. Fig. 2 is a graphical plot for Rb *v.* Zr to show the curve that would be generated by fractional crystallization when the bulk distribution coefficients for Rb and Zr are 0·25 and zero, respectively. The curve is calculated from a starting-point at 100 ppm Rb on the *actual* line and is developed by four successive crystal crops at stages marked by *actual* Zr contents in the Eburru rocks. The highest calculated Rb value on the 'fractionation' curve is 244 ppm, which is only a little more than half the actual value (417 ppm) for the same Zr content. It is glaringly obvious from fig. 2 that either Zr is *not* a reliable index of differentiation, or fractional crystallization *cannot* account for the covariance of Rb and Zr, or *both*. All evidence available to us favours the third conclusion!

*Niobium, yttrium, and chlorine.* There is good correlation between Nb and Yt; the plot, shown in fig. 1, is linear within the limits of experimental error, with a narrow 95 % confidence band. The calculated line does not pass through the origin. If it were assumed that crystal fractionation controls the series, and Nb has a distribution coefficient close to zero, the sample array might be explained by Yt having a significantly higher distribution coefficient. The only phase that might be separating throughout the whole series is alkali feldspar, which would not normally be suspected of fractionating Yt with respect to Nb. Furthermore, neither Nb nor Yt shows a simple linear relation with Zr, which adds further complications to the model.

Nb and Yt both show reasonably linear correlations with Cl. The graphical plot for Nb *v*. Cl, shown in fig. 1, reveals a high positive intercept of the computed line on the Cl axis. This has the same implications for fractional crystallization as the Nb *v*. Yt array. It should be noted that if a fractional-melting evolution model is applied to these data, and Nb is taken to have a distribution coefficient of zero, then the system must be open to the ingress of Yt and Cl.

Yt *v*. Cl gives a similar pattern to Nb *v*. Cl but the line runs through the origin (within the 95 % confidence band).

*Non-linear patterns, and covariance with fluorine and chlorine.* Examination of the correlation matrix (Table II) shows that in addition to the four coefficients better than 0·990, there are a further ten better than 0·900. Nb and Zr are the best of this group with a coefficient of 0·972. But when graphical plots of these pairs of variables are made it emerges that many of these correlation coefficients are not lower (i.e. $< 0{\cdot}990$) due to random deviations from the line (as might be argued, for instance, for Nb *v* Cl, fig. 1). The lower coefficients for many pairs of elements result from *patterned*, but *non-linear* arrays of points. Examples are depicted in fig. 3, in which it may be seen that each computed best-fit line has been achieved by balancing a cluster of points in the middle of the array against points at the extremities. These are certainly not random patterns. The most obvious case is F *v*. Cl, with a relatively low correlation coefficient of 0·862, where a better description of the array would be an inflected line. The fact that this pattern is matched by Nb *v*. Zr, elements of a completely different kind, determined by a completely different method, must rule out the possibility that the arrangement is fortuitous. Fig. 3 confirms what was implicit from fig. 1 and the earlier discussion, namely, that Zr varies linearly with F (and Rb), that Nb varies linearly with Cl (and Yt), but between these groups of elements there is a marked inflection in the pattern of distribution. The complexity of the element covariances within these two groups, coupled with this additional complication of the relationships between the groups, rules out any rational *closed-system* (isochemical) evolutionary model. Such a conclusion is entirely consonant with those reached earlier on the basis of major-element variations (Macdonald *et al.*, 1970) and comparisons of major and trace elements (Bailey, 1973).

Before considering alternative explanations for the chemical variations in the Eburru obsidians, the anomalously high, and seemingly erratic, zinc distribution needs comment (fig. 3). Firstly, Zn can be determined with high precision by XRF. Secondly, the limiting Zn values in fig. 3 were checked by atomic absorption, with good agreement. Thirdly, the high levels, and the variability, of the Zn values in the Eburru samples, are not due to vagaries of sampling, sample preparation, or analytical method, because the second data set (plus signs) in fig. 3 represent comendite obsidians from the Naivasha volcanic area, just south of Eburru. These were collected, prepared, and analysed with the Eburru samples, so we are seeing a genuine Zn anomaly in the Eburru rocks. Fourthly, the broad scatter of the Zn values about the best-fit line in fig. 3 is confirmed by later results on other samples (not yet analysed for F and Cl)—the impression given by this pattern is of a second-order fluctuation in Zn concentration superimposed on a main trend indicated by the line. The general

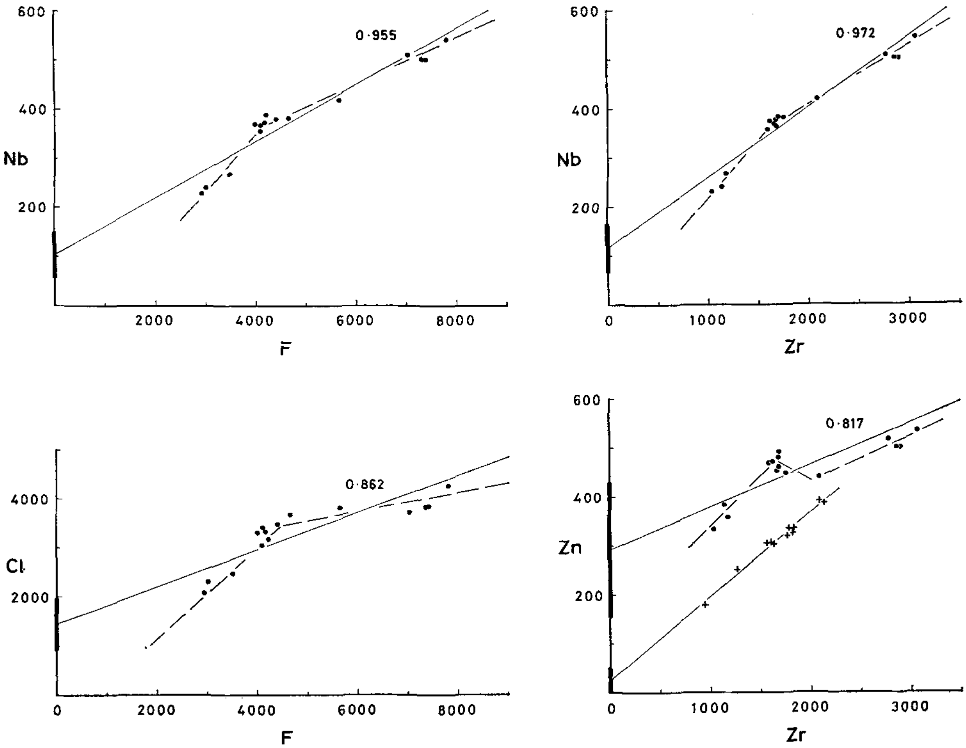

FIG. 3. Four examples of non-linear arrays in the Eburru obsidians. Solid circles, continuous lines, and heavy bars as in fig. 1. The broken lines represent preferred descriptions of the variation in each case. In the Zn *v*. Zr plot the plus signs are comendite obsidians from the Naivasha volcanic area (see text).

form of the Zn distribution, when plotted against Zr, resembles that of Yt, Nb, and Cl against Zr, except that the general high levels of Zn are more obvious. Indeed, Zn shows its strongest correlations with Yt, Nb, and Cl, in that order (see Table II) so that similar factors, either at source or during magma generation, or both, have presumably influenced all four elements, but to different degrees. At present we have no evidence to suggest possible causes of the second-order fluctuations in the Zn pattern.

As a final point it should be noted that inflected patterns similar to those among the trace elements (shown in fig. 3) also emerge when some major elements (and their functions) are plotted against Zr. Examples are $Al_2O_3$, $TiO_2$, and agpaitic index ($Mol(Na_2O+K_2O)/Al_2O_3$).

### *An open-system model*

In our earlier paper on the major-element patterns in the range pantelleritic trachyte to pantellerite (Macdonald *et al.*, 1970) we had to conclude that *if the rocks were an evolutionary series* a phase now missing from the rocks must have played a major part in the evolutionary process. The Eburru obsidians fall into the previously defined major-element patterns and the same conclusion applies. Furthermore, the trace-element patterns are now found to be incompatible with closed-system evolution. We concluded from the earlier major-element studies that if the rocks had been generated by a series of melting episodes then a separate vapour (fluid) phase had contributed Na (and possibly Si and Fe) to successive silicate liquids. Our reasons for preferring a fractional-melting model were given in that account (Macdonald *et al.*, 1970): a further reason in the Eburru rocks is that the chemical variations do not seem to fit any regular pattern in the development of the volcano. It would be premature to try to elaborate this model much further until all our data are in, but some additional conclusions from the present trace-element distributions are in order.

It is clear that a simple fractional-melting model could not generate most of the observed trace-element patterns. For instance, most of the correlation lines do not pass through the origin, which would be the first requirement for 'residual' elements. In such cases, where the correlation is linear (fig. 1) the line could be interpreted as a product of simple mixing, but the true picture must be more complex because some patterns are inflected (fig. 3). The most significant feature is the affinity of Zr and Rb with F, and the *separate* affinity of Nb, Yt, and Zn with Cl: judging by the inflected variation patterns between these two groups they would seem to have some degree of independence throughout the rock series. One possibility is that the metallic elements form preferred complexes with either fluorine or chlorine, and the partitioning of these complexes between vapour (fluid) and silicate melt varies with the melting conditions (e.g. relative volumes of melt to vapour, variations in melt or vapour compositions, temperature, and pressure). We are investigating this and other possibilities by: further analyses of Eburru rocks and extracted gases; experimental determination of melting, crystallization, and volatile exsolution; and by studies of obsidian suites from other volcanoes.

Another remarkable feature of the Eburru rocks is the Rb variation, which shows no recognizable contribution from alkali feldspars in contact with the melt (yet alkali-feldspar phenocrysts are normal). If a coexisting vapour phase contributing Rb (and Zr and F) is accepted, the Rb patterns in the rocks suggest that the effect of this vapour is paramount. It is as if the melts were buffered for Rb. The fact that a key major element such as Al gives inflected variation patterns when plotted against Zr, Rb, and F also suggests that the concentrations of these elements are controlled by some factor other than those that determine the major-element distributions in the magmas.

Finally, one general point may be made concerning F and Cl in peralkaline magmas. It is commonly argued by advocates of fractional crystallization, that the high concentrations of Zr that distinguish peralkaline from subaluminous magmas are due to the solubility of Zr in peralkaline melts, and their consequent failure to precipitate zircon during crystallization. But how, then, is it possible to account for the high concentrations of F and Cl that equally distinguish these same peralkaline melts from other oversaturated magmas? We believe that the very high correlation of Zr and F in our samples exposes this as an artificial dilemma, and we appeal to fellow petrologists and petrochemists to critically reappraise some of the time-honoured concepts of magma evolution.

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## APPENDIX. *Trace-element values (ppm) in 15 Eburru obsidians*

| Sample | F | Cl | Zn | Nb | Zr | Yt | Rb | Co-ordinates | Age group |
|---|---|---|---|---|---|---|---|---|---|
| PCO082 | 4000 | 3300 | 454 | 370 | 1653 | 294 | 212 | AK 966 332 | c |
| PCO083 | 4100 | 3400 | 467 | 367 | 1664 | 296 | 211 | AK 956 323 | c |
| PCO084 | 3000 | 2300 | 384 | 240 | 1137 | 203 | 139 | AK 971 329 | b–c |
| PCO129 | 4650 | 3680 | 448 | 381 | 1748 | 305 | 220 | AK 943 297 | d |
| PCO130 | 4200 | 3190 | 491 | 389 | 1697 | 318 | 213 | AK 933 363 | b |
| PCO131 | 7020 | 3710 | 519 | 508 | 2776 | 371 | 377 | BK 001 398 | a–b |
| PCO132 | 4400 | 3480 | 480 | 379 | 1679 | 305 | 218 | AK 950 279 | d |
| PCO133 | 4150 | 3330 | 472 | 372 | 1608 | 300 | 208 | AK 954 295 | d |
| PCO134 | 5630 | 3810 | 440 | 419 | 2091 | 324 | 273 | AK 965 242 | d |
| PCO135 | 4090 | 3040 | 469 | 357 | 1593 | 292 | 206 | AK 974 229 | a? |
| PCO161 | 7390 | 3930 | 501 | 502 | 2865 | 383 | 397 | BK 037 323 | a |
| PCO162 | 7370 | 3930 | 503 | 502 | 2880 | 375 | 402 | BK 039 329 | a |
| PCO163 | 7800 | 4290 | 537 | 542 | 3058 | 410 | 417 | BK 022 263 | a |
| PCO164 | 3480 | 2480 | 359 | 269 | 1168 | 230 | 162 | AK 910 362 | b |
| PCO165 | 2910 | 2090 | 333 | 230 | 1038 | 195 | 131 | AK 905 374 | b |

*Methods*: F and Cl; determined colorimetrically (Thomas *et al.*, 1975). Zn, Nb, Zr, Yt, Rb; determined by XRF (Parker, unpub.), using U.S.G.S. Standard Rocks (G2, GSP1, AGV1, PCC1, DTS1, BCR1) for calibration.

*Co-ordinates.* 1000 m Universal Transverse Mercator Grid Clarke 1880 (Modified) Spheroid. Grid Zone Designation 37 M. The 100 000 m Sq Identification is given by the prefix letters: easting and northing by the final six digits. As used on Survey of Kenya maps.

*Age groups*: a–d: oldest–youngest. Broad groupings only are possible because many flows do not overlap to give precise relationships.

*Rock descriptions.* The suffix (P) signifies rare feldspar phenocrysts: in such rocks there are usually abundant microphenocrysts. Full modal data will be published later, with the major element analyses.

| | |
|---|---|
| PCO082 | See Macdonald and Bailey (1973), Anal. 82. |
| PCO083 | See Macdonald and Bailey (1973), Anal. 83. |
| PCO084 | See Macdonald and Bailey (1973), Anal. 84. |
| PCO129 | Obsidian |
| PCO130 | Obsidian (P) |
| PCO131 | Obsidian |
| PCO132 | Obsidian |
| PCO133 | Obsidian |
| PCO134 | Glassy lava with abundant phenocrysts of feldspar, quartz, and aenigmatite, and rare clinopyroxene. |
| PCO135 | Glassy lava with phenocrysts of feldspar, aenigmatite, and clinopyroxene. |
| PCO161 | Obsidian |
| PCO162 | Obsidian |
| PCO163 | Obsidian. Same locality as Anal. 89, Macdonald and Bailey (1973). |
| PCO164 | Obsidian (P) |
| PCO165 | Obsidian (P) |