

Systematic Use of Trace Element in Igneous Process

Part I: Fractional Crystallization Processes in Volcanic Suites

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Abstract. This paper describes an extended application of the Rayleigh distillation law to trace element behavior in a fractional crystallization sequence. Using a trace element with a very low bulk partition coefficient as a reference (as suggested by Anderson and Greenland, 1969, and extended by Treuil and Varet, 1973), we can derive bulk partition coefficients for other elements and, in turn, the mineralogical composition of the cumulates. Trace elements with large D , such as Ni and Cr, further constrain the system, and we can deduce the initial composition of the magma. An example of this technique is shown for Terceira Island in the Azores.

I. Introduction

Using hygromagmatophile elements systematics, Treuil and Varet (1973) have shown a way to determine which of several processes (partial melting, mixing or fractional crystallization) is the dominant process in creating the chemical variation in a volcanic suite. This approach shows that a differentiation process following a Rayleigh type law (crystal fractionation in a closed system) is common in volcanic suites, in island arc series (Treuil et al., 1973), in oceanic islands (Schilling and Winchester, 1967), in mid-oceanic ridges (Bougault and Hekinian, 1975; Joron et al., 1976) and in rift valleys (Treuil and Varet, 1973). This process plays also a fundamental role on the moon (Allègre et al., 1976).

The goal of this paper is to show that with a proper set of trace element data for a volcanic suite, it is possible to deduce the principal features of the fractionation process, including an estimate of the initial composition, and the principal minerals precipitating and their respective proportions.

We have developed the mathematical formulation to define the basic model for the application of the inversion procedure which will be published separately

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(Minster et al., in preparation). In the first part of this paper, we will give the principles of our approach. Then we will discuss in more details the different problems which should be solved. Finally, we will present an example of this type of treatment.

II. Principles of the Determination of the Fractional Crystallization Parameters

General Principles

We assume that the fractional crystallization follows the Rayleigh law (Neumann et al., 1954).

$$C_l^i = C_{0,i}^i f^{(\bar{D}^i - 1)}$$

i = index of trace element i
 C_l^i = trace element concentration in liquid
 $C_{0,i}^i$ = trace element concentration in initial liquid
 f = weight fraction of residual liquid
 \bar{D}^i = bulk partition coefficient for trace element i .

If $\bar{D} \ll 1$ (element noted with superscripts \star):

$$C_l^\star = \frac{C_{0,l}^\star}{f} \quad \text{or} \quad f = \frac{C_{0,l}^\star}{C_l^\star}.$$

Then $1/C_l^\star$ is proportional to f .

As shown by Anderson and Greenland (1969) this approximation is realized for the elements which have a great affinity for the liquid and are called hygromagmatophile by Treuil and Varet (1973). These will be called H elements in this paper. They are, e.g., Ta, Th and to a lesser extent Ce and La in differentiation of basaltic magma. Figure 1 shows the domain of validity for this approximation. The concentration of an H element is a measure of f (at a constant factor) and its variation can be used as a differentiation index.

Let us consider now a trace element i . We can write the Rayleigh law in the form:

$$C_l^i = C_{0,i}^i \left(\frac{C_{0,i}^\star}{C_l^\star} \right)^{(\bar{D}^i - 1)}.$$

This can be expressed in logarithmic form:

$$\text{Log}(C_l^i) = \text{Log}(C_{0,i}^i) + (\bar{D}^i - 1) \text{Log}(C_{0,i}^\star) - (\bar{D}^i - 1) \text{Log}(C_l^\star).$$

If \bar{D}^i is constant throughout the process, the graph of $\text{Log}(C_l^i)$ versus $\text{Log}(C_l^\star)$ is a straight line for which the slope is $(1 - \bar{D}^i)$. This allows the determination of \bar{D}^i for any element i (Fig. 2). It must be stressed that if \bar{D}^i is extremely small, the slope of the line is almost one but cannot be greater. Thus, if a situation occurs which violates this, (i.e., slope larger than one), another phenomenon than fractional crystallization should be considered.

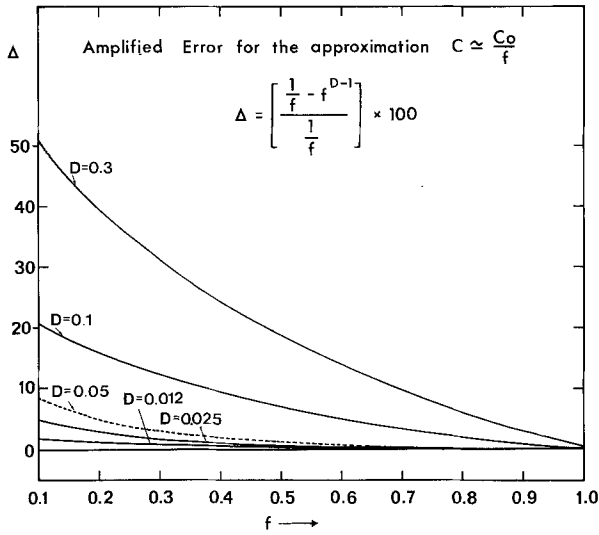


Fig. 1. Plot of $\Delta = \frac{\frac{1}{f} - f^{D-1}}{\frac{1}{f}} \times 100$ against f for different values of the partition coefficient D . This

shows the validity of the approximation $C = C_0/f$ for the Rayleigh law, in the case where D is negligible against 1

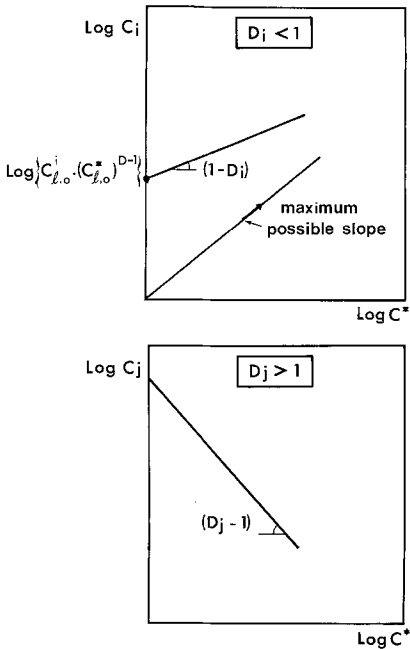


Fig. 2. Schematic diagram showing the path of one element against an H element for which D is extremely small. Case a: the partition coefficient of element i is < 1 . The maximum slope is one. Case b: the partition coefficient of element j is > 1

Determination of the Mean Mineral Assemblage Involved in the Crystallization

We know that the bulk partition coefficient, \bar{D}^i , can be written (Neumann et al., 1954):

$$\bar{D}^i = D_{\alpha/l}^i x_\alpha + D_{\beta/l}^i x_\beta + D_{\gamma/l}^i x_\gamma + \dots$$

$$D_{\alpha/l}^i = \frac{C_\alpha^i}{C_l^i} \dots$$

C_α^i = concentration of trace element i in the phase α

C_l^i = concentration of trace element i in the liquid

x_α = weight fraction of the phase α .

$D_{\alpha/l}^i$ is the partition coefficient between mineral α and liquid. Then, for n trace elements we can write n linear equations which can be written in the matrix form:

$$\begin{bmatrix} \bar{D}^1 \\ \bar{D}^2 \\ \vdots \\ \bar{D}^n \end{bmatrix} = \begin{bmatrix} D_{\alpha/l}^1 & D_{\beta/l}^1 & \dots \\ D_{\alpha/l}^2 & & \dots \\ \vdots & & \\ D_{\alpha/l}^n & & \dots \end{bmatrix} \cdot \begin{bmatrix} x_\alpha \\ x_\beta \\ \vdots \\ \dots \end{bmatrix}.$$

Or:

$$[\bar{D}^i] = [D_{\alpha/l}^i] \cdot [x_\alpha].$$

If we know the partition coefficients between minerals and liquid for several elements, we know the partition coefficient matrix $[D_{\alpha/l}^i]$ and we can solve the set of linear equations to obtain $[x_\alpha]$, which is the mean modal composition of the solid which was removed from the liquid.

Estimation of the Initial Composition of the Magma

The initial composition of the magma (parental magma for a series) is extremely important to know because it can represent the primary magma, the direct product of the mantle partial melting, and hence give access to the partial melting process. Secondly, this determination allows a numerical estimation of the parameter f .

In our first approach to this problem, we note that for certain elements we can easily obtain, not the initial composition, but the ratios of the initial concentrations. When the evolution lines of two elements are parallel in the diagram of $\text{Log}(C_l^i)$ versus $\text{Log}(C_l^{i^*})$, the difference in the intercepts is $\text{Log}(C_{0,l}^i/C_{0,l}^{i^*})$ and gives the initial ratio. All of the H elements are examples of this case.

In a second step, we want to obtain the initial concentration itself. Let us consider an element for which the bulk partition coefficient is large (denoted by superscripts g). The intercept of the $(\text{Log}(C_l^g), \text{Log}(C_l^{g^*}))$ diagram is:

$$A = \text{Log}(C_{0,l}^g) + (\bar{D}^g - 1) \text{Log}(C_{0,l}^{g^*}).$$

Clearly, an estimation of $C_{0,l}^g$ allows a more precise estimation of $C_{0,l}^{g^*}$. For example, for a partition coefficient $\bar{D}^g = 6$, a fluctuation in the value of $C_{0,l}^g$

between 200 and 400 ppm induces a fluctuation of 5% in the corresponding value of $C_{0,i}^{\alpha}$.

It is possible to find elements such as Ni or Cr for which the bulk partition coefficient is large and for which the initial concentration can be inferred indirectly. An application of this method will be given later.

Another possibility would be to consider the ratio of two elements of very different partition coefficients. Noting R the ratio, we can write:

$$\text{Log}(R) = \text{Log}(R_0) + (\bar{D}^i - \bar{D}^j) \text{Log}(C_{0,i}^{\alpha}) - (\bar{D}^i - \bar{D}^j) \text{Log}(C_{0,j}^{\alpha}).$$

The $(\text{Log}(R), \text{Log}(C_{0,i}^{\alpha}))$ plot is a straight line with a slope $-(\bar{D}^i - \bar{D}^j)$. The knowledge of R_0 allows a calculation of $C_{0,i}^{\alpha}$. Ratios like Ni/Sr or Cr/Sc could be used in this way.

III. Geochemical Problems Arising from the Use of this Method

Before giving an example of this type of calculation, let us examine a few problems which might appear.

1. Sampling of the Liquid

In order to apply the above formalism, it is necessary to use samples of the liquid at different stages of fractional crystallization. However, a volcanic rock is in most cases a complex system involving liquid, phenocrysts and xenocrysts. The measured concentration C_{Σ}^i in a whole rock sample can be expressed as:

$$C_{\Sigma}^i = \alpha_M C_M^i + \alpha_{Ph} C_{Ph}^i + \alpha_{Xe} C_{Xe}^i$$

where

C_M^i = concentration of element i in matrix (this is the part which we need)

C_{Ph}^i = concentration of element i in phenocrysts

C_{Xe}^i = concentration of element i in xenocrysts

α = weight proportion of the corresponding phase.

In a simple case where there are only phenocrysts in equilibrium with the liquid and matrix:

$$C_{Ph}^i = \bar{D}^i \cdot C_M^i$$

$$C_{\Sigma}^i = (\alpha_M + (1 - \alpha_M) \bar{D}^i) C_M^i.$$

If \bar{D}^i is small and α_M is large (this condition can be attained in an appropriate petrologic type) C_{Σ}^i is not very different from C_M^i . On the other hand, if \bar{D}^i is large, this effect is disastrous. For example, if $\bar{D}^i = 10$ and $\alpha_M = 0.9$ (e.g. $i = \text{Ni}$, $\text{Ph} = \text{olivine}$), $C_{\Sigma}^i = 1.95 C_M^i$, and in replacing C_M^i by C_{Σ}^i we make a 50% error.

Probably the best method for estimating the liquid composition would be to analyze the center of the automorphic crystals by an ion probe and then, applying the correct set of mineral/liquid partition coefficients to deduce the composition of the liquid.

An alternative method would be a careful choice of the samples. Using petrographic observations, samples without pheno- or xenocrysts will be chosen. A control can be made after the study on a limited number of cases by using those elements for which the partition coefficients are large.

2. Problem of the Constancy of \bar{D}

We have studied several magmatic suites and all of them have shown constant \bar{D} for the series, or for parts of the series. In other words \bar{D} does not vary continuously but stepwise and the $(\text{Log}(C_i^s), \text{Log}(C_i^l))$ diagrams consist of series of segments.

As explained by Bowen (1914) and Presnall (1969), the mineralogical composition of the solid which precipitates during a sequence of fractional crystallization varies in stepwise function. When the curvature of the cotectic line is small (which is generally the case), the proportion of the different minerals stays almost constant. If the partition coefficients between minerals and melt remain constant during a given step, the bulk partition coefficient \bar{D}^i is constant for that step. However, we know that the mineral/liquid partition coefficients are not necessarily constant during such processes. They may vary with both the composition of the host mineral and the melt. For example, we know that during the crystallization process the fayalite content of olivine increases, and at the same time, the MgO content of the liquid decreases. The nickel partitioning between olivine and liquid depends on both the composition of the olivine and the composition of the melt (Hart et al., in preparation). Thus, $D_{\text{ol}/l}^{\text{Ni}}$ should vary during this process and \bar{D}^{Ni} should be strongly dependent on this variation. The situation of strontium partitioning in plagioclase is similar. To illustrate this type of behavior, we have calculated a theoretical curve for a given petrological situation. We considered a basaltic magma crystallizing first olivine, then ol.(70)-cpx.(30), ol.(30)-plag.(30)-cpx.(40) and finally cpx.(30)-plag.(70). Figure 2 shows with exaggerated features the evolution of the concentration of Ni and Sr in the liquid during this sequence.

Unless we have an extremely good sampling and very accurate measurements this effect will be difficult to detect and a mean value of the bulk partition coefficients will be obtained. Imagine however that such a curvature is detected; as shown by Presnall (1969), the solid precipitate is on the tangent to the path of the liquid evolution. This principle has been extensively used by Albarède (1976) in his geometrical treatment of a simple system. It is possible to work on this tangent in the same way as in the constant \bar{D} hypothesis.

3. Problem of the Trapped Liquid

Wager and Deer (1939), Jackson (1961), and Hess (1960) have shown that the solid which precipitates in a magma chamber can trap up to 40% of the liquid. In the case of the Skaergaard intrusion, Paster et al. (1974) have shown that this effect should be taken into account when modeling the trace element distribution

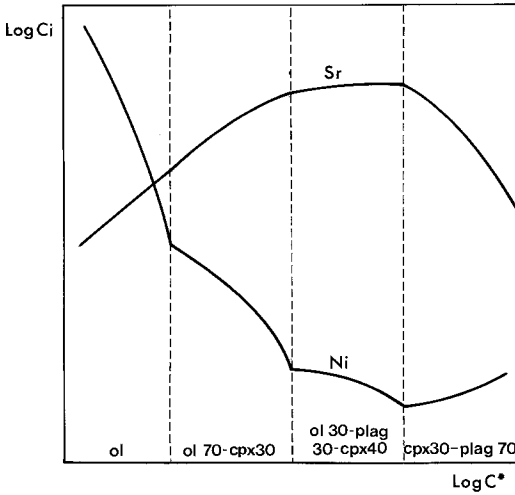


Fig. 3. Schematic diagram showing possible effects of the variation of the composition of the melt and of the crystallizing solid. At the beginning of each sequence, apparition of a new crystallizing mineral assemblage induces a sudden change of the bulk partition coefficient. During the first sequences, the composition of the melt changes (increase of Fe/Mg and SiO₂) and $D_{ol/liq}^{Ni}$ increases. During the last sequence, no more olivine crystallizes and nickel behaves as an incompatible element. During the first sequence strontium is an H element. During the following sequences, $D_{plag/liq}^{Sr}$ increases as plagioclase becomes more sodic. In fact, variation of the composition of both the melt and the solid are simultaneous, and their effects are superimposed

between the minerals of the cumulate. As shown by Albarède (1976), this effect can be expressed by replacing the expression for the bulk partition coefficient by $\langle D \rangle$:

$$\langle D^i \rangle = \bar{D}^i a + (1 - a)$$

where \bar{D}^i is the bulk partition coefficient and $(1 - a)$ is the proportion of trapped liquid which is supposed to be constant. The slope of the liquid path in the $(\text{Log}(C^i), \text{Log}(C^*))$ diagram:

$$(\langle D^i \rangle - 1) / (\langle D^* \rangle - 1) = (\bar{D}^i - 1) / (\bar{D}^* - 1)$$

remains unchanged. This is true even if the distribution coefficients are not constant.

4. Solution of the Matrix Equation

The mineralogical composition of the cumulate is obtained by solving the linear equation system, in other words, by inverting the mineral/liquid partition coefficient matrix. Several difficulties arise at this point. To solve these equations, we need informations on a number of elements equal to or greater than the number of minerals involved. In addition, the elements used in this process must carry independent information. For example, the analysis of 14 REE does not

result in 14 independent information units; almost all of the REE information is contained in La, Sm, Eu and Yb. One way to choose “independent elements” is to choose elements which are characteristic of a mineral, such as Ni for olivine, V for Ti—Fe oxides, Sc for clinopyroxenes, Sr for plagioclase. We will find in this way more elements than minerals and the problem will be overdetermined.

Another problem occurs if we want to take into account the errors on the partition coefficients we use. A complete analysis of this type of problems is given by Albarede and Provost (1976) from a mathematical point of view. In this case a large number of elements is needed, in order to avoid the matrix to be singular in a numerical sense.

5. Presence of a Gas Phase

The gas phase certainly plays a role in the course of magmatic differentiation for several elements. But at the end of the process, this phase escapes from the rocks (except in fluid inclusions). Neglecting the gas phase influence could lead to a misinterpretation of certain results.

Let us consider a simple case and examine the gas phase effect. Gas solubility in a solid is very low compared to that in magma; thus, fractional crystallization leads to the formation of a gas phase. If

$$K_{v/l} = \frac{C_{\text{vapor}}^i}{C_{\text{liquid}}^i}$$

we can write

$$\frac{dx_v}{dv} = K_{v/l} \frac{x}{M}$$

dv = amount of gas escape

x = amount of element in liquid

M = amount of magma

dx_v = amount of element passing into vapor phase.

The crystallization relationship writes:

$$\frac{dx_s}{dM_s} = K_{s/l} \frac{x}{M}$$

dx_s = amount of element passing into solid

dM_s = amount of instantaneous solid.

If we consider, following Holland (1972), that the concentration of gas dissolved in the magma is constant:

$$\frac{V}{M} = G \quad \text{and} \quad dv = G dM$$

$$dx_v = K_{v/l} G \frac{dM}{M}.$$

The total amount of element which is taken out of the magma can be written

$$dx = dx_s + dx_v$$

$$dx = (K_{s/l} + K_{v/l}G) x \frac{dM}{M}$$

Under the condition that the distribution coefficients are constant it follows by integration:

$$C_l = C_{0,l} f^{(K_{s/l} + K_{v/l}G) - 1}$$

f = fraction of residual magma.

Thus, we obtain a Rayleigh law in which:

$$\bar{D}^i = (K_{s/l} + K_{v/l}G).$$

Note here that the gas phase is not considered as an additional phase. In a $(\text{Log}(C_l^i), \text{Log}(C_l^{\#}))$ diagram the path will remain a straight line, but the partition coefficient will include the gas phase effect.

At the present time, such calculations are impossible because we do not know the values of $K_{v/l}$ and G , but they could be obtained in the future. We should, however, consider the possibility of a gas phase influence if, for several elements, the solution of the matrix equation gives inconsistent results.

6. Calculation of C_0 and f

As is pointed out, it is possible to obtain a strong constraint on $C_{0,l}$ and thus f , using an estimate of $C_{0,l}^g$.

Here will follow an example of estimating $C_{0,l}^g$ for Ni. Assuming a concentration in the initial solid, we can calculate the concentration of an element in the liquid derived by partial melting (Gast, 1968; Shaw, 1970).

$$\frac{C_l}{C_0} = \frac{1}{D_0 + F(1 - P)}$$

C_0 = concentration in the initial solid

F = degree of partial melting

$$D_0 = \sum X_\alpha D_{\alpha/l}$$

$$P = \sum x_\alpha D_{\alpha/l}$$

X_α = weight proportion of mineral α in the initial solid

x_α = weight proportion of mineral α entering into the liquid.

For the set of partition coefficients of Ni given in Table 1, a mantle consisting of spinel lherzolite or garnet lherzolite and for a degree of partial melting from 3% to 30%, we obtain C_l/C_0 values ranging from 0.13 to 0.19. If we consider a Ni concentration in the mantle of 2400 ppm as indicated by lherzolite nodules in kimberlite (Boyd, 1973) and intrusive peridotites (Bougault, unpublished results), we obtain a maximum range of Ni concentration from 300 to 450 ppm

in the primary magma. Note that such values are very rare, but not unknown (Shimizu and Arculus, 1975).

Recent experiments (Hart et al., in preparation) have shown tremendous variations of the partition coefficient of nickel between olivine and melt. By using a value of 5 rather than 12, we obtain a concentration of 520 ppm for 30% of partial melting. However, as pointed out earlier, variation of 300–500 ppm Ni as $C_{0,l}^g$ does not change $C_{0,l}$ significantly. Difficulties may appear, related to whether or not a primitive sequence of crystallization is represented by our samples. We know through experimental petrology that in any type of primary magma, at low pressure, olivine precipitates first. Thus, a high value of the partition coefficient of Ni during the first path is a strong indication of “primitiveness”, i.e. closeness to the parental magma. Since, as already noted, $D_{ol/l}^{Ni}$ may be as low as 5, we will assume that when \bar{D}^{Ni} is higher than 4 to 5 we are dealing with a “primitive” sequence.

We want to emphasize that this type of external constraint will probably be given in greater accuracy in the future, and that although the above solution may be proved to be incorrect, this would not invalidate the method.

If we do not have a primitive sequence, we cannot obtain the initial $C_{0,l}^g$ and the absolute value of f . We can still obtain the bulk partition coefficient for the sampled sequence. However, external constraints and the concentrations in the magma at the beginning of this sequence are much more difficult to estimate.

7. Problem of the Partition Coefficient Matrix

Despite the extreme importance of partition coefficients for trace element work, the problem of determining satisfactory mineral/liquid partition coefficients is not solved yet. Schnetzler and Philpotts (1970) supply a list of measured element ratios between matrix and phenocrysts in natural rocks. However, this technique can give misleading results because pure minerals are difficult to get, and that the zoning of minerals (or matrix) creates some difficulties (Albarède and Bottinga, 1972; Hart and Brooks, 1974).

More recently, some equilibrium partition coefficients have been determined by experimental techniques. Difficulties arise whether or not equilibrium is attained. However, it seems that in some cases these difficulties are surmounted, and that reproducible partition coefficients have been measured (Shimizu, 1974; Hart et al., in preparation). To apply these values to natural rocks, we must assume that the phases are in equilibrium, which might not always be correct as suggested by Albarède and Bottinga (1972).

Another complication is the variation of the partition coefficients with the composition of the liquid; this has been shown to occur in plagioclase melt systems for Sr, K, Rb and Ba (Philpotts and Schnetzler, 1970) and in olivine-melt systems for Ni (Hart et al., in preparation). Unfortunately, we have few data related to this effect.

At the present time, the only way to get useful partition coefficients is to criticize all existing results and make a choice between contradictory data. We have made this effort and present a tentative list of values in Table 1. We strongly

Table 1. Matrix of mineral/liquid partition coefficients

	Rb	Sr	Ba	Sc	Ti	Cr	Co	Ni	La	Eu	Tb
Olivine/liquid	0	0.0004	0	0.35	0.3	1.8	3.8	13	0	0	0.009
Op/liquid	0	0.0004	0	1.2	0.7	2.8	3.2	6.6	0.002	0.01	0.04
Cpx/liquid	0.003	0.1	0.002	3.1	1.3	15	1.5	4	0.07	0.3	0.3
Garnet/liquid	0	0.001	0	?	?	13	1.9	0.8	0.005	0.21	3
Plag/liquid	0.05	1.66	0.3	0.03	0.03	0.04	0.1	0.26	0.1	1.2	0.01
		to 13	(?)							to 0.5	
Spinel/liquid	0	0	0	?	0.8	600	40	16	0.04	0.04	0.04
MgIl/Liquid	0	0	0	1	100	10	3	12	0	0	0
Hb/liquid	0.2	0.3	0.5	2.1	?	6	3.8	12	0.2	1.1	1
Ap/liquid	0	2	0.01	0.22	0		0.001	0	8.6	9.6	15.4

emphasize that we consider this table to be provisional. It must be greatly improved in the future if we want to solve the above problem. In particular, error limits would be purely speculative. Another point is that there is a painful lack of information for some minor minerals such as sulfides, which may play an important role in the partitioning of elements like Cu.

We nevertheless applied our technique since none of these difficulties affects the principles of our method.

IV. A Case Study: The Terceira Island (Azores)

As we have stated above, the prerequisites for sampling and analysis are such that almost no published data is suitable. We chose from our work the trace element analysis for Terceira Island (Azores) to illustrate the method; even these rocks were not sampled expressly for such a systematic treatment and do not satisfy the prerequisites very well. It will be shown however that we can describe the evolution of these volcanic rocks fairly extensively through our method.

The Terceira Island in the Azores is a volcanic island composed of a suite (or several suites) of rocks ranging from basalts to trachytes. We have analyzed 17 elements by neutron activation¹, using the method described by Treuil et al. (1973). Those elements are K, Rb, Sr, Ba, Sc, Ti, Cr, Co, Ni, Zr, Hf, La, Eu, Tb, U, Th, Ta; the results are given in Table 2.

To handle these data by following the principles developed previously, we need an appropriate H element. Following Treuil and Varet (1973), we chose Ta because its bulk partition coefficient is very small and that we have measured its concentration accurately. We have plotted all the other elements versus Ta in logarithmic coordinates, as illustrated in Figure 4.

The correlations in these diagrams are rather good, except for Ba and Sr. The variations of the trace elements form two segments, each being approxi-

¹ Rb, K and Sr have been analyzed by isotope dilution

Table 2. Analytical data for Terceira Island (Azores)

Sample	K ₂ O %	Rb	Sr	Ba	Sc	TiO ₂ %	Cr	Co
T7	0.73		516	251	27.5	2.54		45.2
T9	0.89	21	463	402	26	2.66		44.3
T29		27		448	24.8	3.59	200	31
T28	1.09	26	560	492	22	3.78		32
T4	1.19	30	516	578	25	3.49		
T12	1.42	32		343	20.6	3.65		30
T11	1.57	36	561	451	19.3	3.60		25
T25	1.40	35	676	634	16.3	3.09		21
T18		47		469	13.7	2.79	69	17.3
T17	1.56	44	618	467	14.9	2.64	62	15.9
T16	3.07	79		757	7.5	1.21	57	4
T22	4.32	118		566	3		34	0.44
T24	4.62	156	628	107	2.77	0.53	45	0.73
T27	4.27	132	17	52	3.16	0.54	41	0.39
Errors	±2%	±5%	±0.5%	±15%	±3%	±1%	±8%	±3%

mated by a straight line. The break occurs between samples T4 and T12 on the diagram of Ti, Eu, Sc and possibly Cr. It is not apparent on the diagrams involving La, Tb, Rb, K, Zr and Hf, U and Th and Ni. It separates an earlier sequence of basalts from a later sequence of andesites, trachytes and pantellerites.

The first step corresponds to an increase of Ta, Eu, La, U, Th, alkalines, Ba, Zr, Hf, Tb, Ti and Sr (ordered in decreasing relative variations of their concentrations) and to a decrease of Sc, Co and Ni. During the second sequence, Ti and Eu are now depleted and Sc, Co and possibly Cr change their rate of depletion.

Let us go now into the quantitative treatment of the problem to show first the mineralogical controls and then determine the initial conditions.

Determination of the Mineralogical Control

We determine the bulk partition coefficient of each element by the slopes of the (Log, Log) plots and using a least-squares treatment. They have been compiled in Table 3.

As already noted, the matrix of the mineral-liquid partition coefficients is poorly known. During matrix inversion, the errors can be amplified through propagation, resulting in mineral assemblages incompatible with petrology. We will give here a simplified hand-made resolution of the system. The two sequences will be treated separately.

Sequence 1

Despite the absence of plagioclase phenocrysts, the variation of aluminium concentration (Provost et al., in preparation) necessitates plagioclase precipitation.

Ni	Zr	Hf	La	Eu	Tb	U	Th	Ta
230	152	3.2	24	2.1	0.78	0.45	2.2	1.33
257	169	3.5	31	2.8	0.83	0.48	2.5	1.57
41	175	4.5	41	3.3	1.13	0.67	2.75	2.15
34	227	4.6	42	3.9	1.2		2.85	2.19
75	249	4.8	47		1.25	0.77	3.6	2.26
28	305	6.0	47		1.10	1.05	5	2.7
	271	6.1		4.2		0.86	5.2	2.9
12.4	315	6.6	62	4.9	1.57		4.45	3.13
	426	9.5	72	4.3	1.7	1.9	7.25	3.9
2.5	419	10	76	4.5	1.68	2.2	7.53	4.19
0.1	562	14.1	83	3.8	1.61	1.8	11.06	5.19
	801	23	127	3.3	2.35	3.5	16.32	7.94
	806	24.6	181	2.63	2.67	3	17.5	9.87
0.9	950	27	179	3.2	2.48	5.2	20.5	10.36
± 6%	± 3%	± 3%	± 2%	± 5%	± 3%	± 8%	± 5%	± 3%

Orthopyroxene crystallization is quite uncommon in such alkali series. The case for opaque minerals might be questioned. Thus, we write the following simplified system:

$$\bar{D}^{\text{Ni}} = 12x_{\text{ol}} + 4x_{\text{cpx}}$$

$$\bar{D}^{\text{Sc}} = 0.35x_{\text{ol}} + 3.5x_{\text{cpx}}$$

$$\bar{D}^{\text{Sr}} = 0.1x_{\text{cpx}} + 1.5x_{\text{plag}}$$

$$\bar{D}^{\text{Co}} = 3.8x_{\text{ol}} + 1.5x_{\text{cpx}}$$

$$\bar{D}^{\text{Ti}} = 1.0x_{\text{op}} + 1.2x_{\text{cpx}}$$

ol = olivine

cpx = clinopyroxene

plag = plagioclase

op = opaque minerals, identified to magnetite.

A calculation gives from the two first equations (Ni and Sc) ol 0.29, cpx 0.31. The same result is obtained with Ni and Co. Then, plag and magn can be determined by Sr, Ti and the mineral budget: plag 0.38, magn 0.02. These proportions agree with the proportions determined by the major element data (Provost et al., in preparation). The absence of plagioclase in the phenocrysts is noteworthy and as yet unexplained.

Sequence 2

This sequence illustrates the complexity of the problem. The most apparent difficulty is that Co has a bulk partition coefficient by far larger than any mineral/liquid partition coefficient so far known for this element.

The results can be explained in two ways:

A first one consists in considering that the fractional crystallization process

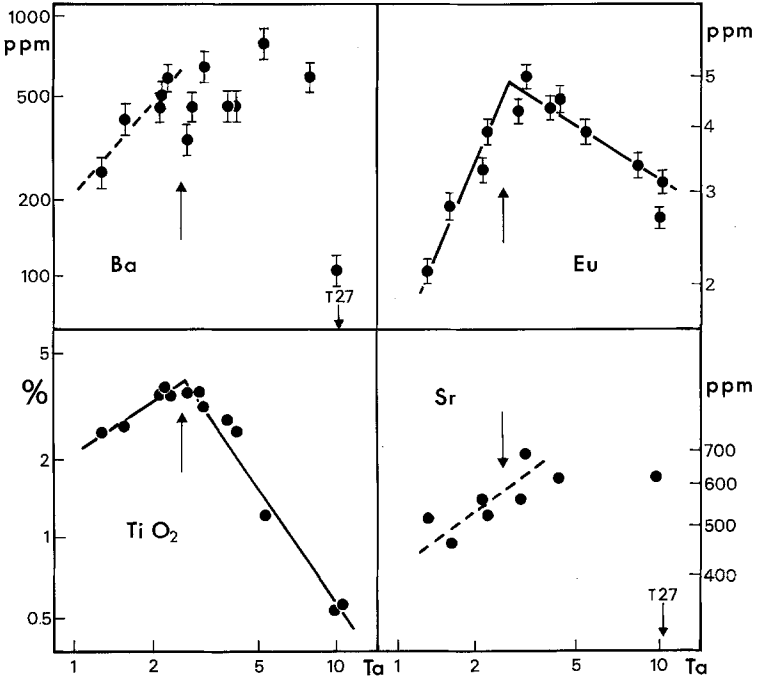
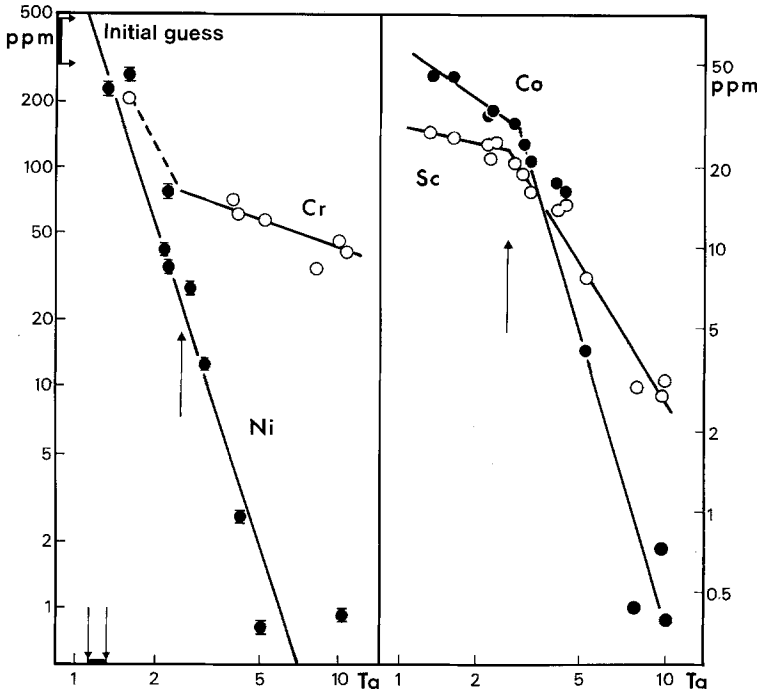


Fig. 4. Logarithmic plot of Ni, Cr, Co and Sc, Ba, Ti, Eu and Sr, K, Rb, U and Th, Zr, Hf, La and Tb against Ta for Terceira Island suite samples. The arrows indicate the approximate position of the change of the bulk partition coefficients. Note on nickel plot the initial guess range values

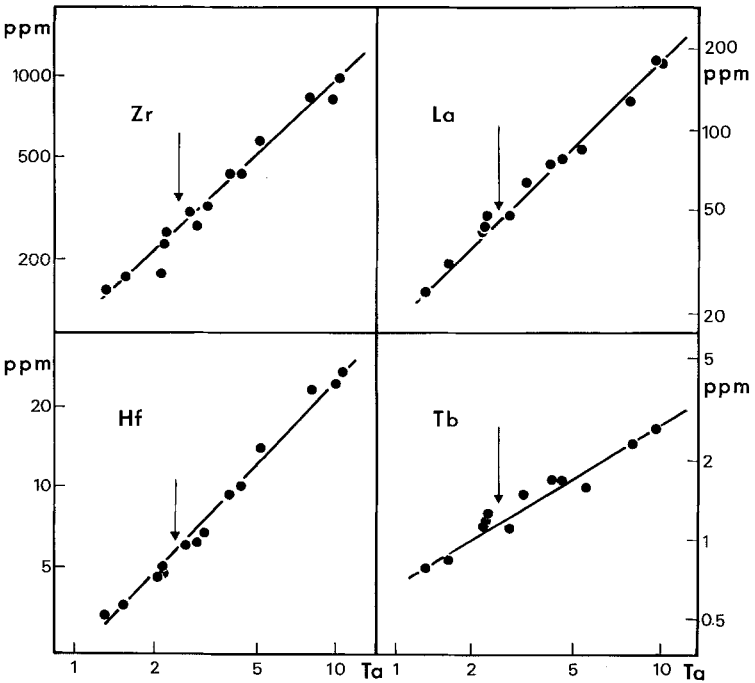
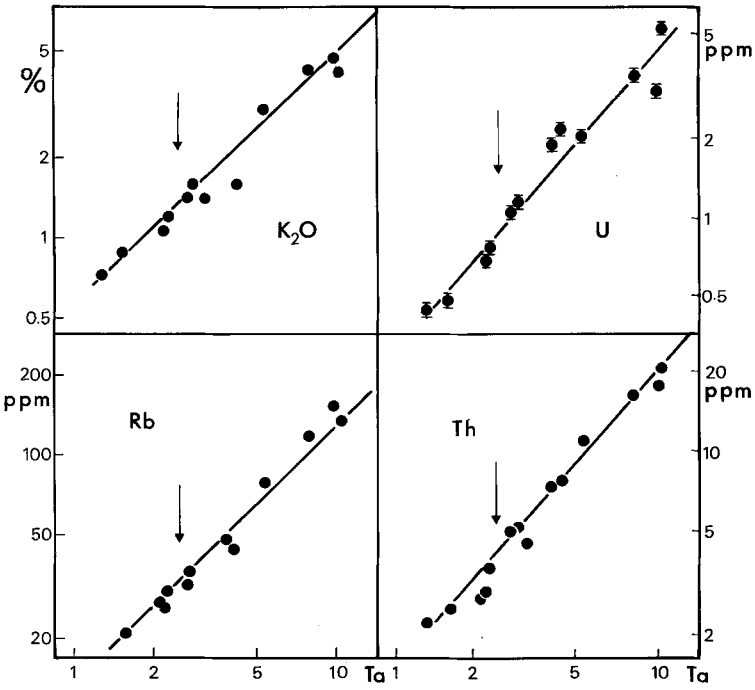


Table 3

	Partition coefficients		Initial concentrations
	1 st sequence	2 nd sequence	
K ₂ O	ϵ	—	0.6 (%)
Rb	ϵ	—	15
Sr	(0.5)	—	(430)
Ba	ϵ	?	240
Sc	1.3	2.9	28
TiO ₂	0.4	2.9	2.3 (%)
Cr	(3)	1.5	(380)
Co	1.8	4.2	51
Ni	4	—	380
Zr	0.1	—	130
Hf	0.1	—	2.6
La	ϵ	—	21
Eu	ϵ	1.3	1.8
Tb	0.2	—	0.7
U	ϵ	—	0.45
Th	ϵ	—	1.8
Ta	ϵ	—	1.15

remains predominant for the trace element variations, and that the incompatibility is related to the partition coefficient values reported in Table 1. Most of these were determined for basic magma, whereas the Fe/Mg ratios of the samples in this sequence are rather high. By comparison with the results of Hart et al. (in preparation) for Ni in olivine, we can assume, for example, that the Co partition coefficient between pyroxene and melt strongly increases when the Fe/Mg ratio of the melt increases, resulting in a higher bulk partition coefficient.

A second explanation would be that a secondary process which cannot be seen by a petrographic examination of the samples, becomes effective in controlling the trace element concentrations. This could be supported by the fact that the slope of the path of Hf and Rb in the (Log, Log) diagram is slightly (although not significantly) higher than one. This process is as yet unknown, but might be for example, contamination by rocks surrounding the magma chamber. That such a process was already present to a lesser extent during the first sequence cannot be ruled out.

This demonstrates the possibilities of such a global analysis of trace elements behavior.

Determination of Parental Magma Concentrations and Description of the Process by f

If we assume 300 to 450 ppm Ni for a primary liquid, we can estimate an initial concentration of Ta of about 1.15 ± 0.1 ppm (see the Ni diagram). From this, we can determine a complete set of initial concentrations (Table 3). We illustrate

Table 4

$K/Rb = 300$
$K/Ba = 20$
$Th/U = 4$
$Ba/La = 11$
$Zr/Hf = 50$

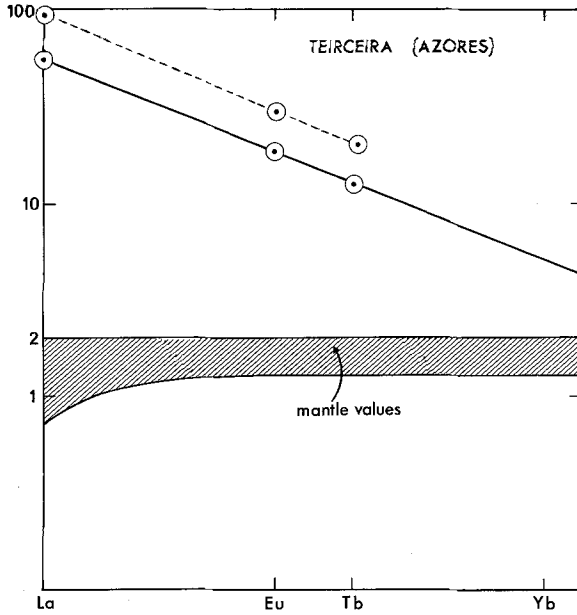


Fig. 5. Chondrite normalized REE diagram for Terceira parental magma. The mantle values are taken from Loubet et al. (1975). Using these values, the degree of partial melting of the primary magma is between 1.2 to 2.5%. Our least differentiated sample (T7) is shown for comparison (dotted line)

these values in a REE diagram (Fig. 5) and a series of ratios which are often used in the geochemical literature (Table 4). We note that the primary magma is similar to our least differentiated sample (T7); if this result is confirmed, it might be possible to sample this magma.

We can now compute the parameter f (weight proportion of residual magma) using the Ta data. For the Terceira volcanism, f varies between about 1 and 0.11. A major break occurs at $f \approx 0.45$.

Summary and Conclusions

We have shown that using several properly chosen trace elements, we can deduce for a sequence of crystallization the principal parameters which describe a sequence. To accomplish this:

1. The sampling should include only aphyric rocks.
2. The sampling should include the entire rock sequence, and in particular, the earlier stage of the differentiation sequence should be sampled with great care.
3. A large number of trace elements is needed, e.g.: Ni and Cr, Co, Sc, Ti or V, Ta, Th, Eu, one light, one heavy REE, Sr, and probably, if we wish to monitor the sulfides, some elements like Cu.
4. We should have a good matrix of mineral/liquid partition coefficients for these elements, and, if possible, the variation of these coefficients with both the composition of the melt and the composition of the minerals. An estimation of the error limits on these coefficients is needed.

In our subsequent paper, we will use the inverse problem technique and information theory to evaluate quantitatively the needs in samples and trace element data.

One of the major conclusions of our study is that we can explain the first differentiation sequence of our example using the Rayleigh distillation law. A second aspect, illustrated by the second sequence, is that a simple differentiation model can be ruled out when the model calculations do not give reasonable results, such as undescribed behavior of some elements, or crystallizing mineral assemblages incompatible with petrology.

However it is also clear that we are in a very primitive stage of the study of the evolution of trace element behavior in a magma chamber. We now need a better sampling procedure as well as more precise analytical data. Such improvements will in turn induce new developments of the models.

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