

PROCEDURES FOR THE CALCULATION OF AXIAL RATIOS ON PEARCE ELEMENT-RATIO DIAGRAMS

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ABSTRACT

The derivation of ratios for plotting on Pearce element-ratio diagrams is facilitated by casting the problem in terms of linear algebra. Two types of systems of linear equations result: systems of homogeneous equations and systems of non-homogeneous equations. Systems of homogeneous equations with a rank less than the number of chemical elements in the ratios lead to diagrams that can test whether chemical variations in a suite of rocks can be explained by sorting of a particular assemblage of minerals. Systems of nonhomogeneous equations with ranks less than or equal to the number of elements in the ratios lead to diagrams that can test whether an individual mineral in a postulated assemblage is required to explain the chemical variations in a suite of rocks. The method of choice for finding the solutions to the systems of equations, which are the coefficients of the chemical elements in the ratios, is singular-value decomposition.

Keywords: Pearce element-ratios, linear algebra, singular-value decomposition, chemical variations, testing hypotheses, igneous petrology.

SOMMAIRE

La dérivation de rapports d'éléments pour la conception de diagrammes de Pearce est facilitée par la formulation du problème en termes d'algèbre linéaire. Deux types de systèmes d'équations linéaires en résultent, soit des systèmes d'équations homogènes et d'autres, d'équations non homogènes. Les systèmes d'équations homogènes ayant un rang moins élevé que le nombre d'éléments chimiques dans les rapports mènent à des diagrammes visant à évaluer si les variations chimiques exprimées dans une suite de roches ignées peuvent s'expliquer par le triage d'un assemblage spécifié de minéraux. Les systèmes d'équations non homogènes ayant un rang plus petit ou égal au nombre d'éléments dans ces rapports mènent à des diagrammes pouvant vérifier l'hypothèse qu'un minéral particulier d'un assemblage proposé est nécessaire pour expliquer la variation dans la composition d'une suite de roches ignées. La méthode préférée pour trouver les solutions à ces systèmes d'équations, qui sont les coefficients des éléments chimiques dans ces rapports, serait la décomposition à valeur singulière.

(Traduit par la Rédaction)

Mots-clés: rapports d'éléments de Pearce, algèbre linéaire, décomposition à valeur singulière, variations chimiques, hypothèses pétrogénétiques, pétrologie ignée.

INTRODUCTION

Pearce element-ratio diagrams (Pearce 1968) are designed to test hypotheses relating the compositions of samples of a rock suite. There is an extensive literature on the application of Pearce element-ratio diagrams to the solution of petrological problems (see Nicholls & Russell 1990, Chapter 2, for a bibliography through 1988). Ernst *et al.* (1988) provided additional examples of the application of Pearce element-ratio diagrams. To make these tests, diagrams that account for the stoichiometry of the phases involved in the mass exchanges that led to the compositional variability are needed. Consequently, a common problem for users of Pearce element-ratio diagrams arises in the design of the ratios for plotting on the axes of the diagrams. Because each suite of

rocks is unique, the ratios to be plotted may also be unique.

For example, suppose the following hypothesis: *The chemical variations in an igneous rock suite are due to the sorting of olivine with compositions represented by $(\text{Mg,Fe})_2\text{SiO}_4$, plagioclase with compositions between albite ($\text{NaAlSi}_3\text{O}_8$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), and clinopyroxene [$\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$].* A diagram is required with axial ratios having the property such that if the hypothesis is false, then the data will not fall on a line with a given slope. Usually, the given slope is set to unity. A pair of ratios that can produce such a diagram are:

$$\begin{aligned} \text{X/K} &= \text{Si/K} \\ \text{Y/K} &= \\ & (0.25 \text{ Al} + 0.5 \text{ FM} + 1.5 \text{ Ca} + 2.75 \text{ Na})/\text{K} \end{aligned} \quad (1)$$

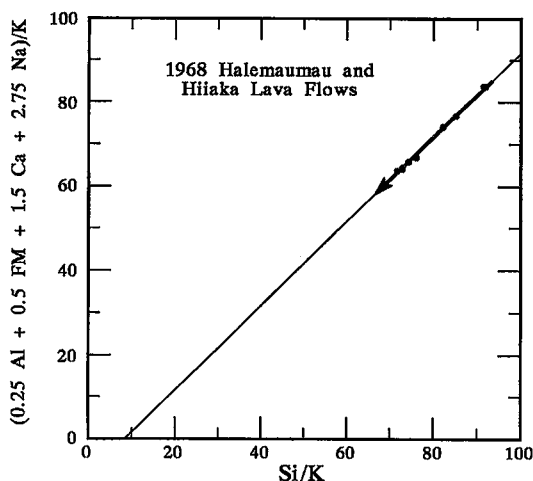


FIG. 1. A Pearce element-ratio diagram designed to test whether the chemical variations in a suite of lava flows from Kilauea Volcano (Wright 1971, Jackson *et al.* 1975, Nicholls & Stout 1988) can be the result of sorting (fractionation and accumulation) of olivine, plagioclase and clinopyroxene. The arrow indicates the trend that the data should follow if fractionation of olivine, plagioclase and clinopyroxene caused the chemical variations in the rocks.

where FM is equal to Fe + Mg. Potassium is chosen as the denominator of the ratios because, by hypothesis, it is a conserved element and does not enter any of the sorted phases invoked by the hypothesis being tested. **X** and **Y** are vectors of the coefficients of the elements that appear in the numerators of the ratios that are plotted on the X axis and Y axis, respectively. Figure 1 shows an example of such a diagram. It is drawn with data from lava flows of the 1968 eruption of Kilauea (Wright 1971, Jackson *et al.* 1975, Nicholls & Stout 1988). One can check that this diagram will produce a line with a slope of one for each of the phases in the mineral assemblage invoked by the hypothesis by calculating, for each phase, the ratios of the components of **X** to those of **Y**:

Olivine:

$$\mathbf{X}/\mathbf{Y} = 1 \text{ Si}/(0.5 \times 2 \text{ FM}) = 1/1 \quad (2)$$

Albite:

$$\mathbf{X}/\mathbf{Y} = 3 \text{ Si}/(0.25 \text{ Al} + 2.75 \text{ Na}) = 3/3 \quad (3)$$

Anorthite:

$$\mathbf{X}/\mathbf{Y} = 2 \text{ Si}/(0.25 \times 2 \text{ Al} + 1.5 \text{ Ca}) = 2/2 \quad (4)$$

Clinopyroxene:

$$\mathbf{X}/\mathbf{Y} = 2 \text{ Si}/(1.5 \text{ Ca} + 0.5 \text{ FM}) = 2/2 \quad (5)$$

Note that end members of the plagioclase series are used separately whereas the end members of the olivine series are combined. The coupled substitution

of Na and Si for Ca and Al makes it impossible to combine the plagioclase end-members into one formula that can represent all plagioclase compositions.

The objective of this note is to provide a systematic method of determining the coefficients for the elements in the ratios (*e.g.*, the numbers: 0.25, 0.5, 1.5 and 2.75 in **Y** and 1.0 in **X**). Stanley & Russell (1989) expressed the problem of finding the ratios for plotting on the axes of diagrams with matrices and linear algebra. They found solutions to the matrix equations by arbitrarily partitioning the matrices such that a determined set of simultaneous equations resulted; there were as many equations as unknowns. Practically, users of their procedure sometimes had to resort to trial-and-error searches to find all the solutions in chemically complex systems. Users could spend considerable time searching for solutions without finding a useful one. The procedures described in this note find all the solutions to the stated problem and reveal immediately where there are no useful ones.

MATRIX FORMULATION: HOMOGENEOUS EQUATIONS

The problem of determining the ratios for the axes of Pearce element-ratio diagrams can be formulated in terms of matrix algebra (Stanley & Russell 1989). The variables in the equations are schematically illustrated on Figure 2, and the general equation, with terms that are matrices, can be written:

$$\mathbf{C} \cdot \mathbf{A} = \mathbf{P} \quad (6)$$

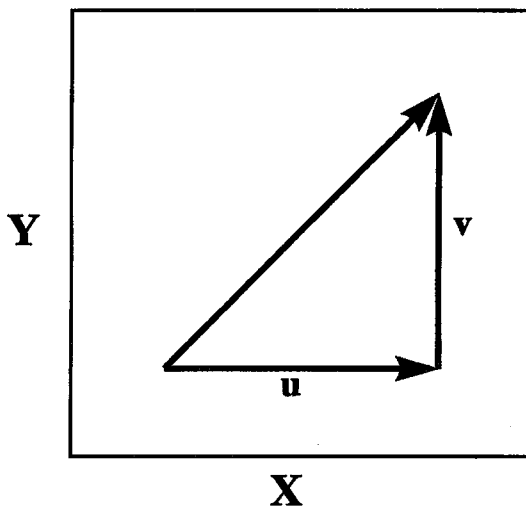


FIG. 2. Schematic diagram showing the notation and relationship of the variables in Eqn. (7).

where C is the $(M \times N)$ matrix of known compositions of phases. M is the number of phases in the system (e.g., $M = 4$ for the assemblage olivine, albite, anorthite and clinopyroxene). N is the number of distinct elements in the phases being sorted (e.g., $N = 5$ in our example: Si, Al, Fe + Mg, Ca, and Na). Note that the rows of C are the compositions of the phases, and the columns correspond to the elements in each phase. A is an $(N \times 2)$ matrix of unknown coefficients of the elements that appear in the numerators of the ratios (e.g., the numbers: 0.25, 0.5, 1.5 and 2.75 in Y and 1.0 in X). The matrix P is an $(M \times 2)$ matrix whose column vectors of length M are the displacement vectors and are symbolized as u and v . The elements of u and v are constrained by the slope of the line required by the hypothesis and are chosen to meet the constraints. In order to construct a Pearce element-ratio diagram, the elements of the vectors that constitute the matrix A (the vectors X and Y) are required. In the general case, these vectors are unknown and are to be determined. The vectors X and Y are the columns of A . For our example, the matrix equation can be written:

$$\begin{array}{c|ccccc} & \text{C} & & \text{A} & & \text{P} \\ & \text{Si Al FM Ca Na} & & & & \\ \hline \text{An} & 2 & 2 & 0 & 1 & 0 & \left| \begin{array}{c} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \end{array} \right. & \left| \begin{array}{c} Y_1 \\ Y_2 \\ Y_3 \\ Y_4 \\ Y_5 \end{array} \right. & = & \left| \begin{array}{c} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \end{array} \right. & \left| \begin{array}{c} v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_5 \end{array} \right. \\ \text{Ab} & 3 & 1 & 0 & 0 & 1 & \\ \text{Ol} & 1 & 0 & 2 & 0 & 0 & \\ \text{Cpx} & 2 & 0 & 1 & 1 & 0 & \end{array} \quad (7)$$

Because the two matrices, A and P , each consist of two column vectors, the last equation [Eqn. (7)] can be split into two equations:

$$C \cdot X = u \quad (8)$$

$$C \cdot Y = v \quad (9)$$

If the desired slopes for all phases represented by the displacement vectors are one (an assemblage test diagram: Stanley & Russell 1989), then the constraints on the slopes as reflected in the displacement vectors, u and v , can be written:

$$u = v \quad (10)$$

hence:

$$C \cdot (X - Y) = 0 \quad (11)$$

Theories in linear algebra show that if a system of homogeneous linear equations, such as Eqn. (11), has a family of solutions in addition to and different from the trivial solution:

$$X - Y = 0 \quad (12)$$

then the rank of C must be less than N (e.g., Ayres 1962). If the number of phases, M , is less than the number of elements in the phases, N , then the rank of C must be less than N . The elements of the solution vectors to Eqn. (11) can be normalized, if desired, so that the coefficient of at least one of the chemical elements in the numerator of the X-axis ratio, say, is equal to one.

Singular-value decomposition (SVD) is a method of solving systems of linear equations, determining the ranks of matrices, and finding solutions to systems of homogeneous equations such as Eqn. (11). The method has been used by petrologists to determine the number of independent components in a mineral assemblage and mass balances (homogeneous equations) relating mineral compositions (Fisher 1989, 1994, Gordon *et al.* 1991). The theoretical basis for the method was derived by Golub & Van Loan (1991, p. 70 and following), and the algorithm and routines for performing the calculations are described by Press *et al.* (1989). Gordon *et al.* (1991) provided a brief description of the use of the method to determine the rank of a matrix. SVD is particularly useful for the problem at hand because the method will always find at least one solution to a set of simultaneous equations. The set can be underdetermined (have fewer equations than unknowns), be exactly determined (have same number of equations as unknowns), or be overdetermined (have more equations than unknowns). In the first case, the only solution may be the trivial one, but where there are nontrivial solutions, the method will find them. In the last case, the solution will be a least-squares solution.

The rank of the matrix C in our example [Eqn. (7)] is four; hence, because there are five unknowns, there is one independent solution-vector in the family of solutions (Press *et al.* 1989). Suppose, however, that the hypothesis called for only three phases or end members: olivine, albite and anorthite. The system of equations then becomes:

$$\begin{array}{c|ccccc} & \text{C} & & \text{A} & & \text{P} \\ & \text{Si Al FM Ca Na} & & & & \\ \hline \text{An} & 2 & 2 & 0 & 1 & 0 & \left| \begin{array}{c} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \end{array} \right. & \left| \begin{array}{c} Y_1 \\ Y_2 \\ Y_3 \\ Y_4 \\ Y_5 \end{array} \right. & = & \left| \begin{array}{c} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \end{array} \right. & \left| \begin{array}{c} v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_5 \end{array} \right. \\ \text{Ab} & 3 & 1 & 0 & 0 & 1 & \\ \text{Ol} & 1 & 0 & 2 & 0 & 0 & \end{array} \quad (13)$$

In vector form, the two solutions to the matrix equation [Eqn. (13)] returned by singular-value decomposition are:

$$\begin{array}{cc} & (X - Y)_1 & (X - Y)_2 \\ \text{Si} & 1.0 & 0.0 \\ \text{Al} & -1.167 & 1.0 \\ \text{FM} & -0.5 & 0.0 \\ \text{Ca} & 0.333 & -2.0 \\ \text{Na} & -1.833 & -1.0 \end{array} \quad (14)$$

Positive values in the solution vectors have been arbitrarily assigned as coefficients of elements in the numerator of the ratio plotted on the X axis, whereas negative values, with the minus sign dropped, have been assigned to coefficients in the numerator of the ratio plotted on the Y axis. The pairs of axial ratios are:

$$\begin{aligned} &(\text{Si} + 0.333 \text{ Ca})/\text{K} \text{ versus} \\ &(1.167 \text{ Al} + 0.5 \text{ FM} + 1.833 \text{ Na})/\text{K} \end{aligned} \quad (15)$$

and

$$\text{Al}/\text{K} \text{ versus } (2 \text{ Ca} + \text{Na})/\text{K} \quad (16).$$

Thus it appears that the number of linearly independent Pearce element-ratio diagrams that can be derived from a matrix of phase compositions, C , is equal to the number of columns in the matrix, N , minus the rank of the matrix, a number called the nullity of the matrix.

Any linear combination of the two vectors [Eqn. (14)] also is a solution of the matrix equation and provides a set of ratios for a Pearce element-ratio diagram. For example, if $1.833(\mathbf{X} - \mathbf{Y})_2$ is subtracted, element by element, from $(\mathbf{X} - \mathbf{Y})_1$, the result is:

	$(\mathbf{X} - \mathbf{Y})_{2-1}$	
Si	1.0	
Al	-3.0	
FM	-0.5	
Ca	4.0	(17)
Na	0.0	

This linear combination can be cast into a pair of ratios:

$$(\text{Si} + 4 \text{ Ca})/\text{K} \text{ versus } (3 \text{ Al} + 0.5 \text{ FM})/\text{K} \quad (18)$$

a pair that will define a trend with a slope of one if the chemical variations are caused by sorting olivine and plagioclase.

Nontrivial solution-vectors of the homogeneous equations are the differences between the elements of the columns of the matrix $(\mathbf{X} - \mathbf{Y})$. Individual values for the components of $\mathbf{X}$ and $\mathbf{Y}$ are required for a Pearce element-ratio plot, however. The components of a solution vector can be arbitrarily partitioned into components of the $\mathbf{X}$ and $\mathbf{Y}$ vectors provided only that their differences equal the components of the solution vector in question. In the example whose result is given by Eqn. (15), the vector difference, normalized to $\Delta\text{Si} = 1$, is:

ΔSi :	$\mathbf{X}_{\text{Si}} - \mathbf{Y}_{\text{Si}} =$	1.000	
ΔAl :	$\mathbf{X}_{\text{Al}} - \mathbf{Y}_{\text{Al}} =$	-1.167	
ΔFM :	$\mathbf{X}_{\text{FM}} - \mathbf{Y}_{\text{FM}} =$	-0.500	(19)
ΔCa :	$\mathbf{X}_{\text{Ca}} - \mathbf{Y}_{\text{Ca}} =$	0.333	
ΔNa :	$\mathbf{X}_{\text{Na}} - \mathbf{Y}_{\text{Na}} =$	-1.833	

The coefficients of the chemical elements used to construct the ratio pair for Eqn. (15) were arbitrarily

partitioned into the $\mathbf{X}$ and $\mathbf{Y}$ vectors by setting:

$$\mathbf{Y}_i = 0 \text{ if } (\mathbf{X}_i - \mathbf{Y}_i) > 0 \quad (20)$$

and

$$\mathbf{X}_i = 0 \text{ if } (\mathbf{X}_i - \mathbf{Y}_i) < 0 \quad (21).$$

These criteria are arbitrary because the only requirement is that the two vectors sum to zero. Consequently, an equally valid diagram with which to test the hypothesis can be obtained by setting $\Delta\mathbf{X}_{\text{Ca}} = 0$, say, with the result that the ratio pair:

$$\text{Si}/\text{K} \text{ versus } (1.167 \text{ Al} + 0.5 \text{ FM} - 0.333 \text{ Ca} + 1.833 \text{ Na})/\text{K} \quad (22)$$

will provide the same test of the hypothesis.

Again, the validity of these ratios, given the hypothesis that variations are due to sorting of plagioclase and olivine, can be checked by calculating the ratios of the numerators for each phase or end member:

$$\text{Ab: } (1.167 \text{ Al} + 1.833 \text{ Na})/(3 \text{ Si}) = 3/3 \quad (23)$$

$$\text{An: } (2 \times 1.167 \text{ Al} - 0.333 \text{ Ca})/(2 \text{ Si}) = 2/2 \quad (24)$$

$$\text{Ol: } (2 \times 0.5 \text{ FM})/(1 \text{ Si}) = 1/1 \quad (25)$$

Figure 3 shows schematically why a shift of the coefficient of an element from one numerator to the other while changing the sign does not change the nature of the Pearce element-ratio diagram.

Deleting $\text{Ca}/3$ from $\mathbf{u}$ and subtracting $\text{Ca}/3$ from $\mathbf{v}$ shortens both vectors by the same amount. Thus, the vector sum of the new vectors, $\mathbf{u}'$ and $\mathbf{v}'$ (Fig. 3), will have the same slope as the vector sum of the original vectors, $\mathbf{u}$ and $\mathbf{v}$. Note, also, that the entire coefficient need not be transferred from one axis to the other. The same element can appear on both axes with different coefficients without changing the properties of the diagram.

Generally, if the number of phases, M , is equal to the number of elements, N , the rank of C will also equal N . In most such instances, the set of homogeneous equations:

$$C \cdot (\mathbf{X} - \mathbf{Y}) = 0 \quad (11)$$

will only have the trivial solution $(\mathbf{X} - \mathbf{Y}) = 0$ or, in other words, the X -axis ratio is the same as the Y -axis ratio. This will produce a plot with a perfect straight line, but it will also contain no information. Exceptions occur if the rank of the coefficient matrix is less than N . If the composition of one (or more) of the phases is a linear combination of some of the other phases, then the rank of C will be less than N .

Suppose, for example, the hypothesis that the variations are due to sorting of plagioclase, clinopyroxene, olivine, ulvöspinel and apatite. The number of phases

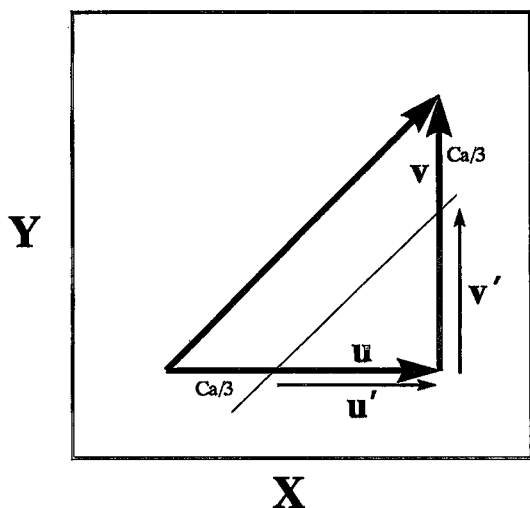


FIG. 3. Schematic diagram showing the effect of moving an element, Ca, from the numerator on the X axis to the numerator on the Y axis.

or end members, M , is 8: An, Ab, Fo, Fa, Di, Hd, Usp, and Ap. The number of elements to be placed in the ratios, N , also is 8: Si, Ti, Al, Fe, Mg, Ca, Na, and P. The rank of the coefficient matrix, C , is less than 8 because there is a linear combination relating the compositions of four of the end members:

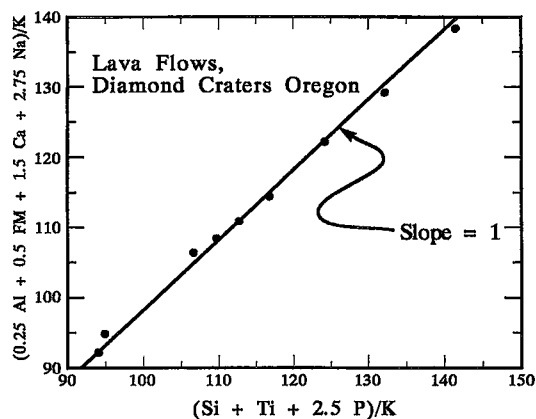
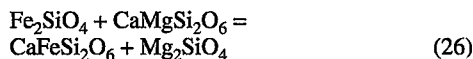


FIG. 4. Pearce element-ratio diagram derived for a phase-composition matrix with N phases (end members) and N elements. The rank of the composition matrix is less than N because of the linear dependence of some of the phases (end members). Data from Russell & Nicholls (1987).

The following ratios will provide a slope of one on a Pearce element-ratio diagram if the variations are due to sorting of plagioclase, clinopyroxene, olivine, ulvöspinel and apatite:

$$(0.25 \text{ Al} + 0.5 \text{ FM} + 1.5 \text{ Ca} + 2.75 \text{ Na})/\text{K} \text{ versus } (\text{Si} + \text{Ti} + 2.5 \text{ P})/\text{K} \quad (27)$$

An example based on this pair of ratios is shown on Figure 4.

The discussion up to this point has been for the case of displacement vectors of equal length and of the same sign. These properties are the ones that make the linear equations homogeneous and also permit elements to be transferred from one numerator to the other with a change in sign.

MATRIX FORMULATION: NONHOMOGENEOUS EQUATIONS

If one wishes to test whether an additional phase also was being sorted by the processes causing the chemical variations, or if the slope of the trend needed to test a hypothesis is not unity, then the displacement vectors will not be equal [*i.e.*, Eqn. (10) will not apply]. As a result, the right-hand side of Eqn. (11) will not be a zero vector, and the system of equations will not be homogeneous, a feature that may make the determination of the ratios more difficult.

Suppose, for instance, we wish to test whether sorting of clinopyroxene is required in addition to sorting of olivine and plagioclase to explain the chemical variations in a suite of rocks. Clinopyroxene [$\text{Ca}(\text{Mg},\text{Fe})\text{Si}_2\text{O}_6$] is then called a rival phase (Stanley & Russell 1989).

The object is to devise a diagram that will produce the greatest divergence of the data from a slope of one if clinopyroxene is sorted as well as olivine and plagioclase. This greatest divergence will occur if the displacement vector for clinopyroxene is at right angles to the displacement vectors for olivine and plagioclase (a phase-displacement test diagram: Stanley & Russell 1989). Such a diagram is shown on Figure 5. The ratios plotted on the axes are:

$$\text{Si}/\text{K} \text{ versus } (2.25 \text{ Al} + 0.5 \text{ FM} - 2.5 \text{ Ca} + 0.75 \text{ Na})/\text{K} \quad (28)$$

The components of the displacement vectors for clinopyroxene (Cpx) must be such that a slope of -1 results for the Cpx-vector on a Pearce element-ratio diagram. Such a feature will occur if $\mathbf{u}_{\text{Cpx}} = -\mathbf{v}_{\text{Cpx}}$.

If we assign the coefficients of the elements in the numerator of the left-hand ratio to X and the coefficients of the elements in the numerator of the right-hand ratio [Eqn. (28)] to Y , then one can show that the resulting vectors satisfy the equation:

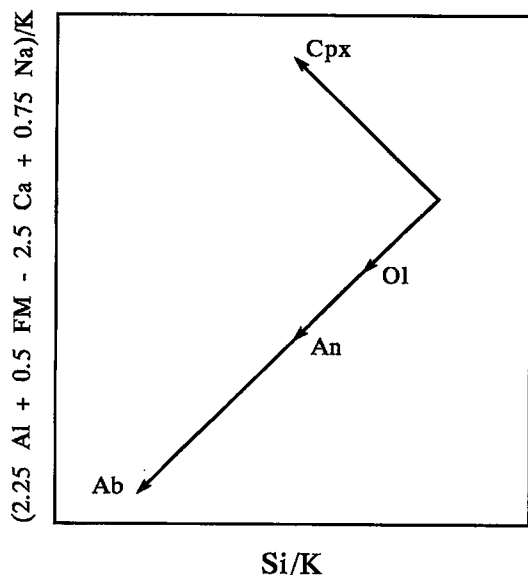


FIG. 5. Schematic diagram showing displacement vectors to test whether clinopyroxene is part of a sorting assemblage that also includes plagioclase and olivine. Symbols: Ab albite, An anorthite, Cpx clinopyroxene, Ol olivine.

$$\begin{array}{c} \mathbf{C} \quad \mathbf{A} \quad \mathbf{P} \\ \text{Si} \quad \text{Al} \quad \text{FM} \quad \text{Ca} \quad \text{Na} \\ \text{Ab} \begin{vmatrix} 3 & 1 & 0 & 0 & 1 \\ 2 & 2 & 0 & 1 & 0 \\ 1 & 0 & 2 & 0 & 0 \\ 2 & 0 & 1 & 1 & 0 \end{vmatrix} \begin{vmatrix} \mathbf{X}_1 & \mathbf{Y}_1 \\ \mathbf{X}_2 & \mathbf{Y}_2 \\ \mathbf{X}_3 & \mathbf{Y}_3 \\ \mathbf{X}_4 & \mathbf{Y}_4 \\ \mathbf{X}_5 & \mathbf{Y}_5 \end{vmatrix} = \begin{vmatrix} 3 & 3 \\ 2 & 2 \\ 1 & 1 \\ 2 & -2 \end{vmatrix} \end{array} \quad (29)$$

Note that the components of the column vectors corresponding to clinopyroxene have opposite signs. The magnitudes of the components of $\mathbf{P}$ were set to the number of moles of Si in the formulae of the corresponding end-members or phases. Again, because of equality in number of elements in the vectors $\mathbf{X}$ and $\mathbf{Y}$ and in the vectors $\mathbf{u}$ and $\mathbf{v}$, this last equation can be written as two:

$$\mathbf{C} \cdot \mathbf{X} = \mathbf{u} \quad (30)$$

$$\mathbf{C} \cdot \mathbf{Y} = \mathbf{v} \quad (31)$$

The coefficients for the $\mathbf{X}$ and $\mathbf{Y}$ vectors for the nonhomogeneous system of equations can be extracted by solving for $\mathbf{X}$ and $\mathbf{Y}$ separately. Solving Eqn. (31) will provide the coefficients for the numerator of the ratio plotted on the X axis, whereas solving Eqn. (30) provides the coefficients for the Y ratio. These two equations are, in general, enough to give a pair of ratios with the desired properties. However, the results commonly are complex.

In part, this complexity arises because the systems of equations [Eqns. (30) and (31)] usually have more unknowns than equations. Consequently, the solutions of the two systems will not be unique; rather, there will be an $(N - M)$ -dimensional family of solutions (Press *et al.* 1989). Because the solutions are not unique, we can commonly rearrange the coefficients in a simpler pattern.

For example, suppose we wish to test whether chemical variations in a suite of rocks can be explained by sorting of plagioclase and clinopyroxene without involving olivine. A matrix equation that reflects this hypothesis is:

$$\begin{array}{c} \mathbf{C} \quad \mathbf{A} \quad \mathbf{P} \\ \text{Si} \quad \text{Al} \quad \text{FM} \quad \text{Ca} \quad \text{Na} \\ \text{Ab} \begin{vmatrix} 3 & 1 & 0 & 0 & 1 \\ 2 & 2 & 0 & 1 & 0 \\ 1 & 0 & 2 & 0 & 0 \\ 2 & 0 & 1 & 1 & 0 \end{vmatrix} \begin{vmatrix} \mathbf{X}_1 & \mathbf{Y}_1 \\ \mathbf{X}_2 & \mathbf{Y}_2 \\ \mathbf{X}_3 & \mathbf{Y}_3 \\ \mathbf{X}_4 & \mathbf{Y}_4 \\ \mathbf{X}_5 & \mathbf{Y}_5 \end{vmatrix} = \begin{vmatrix} 3 & 3 \\ 2 & 2 \\ 1 & -1 \\ 2 & 2 \end{vmatrix} \end{array} \quad (32)$$

A pair of solution vectors for this system can be obtained by singular-value decomposition. They are:

$$\begin{array}{c} \mathbf{X} \quad \mathbf{Y} \\ \text{Si} \begin{vmatrix} 1.1124 & 0.9101 \\ -0.5281 & 0.0225 \\ -1.0562 & 0.0449 \\ 0.8315 & 0.1348 \\ 0.1910 & 0.2472 \end{vmatrix} \end{array} \quad (33)$$

As was done earlier, it is a simple matter to calculate the slope expected from sorting each of the end members or phases (see p. 4):

$$\begin{array}{l} \text{Ab: } 3/3 = 1 \\ \text{An: } 2/2 = 1 \\ \text{Ol: } 1/-1 = -1 \\ \text{Cpx: } 2/2 = 1 \end{array} \quad (34)$$

The pair of ratios that tests the hypothesis are:

$$\begin{array}{l} (1.1 \text{ Si} - 0.525 \text{ Al} - 1.05 \text{ FM} + 0.85 \text{ Ca} \\ + 0.225 \text{ Na})/K \text{ versus} \\ (0.9 \text{ Si} + 0.025 \text{ Al} + 0.05 \text{ FM} + 0.15 \text{ Ca} \\ + 0.275 \text{ Na})/K \end{array} \quad (35)$$

These ratios can be simplified if the rank of the coefficient matrix is less than N . In our example, the rank of $\mathbf{C}$ is 4, whereas N is equal to 5. Consequently, there is a nontrivial solution to the companion homogeneous system of equations:

$$\mathbf{C} \cdot \mathbf{A} = 0 \quad (36)$$

For our example, the solution to the homogeneous system is:

Si	-0.2998	(37)
Al	0.0750	
FM	0.1499	
Ca	0.4497	
Na	0.8245	

We can add a linear combination of the solutions to the homogeneous system to the solution to the companion nonhomogeneous system, and the result will also be a solution to the nonhomogeneous system. In the present example, we can calculate new vectors, X' and Y' , such that the coefficient of Si, say, is equal to one in each axial ratio. This operation is accomplished by adding 0.37492 times the vector in Eqn. (37) to X , and -0.29987 times the vector in Eqn. (37) to Y [Eqn. (33)]. The result, after accounting for round-off error is:

$$(Si - 0.5 Al - FM + Ca + 0.5 Na)/K \text{ versus } Si/K \quad (38)$$

Even if the rank of the coefficient matrix is equal to N , we can re-arrange the coefficients by moving them from one ratio to the other as long as the element appears ONLY in the formulae of phases or end members for which we require slopes of one. In this particular example, Na, Ca, and Al do not occur in the rival phase, olivine. Consequently, these elements could be transferred, with a change in sign, from the X -axis to the Y -axis ratio. In this way, we get a slightly simpler-appearing pair of ratios that still has the same ability to test the hypothesis as Eqn. (38):

$$(1.1 Si - 1.05 FM)/K \text{ versus } (0.9 Si + 0.55 Al + 0.05 FM - 0.7 Ca + 0.05 Na)/K \quad (39)$$

INCORPORATING MINERAL CHEMISTRY IN PEARCE ELEMENT-RATIO DIAGRAMS

Pearce element-ratios are usually calculated for the stoichiometry of ideal mineral formulae or end members. The compositions of minerals actually sorted in rock-forming processes deviate to a greater or lesser extent from the compositions of end members. At best, these deviations will cause small amounts of scatter from the predicted trends on Pearce element-ratio diagrams. At worst, they can produce significant deviations from the predicted trends.

Real minerals, for example, contain defects, minor amounts of trace elements and can show more complex substitutions, such as Al_2 for $MgSi$. Two commonly occurring minerals in mafic rocks, olivine and plagioclase, do not differ sufficiently from the ideal formulae to cause scatter that exceeds that from analytical uncertainty. Listed in Table 1 are the slopes expected for ideal solid-solutions. Also shown are the slopes calculated from compositions of minerals from

TABLE 1. RATIOS IN MINERALS

	Ideal Cases	(Fe + Mg)/Si	
	Formula		
Olivine	$(Mg,Fe)_2SiO_4$	2	
Orthopyroxene	$(Mg,Fe)_2Si_2O_6$	1	
Clinopyroxene	$Ca(Mg,Fe)Si_2O_6$	1/2	
Fe-Ti Spinel	$Fe(Fe,Ti)_2O_4$	Infinity	
Fe-Ti Rhombohedral	$Fe(Fe,Ti)O_3$	Infinity	
	Formula	(2 Ca + Na)/Al	
Plagioclase	$NaAlSi_3O_8 - CaAl_2Si_2O_8$	1	
Clinopyroxene	$Ca(Mg,Fe)Si_2O_6$	Infinity	
Measured Mineral Compositions			
	(Fe + Mg)/Si Slope	Slope in deg	(Ideal)
Olivine	1.980 ± 0.033	$63.2^\circ \pm 0.4^\circ$	(63.4°)
Augite	0.638 ± 0.037	$32.4^\circ \pm 1.5^\circ$	(26.6°)
	(2 Ca + Na)/Al Slope	Slope in deg	(Ideal)
Plagioclase	1.054 ± 0.015	$46.4^\circ \pm 0.4^\circ$	(45.0°)
Augite	13.473 ± 3.347	$85.8^\circ \pm 1.2^\circ$	(90.0°)

Averages and standard deviations calculated from results of 15 analyses of each mineral group.

basaltic rocks. The worst case is an error in slope of 4° for an augite with considerable (Al + Ti) per six oxygen atoms in solid solution. If the sorted assemblage contains minerals of more variable stoichiometry, such as amphibole, then the deviations from the slopes expected for ideal compositions may be more extreme.

The problems of variable mineral chemistry can, in some cases, be overcome by using mineral compositions directly in the element ratios. To introduce chemical compositions into Pearce element-ratios, simply enter the cation numbers from the structural formulae into the composition matrix, C . As an example, Figure 6 shows some Pearce element-ratio diagrams for the 1955 lava flows from Kilauea Volcano, Hawaii. Figure 6a is a diagram that should display a trend with a slope of one if the chemical variations in the rock suite can be accounted for by the sorting of olivine, plagioclase, ideal clinopyroxene, $Ca(Mg,Fe)Si_2O_6$, and a magnetite-ulvöspinel solid solution, Usp_{75} . There is considerable scatter of the data about a line with a slope of one, and at least one uncertainty ellipse does not overlap the expected uncertainty about the line (shaded area). The scatter could be due to sorting of orthopyroxene, which would generate a slope of $1/2$ on the diagram or, possibly, the scatter is due to sorting of augite (Aug, Fig. 6) with some solid solution other than Fe for Mg. The slope for augite and the ratios plotted on Figures 6c and 6d were calculated from a composition of an augite from the 1955 lava flow (Ho & Garcia 1988, Table 2, p. 40, sample 2). The formula entered into the phase-composition matrix, C , was calculated with the program written by Cebriá Gómez (1990) after deleting the value of Cr_2O_3 from the analytical data. As shown, an augite with the composition of phenocrysts in the lava would generate a steeper slope and

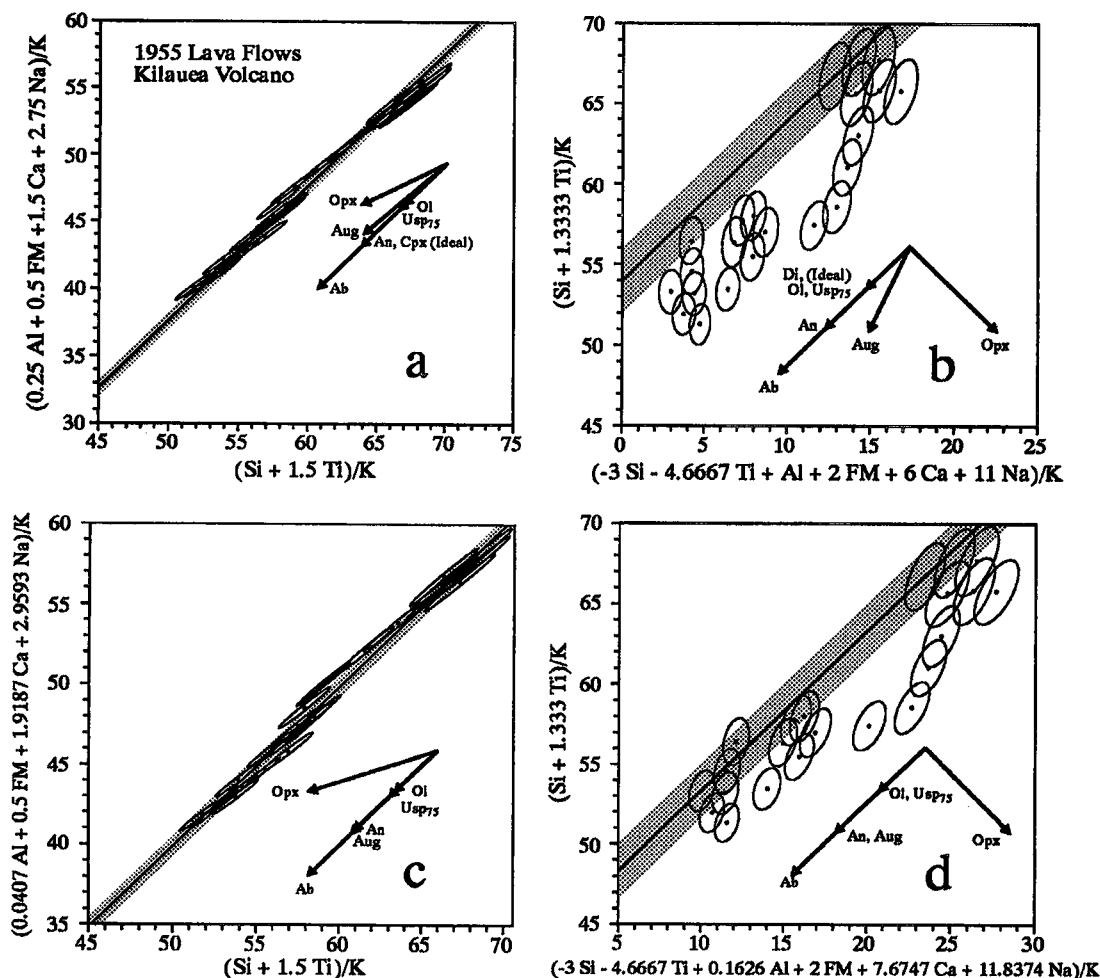


FIG. 6. Pearce element-ratio diagram testing whether orthopyroxene (Opx) is part of the sorted assemblage. Data from Macdonald & Eaton (1964), Wright & Fiske (1971). Symbols: Ab albite, An anorthite, Cpx (ideal) $\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$, Ol olivine, Usp ulvöspinel, Aug augite (Ho & Garcia 1988).

might be the cause of the scatter. The expected slope from sorting such a pyroxene is less than one (Fig. 6a). Figure 6b shows a diagram with orthopyroxene as a rival phase. In order to ensure that the scatter from a line with a slope of one is due to sorting of the rival phase, the other phases should give expected slopes of one.

Figures 6c and 6d are diagrams with the expected slope for the analyzed augite (Ho & Garcia 1988) equal to one. Again, there is greater scatter than expected if the variations are due to sorting of olivine, plagioclase and augite. The scatter on Figure 6d cannot be attributed to augite and is consistent with orthopyroxene being a sorted phase. This interpretation is consistent with the petrography [orthopyroxene

phenocrysts are present in the lava flows (Wright & Fiske 1971, Ho & Garcia 1988, Russell & Stanley 1990)] and with the results of thermodynamic modeling (Russell & Stanley 1990). The latter show that at low to moderate pressures (0 to 0.3 GPa), orthopyroxene begins to crystallize at 100 – 150°C below the liquidus.

SUMMARY

The design of proper ratios for plotting on the axes of Pearce element-ratio diagrams, given a specific hypothesis to constrain the displacement vectors, presents a problem in linear algebra. The common case involves the solution of a system of underdetermined linear equations. If the slopes derived from the dis-

placement vectors that are required by the hypothesis for all phases or end members are one, then the system of linear equations is homogeneous, and nontrivial solutions are possible. Less commonly, the system of homogeneous equations has an $N \times N$ coefficient matrix of phase compositions, where N is the number of chemical elements in the system. In such instances, there are nontrivial solutions only if the rank of the coefficient matrix is less than N .

If the slopes required by hypothesis for one or more phases or end members are different from the slopes required for the remaining phases or end members, then the system of equations is nonhomogeneous. In the usual case, the system of equations is still underdetermined, and unique solutions are not possible. It is possible to transform the problem into systems of nonhomogeneous equations, from which it is possible to extract a pair of ratios that have the properties required by the hypothesis being tested.

Exceptionally, the hypothesis being tested can be cast into a set of nonhomogeneous equations with an $N \times N$ coefficient matrix having a rank equal to N , i.e., the number of equations. The procedures for solving this exactly determined system of nonhomogeneous equations parallel those for the underdetermined systems. The method of choice for solving the systems of equations that arise in constructing Pearce element-ratio diagrams is singular-value decomposition.

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