



1990 GAC Short Course: Theory and Application of Pearce Element Ratios to Geochemical Data Analysis

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INTRODUCTION

In conjunction with the Geological Association of Canada (GAC) and Mineralogical Association of Canada 1990 annual meeting in Vancouver, the GAC presented a short course, entitled "Theory and Application of Pearce Element Ratios to Geochemical Data Analysis", to demonstrate the application of Pearce Element Ratio (PER) diagrams to the study of mass transfer processes in geology. The PER method was introduced by Pearce (1968) as means of illustrating and quantifying constraints placed on mass transfer processes by mineral stoichiometry. The method uses plots of ratios of elements on orthogonal axes. The denominators of the ratios are common to both axes and are conserved elements (elements whose mass does not change during the processes under examination). Unfortunately, Dr. Pearce was unable to attend the course due to illness, but his planned contribution is contained in the course notes, which have been published by the GAC (Russell and Stanley, 1990).

BACKGROUND

PER variation diagrams provide a means of portraying chemical variations within rock suites that removes the effects of data closure. Because major element chemical data are normalized to 100%, a set of n major elements has only $n-1$ independent variables (degrees of freedom) and the concentration of any element can be quickly deduced as being $100 - (\text{sum of } n-1 \text{ elements})$. This property of major elements (and, indirectly, of trace elements) is called the closure effect (e.g., Chayes, 1964). Covariances in closed arrays are biased toward more negative values and this bias increases with the variance

of an element. As a result, many variation diagrams (e.g., Harker, 1909) are empirically useful, providing a summary of compositional ranges of rock suites, but cannot generally be interpreted in terms of petrochemical process. PER diagrams normalize data to a conserved element and, in the process, eliminate data closure. As a result, they enable the quantitative analysis of a variety of open or partially open system processes.

PROCEEDINGS

The course was introduced by K. Russell (U of British Columbia), who provided a discussion of the logic and philosophy of the scientific method. Russell stressed the point that an hypothesis is unscientific if it cannot be tested and used simple examples to illustrate the use of PER diagrams in testing scientific hypotheses.

In a second presentation, Russell went on to develop a set of equations relating chemical variations, expressed as extensive quantities (i.e., mass, volume), to idealized material transfer processes. A variety of mass transfer processes can act on a magma, including differentiation (crystal fractionation, gas transfer, liquid immiscibility), assimilation, Soret diffusion and magma mixing. These processes can be studied assuming that: (1) the magma has a finite size, so that each element has an extensive quantity related to the size of the magma body, and (2) the magma was initially homogeneous. During the operation of a petrochemical process, the extensive quantity of each constituent varies directly with the stoichiometry of the process. In practice, these equations are not directly applicable because petrologists work with data in the form of intensive variables (i.e., mol.%, wt.%), which are independent of the size of the system and form closed arrays. An intensive variable, i.e., wt.% (x), can be related to a corresponding extensive variable, i.e., mass (X), by the size of the system (S) by the relationship: $x = X/S$. Variations in the closed array of intensive variables are not necessarily directly related to the stoichiometry of a material transfer process. However, any ratio of intensive variables equals the analogous ratio of extensive variables (i.e., $x/y = X/Y$) because S cancels from the ratio. The corollary is that variations in ratios of intensive parameters, which petrologists can measure, are identical to the variations in ratios of the corresponding extensive variables. This forms the theoretical basis for the application of PER diagrams.

J. Nicholls (U of Calgary) used simple geological and non-geological examples to help course participants increase their intuitive understanding of the conceptual framework for the PER method. Geochemical data sets can be viewed as samples from finite populations of atoms. Conserved elements must be identified and placed in the denominators of the ratios. The numerators are constructed

from elements that are not conserved by the processes operating on the system and reflect the stoichiometry of the minerals crystallizing in the system. The choice of elements is made from petrological considerations. A simple example is the crystal sorting of olivine from a basaltic magma. The olivine structure excludes Al, Ca, Na, K, Ti and P, which are conserved elements if no other minerals are being sorted. Olivine contains (Fe + Mg) and Si atoms in a ratio very near 2:1. Therefore, on a PER diagram with Si/K on the X-axis and (Fe + Mg)/K on the Y-axis, olivine sorting will produce samples with compositions that define a trend having a slope of two, if this is the only process that has affected the samples. Any process with constant stoichiometry produces a linear trend on a PER diagram, with a slope that depends both on the stoichiometry of the process and the original composition of the system. The significance of a trend on a PER diagram is evaluated from the slope of the line rather than the size of the correlation coefficient, and the required statistics for making decisions about processes can be derived from the analytical uncertainties in the chemical analyses.

T. Pearce's (Queen's U) contribution in the course notes emphasizes several important aspects of PER diagrams. The slopes on some PER diagrams are predictable because they preserve both the magnitude and direction of vectors of chemical change in problems such as chemical reactions and mass transport, and may serve to distinguish various hypotheses. Hypotheses that are poorly constrained on Harker variation diagrams, due to closure effects, are well constrained on PER diagrams. Inter-element distribution coefficients can be extracted from PER diagrams if the data represent only the liquid line of descent. The PER technique is so sensitive that analytical errors are significant in the testing of hypotheses. More precise measurement and reporting of chemical data will allow petrologists to take advantage of this attribute.

The statistical methods required to perform error propagation and regression calculations were presented by C.R. Stanley (Queen's U). The propagation of analytical errors is required to interpret PER diagrams because the common denominators used in the diagrams "induce" correlated errors which could potentially contribute to the variance. Error propagation enables the petrologist to distinguish trends produced by induced correlation from trends produced by petrological processes.

Trace element data provide a means of further testing hypotheses that are consistent with major element data. Trace elements are often more sensitive than major elements as indicators of chemical variations; even with closed arrays of trace element data, different petrochemical processes can sometimes be distinguished (e.g., Allegre

and Minster, 1978). J.K. Russell and A.D. Halleran (U of British Columbia) presented PER diagrams constructed from trace elements, using chemical data from the 1959 eruption of Kilauea Iki, Hawaii. They demonstrated that trace elements formulated as Pearce element ratios can separate processes that have subtle stoichiometric differences. However, the usefulness of trace elements may, in some instances, be hampered by high analytical uncertainties, a less apparent problem with major element data.

R. Ernst (U of Ottawa) analyzed the sensitivity of the PER method to non-conserved behaviour of the denominator element. If the denominator element is truly conserved, then the slope of a line on a PER diagram is a true reflection of the inter-sample variation of the numerator elements. However, if the denominator is not truly conserved, a systematic error is introduced into this slope. Ernst provided a detailed error analysis for various petrochemical processes. One of the generalizations that arise from his analysis is that the method can tolerate a small amount of non-conserved behaviour (e.g., bulk mineral-melt distribution coefficients as high as 0.01 to 0.1, depending on the details of the process) of the denominator element, before significant error is introduced into the slope.

Stanley and Russell presented an elegant methodology for determining the numerators for PER diagrams designed to test scientific hypotheses. The numerators for simple PER diagrams can be developed using simple methodologies and intuition. However, as hypotheses become more complicated, either through the addition of phases or by increasing mineral solid solution complexity, the creation of appropriate diagrams also becomes more complex. Stanley and Russell presented a matrix equation which simplifies this process, and a computer program that can perform the matrix calculations for hypotheses involving mafic rocks.

R. Nielson (Oregon State U) described a computer model that can be used to investigate the ability of PER analysis to distinguish among a range of igneous processes, including fractional crystallization, recharge, assimilation, eruption and periodic mixing. The model was developed using a simulated data set generated from a phase equilibria-based igneous differentiation model. PER analysis was applied to the model results to test the ability of PER diagrams to extract the model parameters. Ambiguities can arise in distinguishing between the above-mentioned processes. For example, it may be difficult to recognize if a system has been periodically mixed. Nielson's results provide a caution for those interested in the application of PER diagrams, or any other method of testing real data against hypothetical processes. If our understanding of these processes is imperfect, our ability to test for their occurrence and distinguish one from another in nature is similarly flawed. Computer modelling is one

way to illustrate the chemical variations that arise through process. Pearce has similarly emphasized the need for computer simulations and pointed out that the sensitivity of the PER method will require that we refine our understanding of the processes involved.

Although most presenters at the course worked with examples of mafic igneous systems, applications to rock alteration were discussed as well. A.D. Fowler (U of Ottawa) introduced this topic with a general overview of the methods available for the determination of mobile and immobile elements in altered rocks, and the potential of PER diagrams to solve some of these problems. A.E. Beswick (Laurentian U) followed with a more detailed discussion of PER methodologies that can be used to distinguish components that are mobile from those that are conserved during the alteration process. PER diagrams can be used to unambiguously identify immobile elements, and primary trends can be determined if two or more conserved elements can be identified. The mobilities of non-conserved components can be quantified as percentage gains and losses relative to primary compositions, using simple mathematical relationships derived from the appropriate PER and logarithmic PER diagrams. Beswick's contribution was a late addition to the course and is not published in the short course volume, although it is published in part elsewhere (e.g., Beswick and Soucie, 1978; Beswick, 1983; DePangher, 1988).

As this short course demonstrated, PER diagrams are a powerful method of investigating a variety of petrochemical processes. Successful application of the method requires some sophistication on the part of the petrologist, which may have prevented more widespread application of the PER method in the past. The short course notes provide the theoretical, conceptual and practical foundations necessary to understand existing applications and develop new ones and would be a valuable resource for any geologist interested in applying the PER method to petrological problems.

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