

QUANTITATIVE ASSESSMENT OF METASOMATIC COMPOSITION-VOLUME CHANGES:  
TECHNIQUES FOR IDENTIFYING ACTUAL PROTOLITHS  
AND CONSERVED COMPONENTS

by

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## ABSTRACT

Quantitative assessment of actual metasomatic changes in mass and volume requires knowledge of (1) chemical compositions and densities of actual protoliths and altered products and (2) the actual bulk volume change of the rock or the actual absolute mass change of any chemical component. Assumed values for (1) and (2) produce metasomatic models that do not necessarily reflect actual metasomatism.

Logarithmic ratio diagrams of the form  $\log_{10} (X/Z)$  versus  $\log_{10} (Y/Z)$  portray metasomatism in an elegantly simple fashion; metasomatism in a three component system where only one of X, Y, or Z is conserved produces a collinear array of points with predictable slope of 0,  $\frac{1}{2}$ , or 1, respectively, independent of protolith composition. Such relationships can be used to identify conserved components and to discriminate altered from unaltered rocks.

Any two conserved components can be identified on the basis of slope and collinearity. Actual conserved components thus identified enable precise calculation of actual rather than model metasomatic changes.

Analyses of 1133 Cenozoic volcanic rocks from a wide variety of tectonomagmatic environments plot as single, well defined trends on certain logarithmic ratio diagrams. By assuming that unaltered pre-Cenozoic volcanic rocks should conform to Cenozoic trends, it is possible to discriminate altered from unaltered volcanic rocks.

Published wall-rock alteration data for the Millenbach mine are evaluated using these new techniques.  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{Al}_2\text{O}_3$  are found to be the most frequently conserved components. Averaged rocks show volume changes of -7.15% to +7.20%, whereas actual samples show volume changes of -22.6% to +32.4%.

Alteration is found to be spatially inhomogeneous but more areally extensive with composition changes generally more extreme than previously recognized.

Improved ability to detect and quantify metasomatism results in better definition of its nature and extent. Lithogeochemical exploration, geochemical modeling of metasomatism, and petrogenetic studies will be enhanced by these new techniques.

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## INTRODUCTION

Quantitative assessment of actual metasomatic changes in mass and volume requires that the following information be known:

- (1) the actual protolith of any specific altered rock;
- (2) the chemical compositions and densities of actual protoliths and altered products; and
- (3) either the actual bulk volume change of the rock mass or the actual absolute change in mass of any chemical component.

Significant difficulties are often associated with identifying actual protoliths, matching actual protoliths to specific altered products, and establishing actual mass-volume reference changes.

Identifying protolith requires demonstrating that a candidate for protolith has not been compositionally altered by the metasomatizing process in question and that it is the actual protolith of the altered rock(s) produced by that same process. It is often difficult to rigorously satisfy these requirements. It has thus become common practice to assume a protolith, the choice sometimes being supported by geologic field relations, petrographic observations, or distance from obvious alteration.

Identifying an actual absolute mass or volume change has proven difficult as well. The almost universal practice has been either to assume a zero mass change for so-called "immobile elements" (Al, Ti, Zr, Y, Nb, and others) or to assume a zero volume change if primary textures are preserved in thin section.

Assumed protoliths and assumed mass-volume reference changes give model results that might not accurately represent actual metasomatism. If actual protoliths and actual mass-volume reference changes could be identified, actual metasomatic mass-volume changes could be calculated precisely.

This paper reviews previous contributions to these problems and presents new and

improved techniques for quantitatively identifying actual protoliths and conserved components in altered rock suites. These new techniques are then applied to published data from the Millenbach mine, an Archean volcanogenic massive sulfide deposit, to comparatively demonstrate their advantages.

Abbreviations of terms used in this study are presented in Table 1.

## HISTORICAL DEVELOPMENT OF QUANTITATIVE TECHNIQUES

### FOR STUDYING METASOMATISM

#### Introduction

Early workers realized that in order to calculate gains and losses in metasomatic processes, it was necessary to identify protoliths and a parameter that either remained constant or had a known dependency upon another parameter throughout the metasomatic process. Historically, it has been assumed that protoliths could be readily identified, with the result that most attention has focussed instead on the recognition of processes having constant volume or constant mass of one or more components.

#### Previous Work

Earliest attempts to quantitatively assess metasomatic mass-volume changes were dominated by the assumption of constant volume (Lindgren, 1918). In this approach, each rock in a metasomatic suite is normalized to 100 cm<sup>3</sup> by multiplying weight percentages by the rock's specific gravity. One rock is then compared to another to determine gains and losses of components. Variations on this constant volume technique have been presented by a number of authors (Reynolds, 1943; Ellis, 1947; Joplin, 1952; Pitcher and Sinha, 1957).

Many authors have criticized the constant volume hypothesis (Van Hise, 1904; Becke, 1913; Eskola, 1948; Ridge, 1949; Ramberg, 1952; Turner and Verhoogen, 1960) and have proposed constancy of chemical components instead. Barth (1948), for instance, proposed constant total oxygen, whereas Poldervaart (1953) proposed constancy of Si and Al.

Akella (1966) reviewed the above mentioned techniques and found serious problems with them all. He proposed a method of calculation based on the correct assumption that the ratios of initial to final weight percentages of elements undisturbed during metasomatism should be identical. Akella (1966) showed that metasomatic mass changes can be assessed without density measurements, which are commonly not available or of low accuracy.

Gresens' (1967) classic paper presented the basic equations relating mass and volume that are necessary for quantitative assessment of metasomatic mass and volume changes. This work established the benchmark requirements by which all subsequent quantitative studies of metasomatism must be measured. Gresens (1967), apparently unaware of Akella's (1966) work, also recognized the potential significance of ratios in identifying conserved components.

Pearce (1968) showed that plotting ratios of components where the divisor component is conserved and is the same for both axes has many advantages over traditional Harker diagrams for interpreting data and discriminating between rival hypotheses to explain chemical variation.

Beswick and Soucie (1978) modified Pearce's (1968) ratio diagrams to a log base 10 molar form in an attempt to detect and correct for metasomatism in Archean volcanic rocks. Using empirically determined reference curves for Cenozoic volcanic compositions and assuming two conserved chemical components, they suggested a method by which volcanic protolith compositions could be identified. This technique has important applications in cases where a volcanic protolith is likely but whose composition is not known. This technique enables calculation of protolith weight percentage composition for any altered volcanic rock when two or more conserved components are known.

Davies et al. (1979) used ratio diagrams modified from Pearce (1968) to establish the "immobility" of chemical components used to fingerprint altered mafic volcanic rocks for stratigraphic correlation. Davies et al. (1979) suggested that data from metasomatically related

rocks produce a collinear array passing through the origin and protolith composition on Cartesian plots of two conserved chemical components ratioed against a mobile divisor component. The array slope is determined by the ratio of the two conserved components in the protolith.

Grant (1987) used the relationship  $M = pV$  to substitute mass for density and volume terms in Gresens' (1967) fundamental equation. The result was a linear relationship between concentrations in protolith and altered product similar to Akella's (1966) basic equation. As with the method of Akella (1966), density measurements are not used and volume changes not assessed. Grant (1987), however, improved on Akella (1966) by presenting the "isocon" diagram as a graphical means of displaying and interpreting data for protolith/product pairs. In this technique, weight percentage data for protolith (X-axis) and altered product (Y-axis) are plotted against each other. Chemical components that are conserved form a collinear array called an isocon, which passes through the origin. The isocon slope is the ratio of the initial total system mass to the equivalent altered total system mass and hence is a convenient measure of the relative net mass change during metasomatism.

MacLean and Kranidiotis (1987) proposed a technique in which weight percentages of pairs of components from a suite of metasomatically related rocks are plotted against each other on binary diagrams. When the two chemical components are conserved, the altered rock points form a collinear array passing through the origin and protolith composition.

### Discussion

The history of the development of quantitative techniques for studying metasomatism has been dominated by attempts to identify a constant parameter against which gains and losses of mass and volume could be calculated.

No technique for empirically identifying a constant volume process has been developed.

Although constant volume has been presumed on the basis of preservation of textures in thin section, even rather large volume changes can be difficult to detect (Costa et al., 1983; Leshner et al., 1986), especially if the volume change was isotropic.

Akella's (1966) ratio technique, Gresens' (1967) composition-volume diagrams, Grant's (1987) isocon diagrams, and the graphical techniques of Davies et al. (1979) and MacLean and Kranidiotis (1987) are the only valid techniques developed thus far for identifying conserved chemical components. These techniques, however, assume prior knowledge of protolith composition to identify conserved components. As some authors have recognized (Beswick and Soucie, 1978; Grant, 1987), correct identification of actual protolith is more difficult than has commonly been assumed. Beswick and Soucie's (1978) technique for identifying volcanic protoliths, however, requires prior knowledge of at least two conserved components.

All quantitative studies of metasomatism to date have thus been hampered by having to make at least one initial assumption about protoliths or conserved components. The result has been that different studies are often not comparable, because they utilize different starting assumptions.

Studies of metasomatism that begin with assumptions about protoliths or conserved components are only models of metasomatism and should be recognized as such.

### "Immobile Elements?"

#### Introduction

Although the "immobile element" concept was popularized outside of the historical mainstream of quantitative metasomatic studies and has existed parallel to and largely in apparent ignorance of it, the impact of the "immobile element" concept on metasomatic studies has been enormous, and no discussion of metasomatic studies would be complete without addressing it.

In the 1970s, the search for chemical discriminators of tectonomagmatic environments gave rise to the widespread notion that certain elements were universally immune to metasomatic changes. Certain elements were declared to be "immobile" if they exhibited either of two behaviors:

- (1) showing little or no change in weight percentage or ppm from unaltered to altered rock (Smith, 1968; Cann, 1970; Hart, 1970; Thompson and Melson, 1970; Hekinian, 1971; Thompson, 1973; Hart et al., 1974; Shido et al., 1974; Hellman et al., 1979; Ludden and Thompson, 1979); or
- (2) generating smoothly curvilinear trends or clusters of low scatter on diagrams whose variables are plotted in terms of weight percentage or ppm (Harker diagrams) (Smith and Smith, 1976; Wood et al., 1976; Coish, 1977; Hellman et al., 1979).

By the end of the decade, Al, Ti, Nb, Y, and Zr were widely considered to be the most important "immobile elements." However, as discussed below, the conclusion that these elements are "immobile" was based largely on circular or erroneous reasoning that is remarkably persistent in the literature.

#### Conservation Versus Immobility: The Effect of Scale

The term "immobile" has commonly (and unrealistically) been used in such a way as to imply absolute inertness over a broad range of physical and chemical conditions. In contrast, the term "conserved" has traditionally carried the thermodynamic meaning of a component's net zero change in a system having well defined properties, parameters, and physical limits. In geochemical practice, a conserved component is one which has experienced neither net gain nor net loss from a system the size of the sample homogenized for analysis.

A component may be conserved on one scale but not on another within the same system

(Carmichael, 1969). For example, in thin section, one might observe plagioclase to be completely replaced by calcite (Fig. 1). Considered on the scale of the original plagioclase crystal,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{CO}_2$  can not have been conserved (Table 2). However, suppose that all of the  $\text{Al}_2\text{O}_3$  has been fixed in secondary minerals within the immediate vicinity of the replaced plagioclase crystal such that there has been no net gain or loss of  $\text{Al}_2\text{O}_3$  from a sample of proportions only slightly larger than the original plagioclase crystal. On this latter scale,  $\text{Al}_2\text{O}_3$  has been conserved while  $\text{SiO}_2$  and  $\text{CO}_2$  may or may not have been (Table 2).

Quantitative assessment of metasomatic gains and losses requires identification of a component whose variation on the scale of the samples taken for analysis is known. It is therefore more useful to speak of conservation and its scale than to use the term "immobile" with its frequently unrealistic connotations.

#### Simple Comparison of Weight Percentage or Ppm Data

In this rather common approach, components showing little or no change in weight percentage or ppm from unaltered to altered rock have been considered "immobile". This method, however, fails to account for a subtle but treacherous quirk of data presented in terms of weight percentage or ppm. Weight percentage and ppm are weight fractions normalized to convenient total masses--  $10^2$  grams for weight percentage and  $10^6$  grams for ppm. The weight fraction,  $\mathbf{W}_j$ , of a component  $\mathbf{j}$  in an  $\mathbf{n}$  component system is defined by the following:

$$\mathbf{W}_j = \mathbf{M}_j / \sum_{i=1}^{\mathbf{n}} \mathbf{M}_i \quad (1)$$

where  $\mathbf{M}$  is mass. Any change in mass of the  $i^{\text{th}}$  component changes the weight fraction of the  $j^{\text{th}}$  component even if the mass of the  $j^{\text{th}}$  component has not changed. The

weight fraction and, hence, weight percentage or ppm of an "immobile" component will therefore change whenever the net mass change for the alteration process is not zero-- a common situation. Direct comparison of weight percentage or ppm data for pairs of altered and unaltered rocks is therefore not sufficient to demonstrate that a component has been "immobile" (Costa et al., 1983), except when it is known that the net mass change during alteration has been zero.

## "Immobility" Deduced by Inspection of Harker Diagrams

In this method, pairs of altered rock components plotting as smoothly curvilinear trends or clusters of low scatter on diagrams whose variables are plotted in terms of weight percentage or ppm (Harker diagrams) have been regarded as "immobile" (Smith and Smith, 1976; Wood et al., 1976; Coish, 1977; Hellman et al., 1979). This method suffers from the weakness of its implicit assumption that alteration can not produce data plotting as coherent trends or tight clusters on Harker-type diagrams. Quite the contrary, high correlations can be imparted to components of any chemical reaction by the reaction stoichiometry (Pearce, 1968). As a number of authors have shown (Davies et al., 1979; Grant, 1987; MacLean and Kranidiotis, 1987), high correlation between weight percentage variables is not enough to establish that a pair of components has been conserved; truly conserved components plotted against each other must produce highly correlated arrays that are **linear**.

## Summary

Most efforts in the field of quantitative metasomatic studies have gone toward identifying the parameter of known variation against which metasomatic gains and losses can be measured. The concept of universally "immobile elements" is based largely on circular or erroneous reasoning. There appears to be no firm basis for believing that volume or any chemical component is universally conserved during metasomatism. Metasomatic models based on assumed protoliths or assumed conserved components might not represent actual metasomatism. A technique that could empirically and independently identify actual protoliths and conserved components would break the cycle of circular assumptions and allow precise calculation of actual metasomatic gains and losses.

## LOGARITHMIC RATIO DIAGRAMS

### Introduction

The techniques presented here for identifying actual protoliths and actual conserved components are based largely on the work of Pearce (1968), who provided the theoretical basis for ratio diagrams, and Beswick and Soucie (1978), who recognized the essential simplicity of logarithmic ratio diagrams for portraying metasomatism. Because of the importance of logarithmic ratio diagrams in this study, the mathematical basis for them is presented first.

### Theory

Consider a system of three components **X**, **Y**, and **Z** subjected to a hypothetical alteration process such that  $\delta X$ ,  $\delta Y$ , and  $\delta Z$  are the changes in **X**, **Y**, and **Z**, respectively. Alteration in this system can be represented on a logarithmic binary diagram where **X** and **Y** are numerators and **Z** is the divisor for both axes. Note that the use of ratios makes the units of **X**, **Y**, and **Z** flexible, provided they are consistent.

Coordinates of protolith:

$$\log(X/Z), \log(Y/Z) \quad (2)$$

Coordinates of altered product:

$$\log((X+\delta X)/(Z+\delta Z)), \log((Y+\delta Y)/(Z+\delta Z)) \quad (3)$$

The slope, **m**, of the line defined by these points is the following:

$$m = \frac{\log((Y+\delta Y)/(Z+\delta Z)) - \log(Y/Z)}{\log((X+\delta X)/(Z+\delta Z)) - \log(X/Z)} \quad (4)$$

Case 1: For **X** metasomatism:  $\delta X \neq 0, \delta Y = 0, \delta Z = 0, m = 0$ .

Case 2: For **Y** metasomatism:  $\delta X = 0, \delta Y \neq 0, \delta Z = 0, m = \infty$ .

Case 3: For **Z** metasomatism:  $\delta X = 0, \delta Y = 0, \delta Z \neq 0, m = 1$ .

### Summary

Geometric relations between these three fundamental metasomatic vectors on a logarithmic ratio diagram are summarized in Figure 2 modified from Beswick and Soucie (1978). The simple elegance of these plots for portraying metasomatism is seen in four areas:

- (1) Use of dimensionless ratios allows **X**, **Y**, and **Z** to be expressed in any units as long as the units are the same for all three.
- (2) Metasomatism involving only one component **X**, **Y**, or **Z** produces a collinear array of points with a predictable slope of 0,  $\infty$ , or 1, respectively.
- (3) Conservation of two out of three components also produces collinear arrays of points that have predictable slopes of 0,  $\infty$ , or 1.
- (4) These slopes are independent of protolith composition and depend only on the changes in **X**, **Y**, and **Z**.

## IDENTIFYING CONSERVED COMPONENTS

### Introduction

Logarithmic ratio diagrams can be used to identify pairs of actual conserved components without prior assumptions, because the slopes of data arrays from metasomatically related rock suites are predictable without prior knowledge of protolith.

### Theory

If **X** and **Y** are conserved, then  $\delta X = 0$  and  $\delta Y = 0$  and eq. 3 becomes:

$$m = \frac{\log(Y/(Z+\delta Z)) - \log(Y/Z)}{\log(X/(Z+\delta Z)) - \log(X/Z)} \quad (5)$$

$$m = \frac{\log Y - \log(Z+\delta Z) - \log Y + \log Z}{\log X - \log(Z+\delta Z) - \log X + \log Z} \quad (6)$$

$$m = \frac{\log Z - \log(Z+\delta Z)}{\log Z - \log(Z+\delta Z)} \quad (7)$$

$$m = 1 \quad (8)$$

The slope, **m**, must therefore be equal to 1 for the case of **X** and **Y** being conserved. It should be noted that if  $\delta Z$  also equals 0, the coordinates of the original and altered composition points are identical because no change in **X**, **Y**, or **Z** has occurred. This implies that conserved numerator components will be most clearly highlighted when the most mobile component of all occurs in the divisor.

Substituting **m = 1** back into eq. 4 and rearranging gives the following:

$$\begin{aligned} \log((X+\delta X)/(Z+\delta Z)) - \log(X/Z) = \\ \log((Y+\delta Y)/(Z+\delta Z)) - \log(Y/Z) \end{aligned} \quad (9)$$

$$\begin{aligned} \log(X+\delta X) - \log(Z+\delta Z) - \log X + \log Z = \\ \log(Y+\delta Y) - \log(Z+\delta Z) - \log Y + \log Z \end{aligned} \quad (10)$$

$$\log(X+\delta X) - \log X = \log(Y+\delta Y) - \log Y \quad (11)$$

$$\log(X+\delta X) - \log(Y+\delta Y) = \log X - \log Y \quad (12)$$

$$\log((X+\delta X)/(Y+\delta Y)) = \log(X/Y) \quad (13)$$

$$(X+\delta X)/(Y+\delta Y) = X/Y \quad (14)$$

$$YX + Y\delta X = XY + X\delta Y \quad (15)$$

$$Y\delta X = X\delta Y \quad (16)$$

$$\delta X/\delta Y = X/Y \quad (17)$$

Equations 8 and 17 show that there are only two ways for the hypothetical alteration process to produce an array of points with a slope of 1. The first is for **X** and **Y** to be conserved components. The second is for **X** and **Y** to be gained or lost in exactly the same proportions as they occur in the protolith -- behavior which will herein be referred to as coherent mobility.

## Coherent Mobility

### Introduction

Coherent mobility, or a slight variant of it, mimics the behavior of conserved components in all existing techniques for identifying conserved components (Akella (1966); Gresens (1967), Davies et al. (1979); Grant (1987); MacLean and Kranidiotis (1987)). Mistaking coherent mobility for conservation generally results in spurious calculations of metasomatic mass and volume changes. It is therefore important to distinguish conservation from coherent mobility for each of the above methods.

### Akella (1966)

Akella's (1966) technique enables calculation of mass changes after identification of a conserved component. Conserved components are identified on the basis of the premise that "the ratio between the initial percentage and final percentage for any oxide (or element) remaining undisturbed during metasomatism will be equal to the ratio for any other oxide (or element) remaining undisturbed during metasomatism" (Akella, 1966). The following are Akella's (1966) fundamental equations:

$$m_i = \frac{W_i^O}{W_i^A} = \frac{C_i^O}{C_i^A} = \frac{M_i^O * M^A}{M_i^A * M^O} \quad (18)$$

$$m_c = \frac{C_x^O}{C_x^A} = \frac{C_y^O}{C_y^A} = \frac{M^A}{M^O} \quad (19)$$

$$\delta M_i = m_c * W_i^A - W_i^O \quad (20)$$

Akella's (1966) method proceeds by first calculating component ratios,  $m_i$ , from equation 18. Clustered values of  $m_i$  are taken as indicating conservation of the clustering components. By definition, conserved components have  $M_i^O = M_i^A$ , so equation 18 reduces to equation 19 for conserved components. The value of  $m_c$  is then used to calculate  $\delta M_i$  values for all components from equation 19.

Rearranging equation 18 and solving for the general case of  $m_x = m_y$ , shows that conservation is not the only way to produce constant component ratios.

$$\frac{\delta M_x}{\delta M_y} = \frac{M_x^O}{M_y^O} \quad (21)$$

Equation 21 is identical to equation 17, which is the mathematical definition of coherent mobility. Coherently mobile pairs will therefore produce constant component ratios that differ, perhaps markedly, from the ratios of actually conserved components. It should also be apparent that a value of  $m_c$  taken from coherently mobile components would produce spurious results for all  $\delta M_i$ .

### Gresens (1967)

Gresens' (1967) method enables calculation of metasomatic mass and volume changes after identification of the bulk volume change of the rock mass or the absolute change in mass of any chemical component. Conserved components are identified through the use of composition-volume (C-V) diagrams. Gresens' (1967) fundamental equation is as follows:

$$\delta M_i = M^O \left( \frac{f_{vi} \cdot p^A \cdot C_i^A}{p^O} \right) - C_i^O \quad (22)$$

For convenience in constructing C-V diagrams, equation 22 can be rewritten by substituting the

relationships  $M^o = 100 \text{ g}$  and  $100 \cdot C_i^o = W_i^o$  from Table 1 and rearranging to slope-intercept form as follows:

$$\delta M_i = \frac{f_{vi} \cdot p^A \cdot W_i^A}{p^o} - W_i^o \quad (23)$$

The first step in Gresens' (1967) method is to generate a C-V diagram by plotting  $\delta M_i$  versus  $f_{vi}$  for each component  $i$  according to equation 23. Clustering of intersections for equation 23 on the  $\delta M_i = 0$  line is taken as indicating conservation of the clustering components. The  $f_v$  value of that clustered intersection is taken as the volume factor for the alteration.

Alternatively, a simplified C-V diagram can be constructed by setting  $\delta M_i = 0$  for the case of conservation and solving equation 23 for  $f_{vi}$ . Clustered values of  $f_{vi}$  are taken as indicating conservation of the clustering components. Once a value for  $f_{vc}$  has been determined, gains and losses of mass are calculated from equation 23. Volume changes are calculated from equation 24.

$$f_{vc} = \frac{V^A}{V^o} = \frac{W_i^o \cdot p^o}{W_i^A \cdot p^A} \quad (24)$$

Two components  $x$  and  $y$  can be related on C-V diagrams by equation 23 in any of three ways:

- (1) intersecting lines --  $W_x^A \neq W_y^A$  and  $W_x^o \neq W_y^o$ . At points of intersection,  $f_{vx} = f_{vy}$  and  $\delta M_x = \delta M_y$ . In this case the two components have identical absolute mobilities;
- (2) parallel lines --  $W_x^A = W_y^A$  and  $W_x^o \neq W_y^o$ ;
- (3) coincident lines --  $W_x^A = W_y^A$  and  $W_x^o = W_y^o$ . This is a variant form of coherent mobility in

which components **x** and **y** have identical weight percentages in the protolith and altered product.

Case 3 is the most important potential source of error in identifying conserved components. An example of it occurs in Gresens' (1967) original example of a C-V diagram (Figures 3 and 4 reproduced here as Figures 3 and 4), where CaO and Na<sub>2</sub>O have such a relationship. These two components form a tight cluster on the  $\delta M_i = 0$  line with a corresponding volume factor of about 0.6. The components K<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>, which Gresens (1967) suggests are conserved, form a much looser cluster corresponding to a volume factor of about 1.25. If clustering alone is the criterion for conserved components, CaO and Na<sub>2</sub>O would have to be interpreted as conserved. The reason they are not so interpreted is the assumption that "if metasomatism involves both gains and losses, then the extreme endpoints on the graph must be the components that are lost or gained" (Gresens, 1967). One could just as well have made the interpretation that CaO and Na<sub>2</sub>O were conserved, and that metasomatism involved only gains of the other components.

#### Davies et al., (1979)

Davies et al. (1979) used ratio diagrams modified from Pearce (1968) to identify pairs of conserved components. Their technique is not designed for calculating metasomatic mass and volume changes. Although Davies et al. (1979) do not present the mathematical basis for their technique, the fundamental relationship between conserved components **x** and **y** and mobile component **z** on their diagrams is as follows:

$$\frac{C_y^A}{C_z^A} = m_c * \frac{C_x^A}{C_z^A} \quad (25)$$

Equation 25 is in slope-intercept form where  $m_c = M_y^0/M_x^0$ . Two conserved components ratioed against a mobile component generate a collinear array passing through the origin and protolith composition when plotted according to equation 25. The number of points that can be plotted on a single diagram is unlimited.

Equation 24, however, can be rearranged to the following form:

$$\frac{\delta M_x}{\delta M_y} = \frac{M_x^0}{M_y^0} \quad (26)$$

This is the by now familiar definition of coherent mobility. Davies et al. (1979) recognized that coherent mobility would mimic conservation. However, they considered coherent mobility to be an unlikely problem, because they plotted many samples together, all of which would fortuitously had to have gained or lost various **x** and **y** components in exactly the same proportions as those in the protolith.

### Grant (1987)

Grant's (1987) method enables calculation of metasomatic changes in mass after identification of a conserved component or the net mass change of the rock. Conserved components are identified through the use of isocon diagrams. The following are Grant's (1987) basic equations:

$$C_i^A = m_i * (C_i^0 + \delta C_i) \quad (27)$$

$$m_c = \frac{M^o}{M^A} \quad (28)$$

$$\frac{\delta C_i}{C_i^o} = \frac{1}{m_c} \frac{C_i^A}{C_i^o} - 1 \quad (29)$$

The first step in Grant's (1987) method is to construct an isocon diagram by plotting  $C_i^A$  (Y-axis) versus  $C_i^o$  (X-axis). Components that form a collinear array passing through the origin are usually interpreted as conserved. The slope of such a collinear array gives the value of  $m_c$  used to calculate mass changes from equation 27 or, more commonly, percentage mass changes from equation 29.

Rearranging equation 27 and solving for the general case of  $m_x = m_y$  reduces to the following familiar definition of coherent mobility:

$$\frac{\delta M_x}{\delta M_y} = \frac{M_x^o}{M_y^o} \quad (30)$$

Grant (1987; Fig. 2 reproduced here as Fig. 5) contains an excellent example of this phenomenon. An isocon diagram is shown in which  $H_2O$ , Zr,  $TiO_2$ , total Fe as FeO, Cu,  $Al_2O_3$ , and  $SiO_2$  are collinear with the origin and are interpreted as conserved components. However, Rb,  $Na_2O$ ,  $CO_2$ ,  $K_2O$ , and Sr also are collinear with the origin and have a quite different slope. The different values of  $m_c$  taken from these different collinear arrays would result in drastically different calculations of metasomatic mass changes.

#### MacLean and Kranidiotis (1987)

MacLean and Kranidiotis (1987) used Cartesian plots of weight percentage data to identify

conserved components and then calculate metasomatic mass changes. Components are interpreted as conserved when four conditions are met:

- (1) conserved components are plotted against each other;
- (2) conserved components have high linear correlations;
- (3) altered rock data points are collinear with the origin; and
- (4) altered rock data points are collinear with protolith composition.

The only equation presented by MacLean and Kranidiotis (1987) is as follows:

$$M_i^A = \frac{W_i^A}{W_c^A} * M_c \quad (31)$$

By substituting the relationships  $M_i^A = M_i^O + \delta M_i$  and  $M_c^O = W_c^O$  (for a 100 g protolith reference mass), equation 31 can be rewritten in the following form for calculating metasomatic mass changes:

$$\delta M_i = m_c * W_i^A - W_i^O \quad (32)$$

where  $m_c = W_c^O/W_c^A$ . Equation 32 is identical to equation 20 above from Akella (1966).

When weight percentage values are plotted in Cartesian space, the equation of a line passing through the origin and a protolith is determined by those two points and is of the following general slope-intercept form:

$$W_y^A = \frac{W_y^A - W_y^O}{W_x^A - W_x^O} * W_x^A \quad (33)$$

However, equation 32 reduces to the following familiar definition of coherent mobility:

$$\frac{\delta M_x}{\delta M_y} = \frac{M_x^o}{M_y^o} \quad (34)$$

Thus it is apparent that coherent mobility mimics conservation for the method of MacLean and Kranidiotis (1987).

### Discussion

For coherent mobility to occur in actual alteration, equation 17 requires that all chemical reactions in the rock that involve phases containing X or Y must proceed in such a way that the ratio of X/Y remains the same as the bulk X/Y ratio of the protolith. Protolith proportions of X and Y are determined by mineral compositions and abundances -- parameters determined by original rock forming processes. Proportions of X and Y mobilized during metasomatism are determined by the sum of all alteration reaction stoichiometries -- parameters determined by intensive properties of the alteration system. Protolith and altered product proportions of X and Y are thus independently determined and are therefore unlikely to coincide except in special circumstances.

Coherent mobility is most likely to be observed in protoliths with exceptionally low variance mineral assemblages. Two such cases should be most common:

- (1) mobile X and Y occur in only one mineralogic phase in the protolith, which is removed during alteration (i.e., removal of Ca and CO<sub>2</sub> in a 1:1 molar ratio as calcite cement is dissolved out of an otherwise pure quartz sandstone); or
- (2) mobile X and Y are absent from the protolith but are added during alteration to form a single mineral phase that has a constant ratio of X/Y (i.e., precipitation of sphalerite in limestone, adding Zn and S in 1:1 molar ratio).

Chemical components that exist in multiple solid phases in a single protolith are extremely unlikely to exhibit coherent mobility, because multiple independent alteration reaction

stoichiometries would have to combine in such a way as to reproduce the protolith X/Y ratio.

The chance of mistaking coherent mobility for conservation is also greatly reduced as the number of variably altered samples examined together increases, because each independent sample would have to fortuitously reproduce the protolith X/Y ratio. Coherent mobility is therefore more likely to manifest itself in methods that examine only pairs of samples (Akella, 1966; Gresens, 1967; Grant, 1987) than in methods that take a synoptic view of a large number of samples (Davies et al., 1979; MacLean and Kranidiotis, 1987).

#### Application of This Technique

The technique presented here for identifying conserved components has been developed as a FORTRAN 77 program called "CONSERVE." The logic of the program is explained below.

An unlimited number of samples derived from a common protolith can be evaluated together. Slopes and correlation coefficients are calculated for all permutations of components, three at a time, in the form  $(\log (X/Z), \log (Y/Z))$ . Small tolerances are allowed to account for inhomogeneities in the protolith and in the metasomatic process. Cutoff values for slope and correlation coefficient in natural data have been established by testing mathematically altered model compositions having known conserved components. Such testing has shown that conservation is most easily identifiable in natural data when a combination of three components produces a slope of  $1.00 \pm 0.05$  and correlation coefficient of 0.98 to 1.00. The program CONSERVE identifies all combinations of three components meeting these criteria.

CONSERVE calculates a conservation index, which is used to rank components by the degree to which they achieve ideal conservation. The conservation index for a perfectly conserved component is given by the following formula:

$$\text{perfect score} = (n - n) * P_2^n \quad (35)$$

where  $P_2^n = n!/2*((n-2)!)$  and  $n$  = the number of conserved components. Interpretation of this score is sometimes complicated by coherently mobile components and by marginally conserved components.

Frequent occurrence of a component as a numerator suggests its conservation or coherent mobility, whereas occurrence as a denominator suggests its mobility. In general, the component pair having highest frequency of occurrence in the numerator, closest average approach to 1.00 of both slope and correlation coefficient, and no occurrences in the denominator represents the closest approach to ideal conservation.

In some cases, no pair of components is identified as conserved. It must be remembered that this technique and all previous techniques can only identify conserved component pairs. No technique has yet been developed for identifying single conserved components. In such cases, independent knowledge of mass or volume changes in the surrounding system might be used to constrain subsequent calculations of metasomatic gains and losses.

It should be apparent that the chances of identifying a conserved component pair rise with the number of components available for examination. It is therefore advantageous to evaluate as many major, minor, trace, and REE components as possible.

### Testing the Program CONSERVE

Three types of tests, in which conserved components were independently known, were conducted for the program CONSERVE:

- (1) identifying conserved components in mathematically altered rocks;
- (2) identifying conserved components in thermodynamically calculated water:rock interaction; and
- (3) identifying conserved components in laboratory experiments of water:rock interaction.

Test case type 1 was conducted by mathematically altering actual rock compositions using a program called ALTER, which calculates the altered weight percentage composition of a rock from an initial composition and absolute changes in moles of oxides input by the user. The protolith and altered compositions were then evaluated by CONSERVE. CONSERVE correctly identified the actual conserved components in every test conducted.

Test case type 2 was performed on the data of Reed (1983) to test CONSERVE's ability to correctly identify actual conserved components in model water:rock interaction controlled by the laws of thermodynamics. Table 3 gives component mobilities calculated from the raw data of Reed (1983). Table 4 compares the data from Table 3 with the results from CONSERVE.

Test case type 3 was performed on data from laboratory experiments of Bischoff et. al. (1981) for the interaction between graywacke and seawater. Table 5 shows the mobilities calculated from the raw data. Table 6 compares the data from Table 5 with the results from CONSERVE. The above testing broadly demonstrates CONSERVE's ability to correctly identify conserved components. This is not surprising in view of the simplicity of the mathematical proof on which CONSERVE is based. An important implication of this testing is that gains and losses calculated from actual conserved components can be used to constrain thermodynamic models of actual geochemical processes. Model parameters can be varied until the gains and losses predicted by the model match the actual ones. This approach could provide information about the intensive parameters of alteration.

### Discussion

All previous techniques for identifying conserved components require prior knowledge of protolith composition. Many of these techniques are also limited to comparison of only two samples at a time -- one of which must be the already known protolith. The technique presented here

is an improvement over all previous techniques because it does not require prior knowledge of protolith composition, and there is no limit to the number of samples that can be evaluated together.

The advantage of not having to know protolith beforehand is that actual conserved components can be identified without having to make any prior assumptions. In fact, the simple geometric relationships of metasomatism on logarithmic ratio diagrams actually help to identify protoliths. On a logarithmic ratio diagram with conserved numerator components, the protolith must lie on the regression line defined by the metasomatic array. Thus it is sometimes possible to identify the most likely protolith from a number of candidates. Perhaps even more significant, this technique opens the door for precise identification of actual volcanic protoliths by the method of Beswick and Soucie (1978).

The advantage of simultaneous evaluation of a large number of samples is that it provides a synoptic view of the chemical data, which reduces the risk of misinterpretation that might arise in cases of sampling or analytical errors and coherent mobility.

### Summary

The techniques of Akella (1966), Gresens (1967), Davies et al. (1979), Grant (1987), and MacLean and Kranidiotis (1987) are all valid techniques for identifying conserved components. However, their abilities to recognize conserved components depend on prior knowledge of protolith composition.

Coherent mobility mimics conservation in all these techniques and is a much more likely problem in methods that evaluate only two samples at a time (Akella, 1966; Gresens, 1967; Grant, 1987) than in methods that take a synoptic view of a large number of samples (Davies et al., 1979; MacLean and Kranidiotis, 1987).

The technique presented here and embodied in the program CONSERVE requires no prior knowledge of protolith composition and has no limit on the number of samples that can be evaluated together. It is thus capable of identifying actual conserved components, which opens the door to identifying actual protoliths and being able to calculate actual metasomatic gains and losses precisely.

## IDENTIFYING PROTOLITHS

### Introduction

Identifying protoliths for studies of metasomatism generally requires three steps:

- (1) identifying geologically reasonable protolith candidates,
- (2) discriminating between altered and unaltered candidates, and
- (3) choosing the composition that best represents the actual protolith of the altered rocks in question.

Although the first step can usually be accomplished through careful geologic mapping, the second and third steps present some difficult problems. Discrimination has usually been done graphically by comparing sample positions with empirically documented fields in 2- or 3-dimensional space. However, whole-rock analyses used in quantitative metasomatic studies usually include at least 11 major and minor oxides and often a handful of trace elements. Such multicomponent systems are difficult to completely represent in traditional 2- or 3-dimensional portrayals. Strategies for reducing the number of components (factor analysis or principal components analysis) are of no help here, because protolith candidates must be tested for metasomatism of each specific component. One solution would be to sequentially compare the sample to as many plots as it takes to represent all components. Because of their elegant simplicity and straightforward interpretation, logarithmic ratio diagrams are ideally suited to this task. Because the vectors for **X** or **Y** or **Z** metasomatism are always predictable in advance and are independent of protolith composition, each protolith candidate can be tested for metasomatism of each specific component. Size, shape, and orientation of a protolith field relative to the three fundamental alteration vectors (Fig. 2) are the critical factors determining the protolith field's usefulness as a discriminator of altered from unaltered rocks. For maximum usefulness, a

protolith discrimination field must be oriented relative to the three fundamental metasomatic vectors such that the slightest alteration of the component being tested will produce an altered rock data point outside the protolith field. Discrimination of altered from unaltered can be done in this manner for any rock type, provided the natural variation of the protolith can be documented and suitable unaltered fields defined.

### Application to Volcanic Rocks

#### Previous Applications

On the basis of suggestions by Touminen (1964) and Pearce (1968), Beswick and Soucie (1978) plotted 543 Cenozoic volcanic rock analyses on a series of log base 10 molar ratio diagrams using the components  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and Fm, where Fm is the total of  $\text{FeO}$ ,  $\text{MgO}$ , and  $\text{MnO}$ . They found that certain combinations of components plot as single, well defined trends. Assuming that unaltered pre-Cenozoic volcanic rocks should conform to the Cenozoic trends, they proposed a graphical procedure using a series of five diagrams to identify and correct for metasomatism in greenstones. Glikson and Hickman (1981) and Jahn et al. (1982) used Beswick and Soucie's (1978) diagrams in an attempt to discriminate altered from unaltered volcanic rocks.

### Data for Cenozoic Volcanic Trends (CVTs)

The first goal of this part of the study was to expand the method of Beswick and Soucie (1978) to include more individual components and to document CVTs for a larger, more representative sample population. Data for this purpose were extracted from PETROS (Mutschler et al., 1981) according to a tectonomagmatic classification scheme (Fig. 6) devised to ensure that all significant volcanic rock types were represented. Because PETROS (Mutschler et al., 1981) contains over 40,000 igneous rock analyses and only analyses of unaltered volcanic rocks were desired, data were selected according to the following criteria:

- (1) The youngest volcanic suite typical of each tectonomagmatic category was selected.
- (2) Only analyses of extrusive, non-pyroclastic volcanic rocks were used. Analyses of pyroclastic rock were avoided because of the possibility that mechanical processes operating during deposition might obscure the effects of primary physico-chemical processes.
- (3) Only samples having separate analyses for  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{H}_2\text{O}^+$ , and  $\text{H}_2\text{O}^-$  were used. Total  $\text{H}_2\text{O}$  and total Fe as FeO were calculated from this information.
- (4) In order to minimize biasing by any single tectonomagmatic category, the total number of analyses per category was kept to approximately 100. The approximately 100 youngest rocks from each category were chosen as the final representatives. The resulting data set consisted of 1133 Cenozoic volcanic rock analyses.

### CVTs Used in This Application

Complete representation on log base 10 molar ratio diagrams of the 15 oxide variables listed above requires a total of 1365 diagrams. All 1365 diagrams were plotted at the same scale to inspect the extent of natural variation in Cenozoic volcanic rocks as represented by the PETROS calibration set.

Visual examination of the 1365 diagrams confirms the findings of Beswick and Soucie (1978) that, for certain combinations of components, Cenozoic volcanic rocks from a wide variety of tectonomagmatic environments plot as single, well defined trends. The vast majority of combinations, however, produce fields that are somewhat elongate and curvilinear with low correlation (values of  $R^2$  between 0.0 and 0.5) and regression slopes of approximately 1. A few combinations produce fields that are hyperbolic, sinusoidal, or bifurcate.

Because most CVTs have slopes close to 1 over much of their extents, and alteration involving the divisor component alone would commonly produce an array coincident with the CVT (case 3 above), most CVTs are not very sensitive to alteration involving the divisor component. Maximum sensitivity for this technique is therefore achieved by using enough CVTs such that all components occur at least once as a numerator. Toward this end, all CVTs were first visually examined to find the trends having obviously highest correlations between variables. After this inspection, linear, quadratic, and cubic regression curves were fit to the approximately 150 most highly correlated trends (SYSTAT software; Wilkinson, 1985). Correlation coefficients ( $R$  and  $R^2$ ) were calculated and used to rank the CVTs in descending order of  $R^2$  with diagrams of highest correlation giving the most restrictive discrimination field boundaries. Only 46 of the 1365 combinations of components produce diagrams having  $R^2$  values of 0.9 or greater. Combinations with slopes closest to 1 were chosen to maximize sensitivity to alteration of numerator components. Seven diagrams were finally selected as the basis for a computer program called "SCREEN"

that performs the discrimination procedure for  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ , total Fe as FeO, MnO, MgO, CaO,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ , and total  $\text{H}_2\text{O}$ .

### Calibration of CVT Boundaries

To discriminate between altered and unaltered rocks, it is necessary to define boundaries for the CVT fields. A typical CVT is shown in Figure 7. Equations for the CVT field boundaries used in the program SCREEN are summarized in Tables 7-9. Although selection criteria were designed to minimize inclusion of erroneous or altered rock analyses, a small number may have inadvertently been included. Such analyses may plot outside the boundaries of one or more CVT fields. The number and percent of analyses plotting inside the boundaries of each CVT are shown in Table 10.

### Discussion

The fundamental premise of this discrimination procedure is that any composition plotting outside a CVT field does not have chemical systematics consistent with unaltered Cenozoic volcanic compositions. A volcanic rock plotting outside a CVT field must therefore have been altered with respect to one or more of the three components represented by that CVT. Thus, for rocks known to have originally been volcanic, a distinction can be made between altered and unaltered compositions.

Previous attempts to discriminate altered from unaltered volcanic rocks using molecular proportion ratio diagrams (Beswick and Soucie, 1978; Glikson and Hickman, 1981; Jahn et al., 1982) have relied on the original diagrams of Beswick and Soucie (1978). Their diagrams, however, involve only  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , CaO, and Fm (total Fe + MgO + MnO) as numerators and are therefore not sensitive to alteration involving any other components. The technique presented

here is a significant improvement in that it is calibrated with a much larger and more representative Cenozoic volcanic rock data set, and it is sensitive to alteration involving 13 different components. It has a strong theoretical and empirical basis that does not suffer from the problems sometimes thought to be associated with ratio diagrams (Rollinson and Roberts, 1986, 1987; Vines, 1987; Pearce, 1987).

The CVT discrimination fields determined in this study should provide reasonably accurate empirical limits for the range of unaltered Cenozoic volcanic rocks. The program SCREEN has been used together with geologic and geochemical relationships to successfully identify unaltered volcanic protoliths in studies of mass-volume changes during metasomatism around volcanogenic massive sulfide ore deposits (Petersen and DePangher, 1986; DePangher and Petersen, 1987).

Although the present application involves only volcanic rocks, logarithmic ratio diagrams are well suited for discriminating altered from unaltered rocks of any kind, provided the unaltered rocks define suitable discrimination fields in the first place.

## Summary

1. On certain log base 10 molar ratio diagrams, Cenozoic volcanic rock analyses representing a wide range of tectonomagmatic environments plot as single, well defined trends.
2. Logarithmic ratio diagrams according to Pearce (1968) and Beswick and Soucie (1978) have the useful property that alteration of the three components involved can be represented by combinations of only three fundamental vectors.
3. Volcanic rock alteration is detectable by systematic comparison of analyses to a comprehensive series of CVTs plotted on logarithmic ratio diagrams. The computer program SCREEN performs the systematic comparison.
4. The technique presented here has potentially broad application to all studies involving ancient and modern volcanic rocks where it is necessary to identify an unaltered volcanic protolith.
5. Similar applications of this technique to data for other lithologies should permit discrimination of altered from unaltered rocks of various kinds.

# AN APPLICATION OF NEW TECHNIQUES TO WALL-ROCK ALTERATION STUDIES

## Introduction

To demonstrate the impact of these new techniques on quantitative metasomatic studies, a test data set has been selected from the literature. Riverin and Hodgson (1980) studied wall-rock alteration at the Millenbach copper-zinc mine, an Archean volcanogenic massive sulfide deposit in the Noranda mining district, northwestern Quebec, Canada. The techniques presented herein are applied to the data of Riverin and Hodgson (1980) to identify actual conserved components and actual protoliths. Calculations of metasomatic gains and losses according to Gresens (1967) are then compared to demonstrate the consequences.

## Previous Work

Riverin and Hodgson (1980) concentrated their study on pipe-shaped alteration zones underlying two stratabound massive sulfide ore lenses at the Millenbach mine where they recognized six wall-rock alteration facies: fresh, weakly altered, spotted, giants spots, silicified, and anthophyllite or massive chlorite. Using data from Riverin (1977) they recalculated 114 whole-rock analyses and their specific gravities to a sulfide-free basis, estimated H<sub>2</sub>O contents from normative calculations of assumed original alteration mineral assemblages, and normalized to 100 weight percent. Average rocks for each alteration facies of each rock unit -- the Quartz Feldspar Porphyry, Millenbach Andesite, Amulet Rhyolite, and Amulet Andesite -- were then calculated.

For calculations of metasomatic gains and losses, Riverin and Hodgson (1980) regarded rocks of the fresh facies as protoliths and assumed volume conservation on the basis of preservation of delicate rock textures.

### Identification of Conserved Components

The same data used by Riverin and Hodgson (1980)-- whole-rock analyses of 59 samples of the Quartz Feldspar Porphyry, 25 samples of the Millenbach Andesite, 14 samples of the Amulet Rhyolite, and 16 samples of the Amulet Andesite (Riverin, 1977) -- were evaluated by the program CONSERVE. Table 11 is output from the program CONSERVE using Riverin's (1977) data for the Quartz Feldspar Porphyry at the Millenbach mine, Canada. These data suggest that  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  have been conserved with the  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$  pair representing the closest approach to ideal conservation. The data also suggest that total Fe as  $\text{FeO}^*$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{P}_2\text{O}_5$  have not been conserved. These conclusions are consistent with those recently reached by Grant (1987) using isocon diagrams. A summary of most frequently conserved component pairs at Millenbach, as determined by the program CONSERVE, is presented in Table 12. Since Riverin and Hodgson (1980) used calculated average compositions to represent their rock units, conserved components were determined using all Riverin's (1977) samples simultaneously for the rock unit in question. Volume factors (Gresens, 1967) used in subsequent calculations are averages of the two volume factors represented by the conserved component pairs. In the case of the Amulet Rhyolite, where no pair of conserved components was identified, volume factors have been used which are averages of the volume factors for the other three rock units of the same alteration facies.

### Identification of Protoliths

Riverin and Hodgson's (1980) calculated average protoliths and all analyses of rocks in the fresh facies (Riverin, 1977; Appendix III) from which the averages were derived were evaluated by the computer program SCREEN. The results are presented in Table 13. It is apparent that calculated average fresh rocks at Millenbach are generally not the best choices for unaltered

protoliths. The calculated average fresh rock for the Quartz Feldspar Porphyry is a particularly poor choice for unaltered protolith. It appears that a truly unaltered protolith can be found if a sufficient number of samples distant from the most intense alteration are collected. It is likely that a few more well chosen samples of the Amulet Rhyolite would include a truly unaltered protolith.

All individual rock analyses from Riverin (1977; Appendix III) were subsequently evaluated by the program SCREEN. Inspection of Millenbach Andesite and Amulet Andesite analyses classified as unaltered (Table 14) shows that both rock units are composed of at least two chemically distinct protoliths.

Graphical presentations of the technique embodied by the program CONSERVE are useful for further delimiting the probable protoliths. On logarithmic ratio diagrams with conserved numerator components, the actual protolith must lie on the linear regression curve defined by the metasomatic array. The case of the Millenbach Andesite is shown in Figure 8. Of three eligible candidates for Millenbach Andesite protolith, only sample 4-7 lies on the metasomatic array. The other two candidates clearly do not coincide with the metasomatic array and therefore can not represent the actual protolith.

The case of the Amulet Andesite is shown in Figure 9. In this instance, all three eligible candidates for protolith lie near each other on the metasomatic array. Sample 4-12 plots at the extreme lower left end of the array, while the most intensely altered rocks plot at the opposite end of the array. The other two candidates, samples 1730-10 and 4-10, plot at intermediate positions. Because sample 4-12 plots at the opposite extreme from the most altered rocks in a position consistent with the ubiquitous pattern of CaO loss seen in the other rock units, it is chosen as the unaltered protolith.

#### Comparative Calculations of Metasomatic Mass-Volume Changes

Metasomatic gains and losses were calculated according to the method of Gresens (1967) for the average altered rocks of Riverin and Hodgson (1980; Table 3) using their average fresh rocks as protoliths and assuming volume conservation (volume factor = 1.0). Comparative calculations were also made for Riverin and Hodgson's (1980; Table 3) average altered rocks using protoliths (Table 15), conserved component pairs (Table 12), and resultant volume factors (Table 16) determined from the original data (Riverin, 1977; Appendix III) by the programs CONSERVE and SCREEN. Since SCREEN identified some of Riverin and Hodgson's (1980) average fresh rocks as actually being altered, calculations were also made for transformations of actual protoliths to Riverin and Hodgson's (1980) average fresh rocks. Tables 17 through 20 show comparative metasomatic gains and losses as percentage changes by weight of oxide (grams gained or lost divided by original grams). Comparison of the results of the two different approaches shows three main features:

- (1) Some of Riverin and Hodgson's (1980) average fresh rocks are significantly altered.
- (2) The relative sense of gains and losses from one alteration facies to another is generally similar for the two methods. Both studies generally agree that FeO, MgO, and H<sub>2</sub>O are gained and CaO and Na<sub>2</sub>O are lost as the center of the alteration pipe is approached.
- (3) In most cases (except H<sub>2</sub>O), Riverin and Hodgson's (1980) approach underestimates the magnitude of a component's gain or loss compared to the present study.

### Discussion

In a broad sense, both methods show general agreement on many of the gross characteristics of wall-rock alteration at the Millenbach mine. Closer comparison shows, however, that the magnitudes of MgO and H<sub>2</sub>O fluxes differ significantly between the two approaches. Since volume factors determined in this study do not depart greatly from Riverin and Hodgson's (1980) assumed

value of 1.0, these differences are more likely attributable to the use of different protoliths. In the extreme case of the Quartz Feldspar Porphyry, Riverin and Hodgson (1980) underestimated MgO flux by anywhere from 274% to 1343% (Table 17). Riverin and Hodgson (1980) also consistently overestimated H<sub>2</sub>O flux for all rock units. The extreme case is the Millenbach Andesite where they overestimated H<sub>2</sub>O flux by anywhere from 86% to 1260% (Table 18). This suggests that at least some aspect of their method for assigning H<sub>2</sub>O contents based on normative calculations of assumed original minerals is inadequate. One possibility is that Riverin and Hodgson's (1980) normative hydrous phases (sericite and chlorite) do not adequately represent the H<sub>2</sub>O in clays and zeolites that might have been in the original alteration mineral assemblage (Date et al., 1983).

Volume factors (Table 16) calculated for the conserved component pairs SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>:TiO<sub>2</sub> (Table 12) all imply bulk volume changes. Volume is therefore apparently not conserved in the actual wall-rock alteration at the Millenbach mine. Volume changes documented for average rocks range from a 7.15% volume decrease for spotted Millenbach Andesite to a 7.2% volume increase for silicified Millenbach Andesite. Apparently such volume changes do not necessarily result in observable changes in primary rock textures.

### Detailed Study of Quartz Feldspar Porphyry (QFP)

#### Calculation of Metasomatic Gains and Losses

Metasomatic gains and losses were calculated for each of Riverin's (1977; Appendix III) 59 samples of the Quartz Feldspar Porphyry using sample 4-8 (Table 15) identified as the actual protolith composition of the QFP. Conserved components were chosen individually for each sample pair by taking the component pair whose volume factors and isocon slopes agreed most closely out of the three most frequently conserved components -- SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>. Metasomatic gains and losses are presented in Figure 10. Volume changes range from -22.6%

to +32.4%.

### Coherent Mobility

Certain QFP samples produced results ordinarily indicative of conservation for the component pairs  $\text{Na}_2\text{O}:\text{CaO}$  and  $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$  but had corresponding volume factors ranging from 0.19 (81% volume decrease) to 10.39 (939% volume increase). Coherent mobility was thus suspected.

Discerning between conservation and coherent mobility at Millenbach was accomplished by comparing the results of CONSERVE with corresponding C-V diagrams (Gresens, 1967). Simultaneous evaluation of all 59 samples by the program CONSERVE (Table 11) indicated that  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{Al}_2\text{O}_3$  were the most frequently conserved components. Implied volume factors ranged from .906 (9.4% volume decrease) to 1.050 (5.0% volume increase). The common appearance of  $\text{Na}_2\text{O}$  and  $\text{CaO}$  as denominators in output from CONSERVE (Table 11), the extraordinarily large volume changes implied by their volume factors, and the disagreement of these implied volume changes with those implied by well documented  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{Al}_2\text{O}_3$  conservation suggests that  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ , and  $\text{P}_2\text{O}_5$  were coherently mobile in these few, isolated pairs of samples.

### Discussion

Metasomatic gains and losses calculated for individual samples show that alteration within any given alteration facies is inhomogeneous on the scale of sampling. Figure 11 is a graphical demonstration of the inhomogeneity of alteration within the QFP. In the submarine hot spring environment of deposition envisioned by Riverin and Hodgson (1980), strong vertical and lateral gradients of temperature and water:rock ratio are likely. It is possible that such gradients might significantly contribute to alteration inhomogeneity.

## Summary

1.  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  are the most frequently conserved components in alteration at the Millenbach mine.
2. Volume is not conserved for most alteration at the Millenbach mine.
3. The use of averages for protoliths at the Millenbach mine results in reduction of the calculated magnitudes of metasomatic gains and losses.
4. The use of averages for altered products at the Millenbach mine results in almost total loss of ability to see the actual, spatially inhomogeneous nature of alteration.
5. Erroneous selection of an altered rock as protolith generally results in calculation of a reduced apparent spatial extent of alteration compared to that calculated from the actual protolith. The detectable limits of alteration at Millenbach are shown in this study to extend beyond the limits of Riverin's (1977) sampling.

## SUMMARY

All techniques utilizing assumed protoliths or assumed conserved components can only produce models of alteration that do not necessarily represent actual metasomatism. The techniques presented here offer a means of identifying actual protoliths and actual conserved components and thereby enable precise calculation of actual metasomatic gains and losses.

Accurate identification of conserved components leads directly to an improved ability to accurately calculate gains and losses for actual rather than hypothetical metasomatic processes. Writing a balanced chemical reaction requires that the net change in volume or the change in mass of a chemical component be known. Accurate knowledge of actual gains and losses enables one to write balanced net chemical reactions that represent actual net mass and volume changes. This puts geochemical modeling of metasomatism on demonstrably firmer footing than the hypothetical approach. In cases where conserved components can be identified, actual volume changes for actual metasomatic processes can be calculated. The common assumption of volume conservation can thus be quantitatively evaluated. Similar common assumptions about so-called immobile elements can be quantitatively evaluated as well. As more such quantitative evaluations are done, more will be learned about the nature of mass and volume changes in metasomatic processes. This should in turn place empirical constraints on estimates of mass and volume changes when quantitative information is unavailable.

The ability to identify actual altered protoliths leads directly to an improved ability to delimit the actual spatial extent of alteration and possibly the size of the system that produced it. It is possible that ore-related wall-rock alteration might be detectable at a distance from ore significantly greater than previously suspected. This has obvious application to exploration. Knowledge of actual gains and losses might also be used to geochemically fingerprint the altera-

tion patterns for a given deposit type. If successful, this could be an important exploration tool.

This study has also shown that there are at least two chemically distinct protoliths in the Millenbach Andesite and the Amulet Andesite. Knowledge of the range of compositions of protoliths in these formations could provide information useful in better understanding their petrogenesis and tectonomagmatic environments of deposition.

This study has shown that the use of assumed protoliths, assumed conserved components, and assumed volume changes results in calculated hypothetical gains and losses which can differ significantly from gains and losses calculated from actual protoliths, actual conserved components, and actual volume changes. Such use of assumed parameters can lead to an inaccurate understanding of the spatial limits and character of the alteration and the geochemical processes which caused it.

Whenever possible, actual rather than hypothetical protoliths, conserved components, and volume changes should be used in order to gain the most accurate possible understanding of the metasomatism being studied.

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TABLE 5. Mobilities of Chemical Components in Experimental Alteration of Graywacke With Seawater<sup>1</sup>

Component	Percentage Change <sup>2</sup>
Ca	-69.1
K	-21.9
Na	14.6
Mg	31.1
CO <sub>2</sub>	-84.5
C <sub>org</sub>	-76.6
Fe	- 1.9
Mn	-24.4
Zn	- 9.1
Ni	- 8.8
Cu	- 5.0
Pb	0.0
Sb	-90.0
Cd	0.0

<sup>1</sup> Data from Bischoff et al. (1981; Table 7).  
<sup>2</sup> Calculated according to the following: (final rock - original rock)/original rock.

TABLE 6. Evaluation of CONSERVE's Ability to Identify Conserved Components in Experimental Alteration of Graywacke With Seawater

Mobility	Experiment <sup>1</sup>	CONSERVE
Conserved	Pb, Cd,	Pb, Cd
Intermediate	Fe, Cu, Ni, Zn	Cu, Ni, Zn, Fe
Mobile	Na, K, Mn, Mg, Ca, C <sub>org</sub> , CO <sub>2</sub> , Sb	K, Mn, Na, Mg, Ca, C <sub>org</sub> , CO <sub>2</sub> , Sb

<sup>1</sup> Data from Bischoff et al. (1981; Table 7).

TABLE 7. Correlation and Regression Coefficients for the Cenozoic Volcanic Trend Equations Used in the Program SCREEN

CVT Components				Coefficients				
CVT	X	Y	Z	Corr. R	Regression <sup>1</sup> a b c d			
1	Si O <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	0.996	-0.070	0.241	0.950	0.737
2	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	0.980	-0.011	0.118	0.807	0.277
3	MnO	FeO <sup>2</sup>	K <sub>2</sub> O	0.958	-0.016	0.156	0.644	-1.546
4	Ti O <sub>2</sub>	FeO <sup>2</sup>	K <sub>2</sub> O	0.968	-0.082	0.174	0.969	-0.929
5	MgO	CaO	K <sub>2</sub> O	0.983	-0.013	-0.066	1.359	-0.365
6	Ti O <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	0.915	-0.109	-0.179	1.192	1.124
7	Si O <sub>2</sub>	H <sub>2</sub> O <sup>4</sup>	MgO	0.890	-0.025	0.209	0.796	1.176

<sup>1</sup> Regression equations are of the form: (X/Z) = a(Y/Z)<sup>3</sup> + b(Y/Z)<sup>2</sup> + c(Y/Z) + d, where X/Z and Y/Z are log base 10 molar ratios.

<sup>2</sup> Total Fe as FeO

<sup>3</sup> Total H<sub>2</sub>O

TABLE 8. Boundary Displacement Values of X/Z for CVTs  
Used in the Program SCREEN

CVT	X/Z
1	±0.200
2	±0.342
3	$\pm(-0.032(Y/Z)^2 - 0.022(Y/Z) + 0.414)$
4	±0.334
5	±0.425
6	±0.750
7	±0.675

CVT field boundary values of X/Z are given as positive and negative log base 10 molar ratio displacements of X/Z from the regression curve X/Z values. Most of the X/Z values are constant, although displacements for CVT #3 are given as a function of Y/Z.









TABLE 13. SCREEN Classification of Fresh Facies Rocks at the Millenbach Mine

Rock Unit	Unaltered			Altered <sup>1</sup>			# Samples
	Weak			Moderate			
	Strong						
Quartz Feldspar Porphyry <sup>2</sup>	1	2	0	7			10
Av. Quartz Feldspar Porphyry <sup>3</sup>				X			
Millenbach Andesite <sup>2</sup>	3	6	0	2			11
Av. Millenbach Andesite <sup>3</sup>				X			
Amulet Rhyolite <sup>2</sup>	0	2	0	0			2
Av. Amulet Rhyolite <sup>3</sup>				X			
Amulet Andesite <sup>2</sup>	2	2	1	0			5
Av. Amulet Andesite <sup>3</sup>				X			

<sup>1</sup>Altered rocks have been subdivided into weakly, moderately, and strongly altered based on how many Cenozoic Volcanic Trend fields they plot outside of and how far outside they are.

<sup>2</sup>Data from Riverin (1977) Appendix III.

<sup>3</sup>Calculated average rock data from Riverin and Hodgson (1980; Table 3).

TABLE 14. Weight Percentage Chemical Compositions of All Millenbach Andesite and Amulet Andesite Samples Classified As Unaltered by the Program SCREEN

Sample <sup>1</sup>	Millenbach Andesite			Amulet Andesite		
	4-6	4-5	4-7	4-10	4-12	1730-10
SiO <sub>2</sub>	53.57	53.80	59.92	56.01	49.46	53.76
TiO <sub>2</sub>	1.84	1.90	1.20	1.56	1.31	1.19
Al <sub>2</sub> O <sub>3</sub>	13.23	14.39	14.45	14.28	15.30	16.58
FeO*	11.81	11.96	6.79	8.31	11.20	9.42
MnO	0.20	0.20	0.14	0.23	0.22	0.10
MgO	5.62	5.92	3.47	3.89	5.30	6.65
CaO	4.92	4.84	3.71	7.51	9.28	6.32
Na <sub>2</sub> O	3.78	3.78	5.10	3.46	2.56	3.13
K <sub>2</sub> O	2.07	1.99	1.42	0.77	0.65	1.84
P <sub>2</sub> O <sub>5</sub>	0.37	0.33	0.16	0.27	0.22	0.17
H <sub>2</sub> O	1.74	1.48	1.70	1.26	1.76	3.76
Total	99.15	100.59	98.06	97.55	97.26	102.92
Density	2.81	2.78	2.78	2.80	2.94	2.95

<sup>1</sup>Data from Riverin (1977) Appendix III. Twenty-five samples of Millenbach Andesite and 16 samples of Amulet Andesite representing all 6 alteration facies were evaluated by the program SCREEN. All samples classified as unaltered come from the fresh facies of Riverin (1977) except 1730-10 which comes from the weakly altered facies.

\*Total Fe as FeO.













I. Plate Margin (647)	
A. Convergent (215)	
1. Oceanic/oceanic (108)	
a. Marianas	( 16)
b. Lesser Antilles	( 58)
c. Tonga	( 20)
d. Kermadec	( 14)
2. Oceanic/continental (107)	
a. Cascades	( 84)
b. Aleutians	( 23)
3. Continental/continental -- no data	
B. Divergent (432)	
1. Oceanic (193)	
a. mid-ocean ridges	(167)
1. fast spreading	
a. East Pacific Rise	( 51)
2. slow spreading	
a. Mid-Atlantic Ridge	(116)
b. back arc basin crust ( 26)	
1. Philippine Sea	( 26)
2. Continental (239)	
a. rift zones (141)	
1. African Rift	( 87)
2. Rio Grande Rift	( 54)
b. broad extensional zones (98)	
1. Mojave Desert	( 25)
2. Nevada	( 3)
3. Marysvale, Utah	( 1)
4. San Francisco Mtns.	( 57)
5. Southwest Utah	( 12)
II. Intraplate (486)	
A. Oceanic (117)	
1. Hawaii	(107)
2. Canary Islands	( 10)
B. Continental (369)	
1. Plateau areas (103)	
a. Columbia River	( 29)
b. Snake River Plain	( 74)
2. Calderas in tectonically stable areas (161)	
a. Yellowstone	( 19)
b. San Juan Mountains	(142)
3. Calderas in tectonically unstable areas (105)	
a. Goldfield, Nevada	( 21)
b. McDermitt, Nevada	( 7)
c. Silver Peak, Nevada	( 28)
d. Central Nevada	( 1)
e. Timber-Oasis, Nevada	( 48)
	<hr/>
	Total # Samples
	1133

Figure 1. Hypothetical alteration of plagioclase to calcite. System A is enclosed by the outer surface of the plagioclase crystal. System B is enclosed by the outer circular boundary. Volumes of systems A and B are conserved in this hypothetical alteration.

Figure 2. Geometric relations between the three fundamental alteration vectors on a log base 10 ratio diagram.

Figure 3. Composition-volume diagram of Gresens (1967) demonstrating coherent mobility. Reprinted with permission.

Figure 4. Abbreviated composition-volume diagram of Gresens (1967) demonstrating coherent mobility. Reprinted with permission.

Figure 5. Isocon diagram of Grant (1987) demonstrating coherent mobility.

Figure 6. Tectonomagmatic classification scheme and geographic distribution of PETROS analyses used in this study. Number of samples from each locality is in parentheses.

Figure 7. Typical Cenozoic Volcanic Trend (CVT)

Figure 8. Plot of  $\log_{10}$  molar  $\text{TiO}_2/\text{K}_2\text{O}$  versus  $\log_{10}$  molar  $\text{Al}_2\text{O}_3/\text{K}_2\text{O}$  for all samples of the Millenbach Andesite. The program SCREEN has been used to classify samples as unaltered (open triangles) or altered (open circles).

Figure 9. Plot of  $\log_{10}$  molar  $\text{SiO}_2/\text{CaO}$  versus  $\log_{10}$  molar  $\text{Al}_2\text{O}_3/\text{CaO}$  for all samples of the Amulet Andesite. The program SCREEN has been used to classify samples as unaltered (open triangles) or altered (open circles).

Figure 10. Histogram of metasomatic gains and losses in the Quartz Feldspar Porphyry. Gains and losses are in percentage by weight. Vertical dimension of the histogram indicates the relative number of samples in each class.

Figure 11. Plot of  $\log_{10}$  molar  $\text{Na}_2\text{O}/\text{MgO}$  versus  $\log_{10}$  molar  $\text{K}_2\text{O}/\text{MgO}$  for all samples of the Quartz Feldspar Porphyry. The plot shows inhomogeneity of alteration within each alteration facies for the components  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{MgO}$ . Letters A-F correspond to the fresh, weakly altered, spotted, giant spots, silicified, and massive chlorite/anthophyllite facies, respectively, of Riverin and Hodgson (1980). Open triangle encloses the unaltered Quartz Feldspar Porphyry protolith used in this study. Also shown is the regression curve (solid line) for CVT #2 (Table 2). This particular plot clearly shows the fact that rocks of the fresh facies are actually altered.