

Mass change calculations in altered rock series

W.H. MacLean

Department of Geological Sciences, McGill University, Montreal, Quebec, Canada H3A 2A7

Abstract. A technique is presented whereby precursors of altered rocks in a fractionated rock series can be identified, and changes in chemical components, mass and volume accurately calculated. The procedure utilizes elements with high degrees of immobility in hydrothermal and associated interactive water-rock systems. Igneous rock series, and sedimentary and metamorphic rocks with primary continuity of chemical composition, are amenable to this treatment. In the procedure for igneous rocks, best-fit fractionation lines are established for an immobile igneous compatible-incompatible element pair, the latter element functioning as the fractionation monitor. Alteration paths are linear and pass through the origin. Intersections of the fractionation and alteration lines yield the immobile element concentrations in the precursors to the altered rocks; mobile components are determined from fractionation lines and monitor values. Total mass changes are proportional to the displacement of altered samples from the fractionation line. Masses of other elements in an altered sample (reconstructed values) are recalculated to the concentration of the monitor element in the precursor. Chemical changes are the differences between the calculated precursor compositions and the reconstructed altered rock compositions. Errors are mainly a function of the positioning of the fractionation lines.

Rocks that have been hydrothermally altered gain and lose mass and chemical constituents, and commonly it is difficult or impossible to identify the parent rock. In this paper a technique is presented which can be used to determine a precise chemical composition of the parent rock for each altered sample and to calculate the change in each chemical constituent. A quantitative knowledge of these changes is often needed for modeling metasomatism, alteration and ore genesis, which have application to problems in mineral exploration.

Where the parent of an altered rock is a well-defined, chemically homogeneous unit (a single precursor), mass

and chemical changes can be calculated from changes in concentrations of immobile elements (MacLean and Kranidiotis 1987). The single precursor technique can be applied to alteration studies on any homogeneous rock type, igneous, sedimentary or metamorphic, that contains immobile elements in measurable amounts.

If altered rocks are derived from unrelated precursors, or from rocks ranging widely in composition, the problem of identifying precursors and measuring mass and chemical changes is commonly insolvable. However, when compositional variation in the parent rocks is continuous and predictable, as it is in most igneous rock series, the problem is alleviated, and changes owing to alteration can be closely monitored. In this paper the geologic basis of the method and derivation of formulae and calculation procedures are outlined.

Methodology

Elements that are immobile during hydrothermal alteration and other interactive water-rock systems are concentrated during net mass loss and diluted by net mass gain. Calculation of these changes (material changes) requires different approaches when the altered rocks are derived from one, or more than one parent rock (single or multiple precursors). In single precursor systems the changes are calculated as displacements from a uniform rock composition (MacLean and Kranidiotis 1987), whereas in multiple precursor systems they are calculated as displacements from a primary chemical mixing line or an igneous fractionation line.

In a single precursor system residual concentration and dilution of immobile elements produce linear arrays of data on binary diagrams that contain the precursor composition and extrapolate to the origin. The correlation coefficient is used as a gauge of mobility. Elements having chemical affinity must be avoided in such tests because of unrelated correlation. Mass changes are calculated from the concentration ratio of an immobile element in an altered samples and its precursor. The

above methodology was used by MacLean and Kranidiotis (1987) and MacLean (1988) to show that Al, Ti, Zr, Nb, Y, Yb and Lu were highly immobile in the alteration zone below the Phelps Dodge massive sulphide deposit.

Multiple precursors

Material changes in multiple precursor systems are most easily determined for igneous rocks series that exhibit initial chemical continuity between fractionated units, although certain sedimentary and metasomatic rock suites should also be amenable to this treatment. Within igneous suites, volcanic rocks closely represent fractionated magmatic liquids and yield more accurate results than their plutonic counterparts.

Tests for immobility of the incompatible elements (distribution coefficient, mineral/melt, $D < 0.1$) are made in the same way in multiple as in single precursor systems. When one of an immobile pair is compatible (that is, it fractionates) during crystallization of the magma (e.g. Al, Ti), the incompatible element functions as a monitor of igneous fractionation and yields (Harker-type trends in the chemical data (Fig. 1). On the Harker diagrams, alteration paths are separate for each sample or homogeneous volcanic unit in a series. The paths produce radial arrays of lines that emanate from the origin and intersect the fractionation lines. The intersection of the alteration and fractionation lines provides a means of identifying altered rock precursors (Finlow-Bates and Stumpfl 1981; MacLean and Kranidiotis 1987). The immobility of compatible elements must be determined on a homogeneous unit within the series, although if this is not feasible, elements of proven immobility in similar systems can be used with appropriate reservations. Tests for immobility of elements were made on altered rocks associated with massive sulphide deposits at Phelps Dodge (MacLean and Kranidiotis 1987; MacLean 1988), Matagami (unpublished data; MacLean 1984), Kidd Creek (data from Campbell et al. 1984) and Noranda (data from Gibson et al. 1983). These tests have shown that Al and Ti were extremely immobile during hydrothermal alteration of volcanic host rocks.

Once the immobile monitor has been selected for either a single or multiple precursor system, total mass change is calculated. This change is directly proportional to the concentration of the monitor element in the precursor (a' , Fig. 1) compared to the altered sample (a , Fig. 1; MacLean and Kranidiotis 1987). The reconstructed composition (R-C) of the altered sample, calculated at the constant concentration of the monitor element, is computed for each component as

$$R-C = \% \text{ component, altered rock} * \frac{I-M (\text{precursor})}{I-M (\text{altered rock})} \quad (1)$$

where I-M = immobile element monitor. When the precursor mass is taken as 100, mass additions and subtractions are equivalent to weight percent changes. The basic principle of the reconstructed composition concept is il-

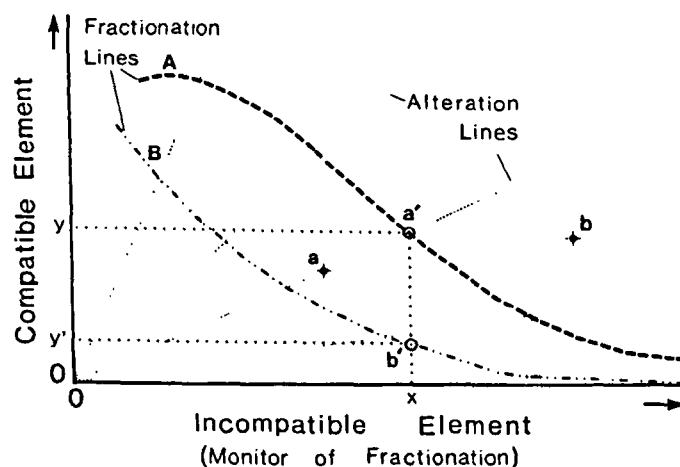


Fig. 1. Schematic diagram illustrating the effects of alteration on mobile and immobile igneous compatible elements. The incompatible element monitor of fractionation is immobile. Fractionation line A is for an immobile compatible element, and line B for a mobile compatible element. Alteration paths (lines) for immobile elements are linear (owing to mass gains and losses) and pass through the origin at infinite dilution. Point a is a plot of the concentration of an immobile element in an altered rock that has gained mass; a' is the projected precursor composition on line A (x , y). The compatible component plotting at b is mobile, and its position has no direct relation to fractionation line B, as it can be added to or removed from the system as well as being affected by mass changes. The precursor composition (x , y') is calculated by projecting the immobile monitor composition (x) to fractionation line B

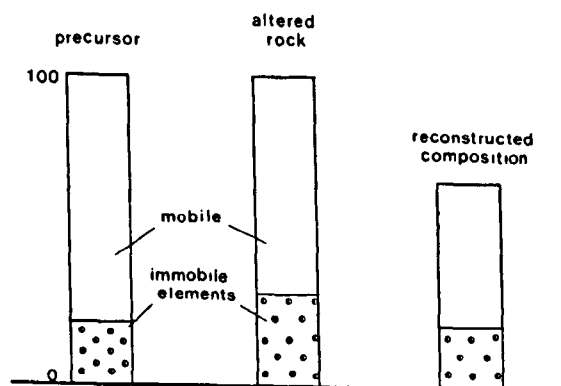


Fig. 2. Illustration of the relation of a reconstructed composition to precursor and altered rock compositions. The precursor and altered rock columns are normalized chemical compositions (wt%). The reconstructed composition of the altered rock is calculated by reducing the content of the immobile elements in the altered rock to the level in the precursor. The mobile elements are reduced in amounts in the same proportion

lustrated in Fig. 2. The reconstructed composition represents the net mass of a unit or rock that has gained or been depleted in mobile components.

Changes in individual components are the differences between the precursor and the reconstructed compositions. So far in these calculations, the reconstructed compositions and the immobile element contents of the precursors have been calculated. Changes in the mobile element contents of the precursors are also obtained from igneous fractionation lines, but the calculation procedure is different.

Fractionation lines

Fractionation lines for a magmatic series are based on samples from least altered units within the alteration zone and from adjacent stratigraphy. The positioning of the lines is critical in limiting error in the material change calculations. The lines can be expressed mathematically by linear, exponential or polynomial equations.

The immobile fractionation monitors should be tested for compatibility. Zr is the most commonly used monitor for igneous rocks because it is highly immobile (MacLean and Kranidiotis 1987), abundant (~10–500 ppm) and is accurately analysed by the X-ray fluorescence method (pressed powder pellets). Zr is highly incompatible in tholeiitic rocks, but compatible in many calc-alkaline rock series (Watson and Harrison 1983), and other less abundant incompatible elements (Nb, Hf, Ta, Th) may have to be used.

Precursor compositions

As outlined above, a straight line connecting the bulk composition (a, Fig. 1) and the origin defines the alteration path for an immobile element pair. The intersection of the alteration and igneous fractionation lines (a') yields the immobile element precursor composition for these elements in each sample. The line intersections can be solved graphically or mathematically. Polynomial equations for the fractionation lines were most amenable to mathematical solution. The data reduction is readily adapted to a spreadsheet computer program (a sample program is available on request). The line equations can be updated easily with new data, so that as a project advances, the the calculated mass changes become more accurate.

The mobile element compositions of the precursors are determined from the fractionation lines and the immobile monitor compositions calculated above. Since all igneous rocks of a series are constrained to plot on the fractionation lines, so must the altered rock precursors. The incompatible monitor precursor composition (x, Fig. 1) of an altered rock (b) is simply projected from the monitor axis to the fractionation line (b') to obtain the mobile element precursor composition (y'). This is equivalent to substituting the monitor value (x) into the fractionation equation and solving for the mobile element (y').

Mass change calculations

Gains and losses of components are calculated as the differences between the precursors and the reconstructed compositions (R-C) given by Eq. (1):

$$\text{material change} = R - C - \text{precursor composition.} \quad (2)$$

The accuracy of the calculations depends on the estimated values of the precursor compositions, which, in turn, are functions of the precision of the fractionation lines. Factors which must be taken into consideration

when positioning the fractionation lines include phenocryst accumulation, multiple magmatic series, contamination and alteration. Close petrographic inspection will generally detect these abnormalities.

Mass changes at the Horne mine

Chemical data from altered wallrocks at the Horne mine, Noranda, Quebec, are used to illustrate the material change calculations for a multiple precursor system. The data were collected as part of a comprehensive study of the Horne and Quemont mines by the Mineral Exploration Research Institute (Cattalani et al. 1988) for the Ministry of Energy and Resources of Quebec. Details of the mine stratigraphy and alteration are the subject of a separate paper.

The Horne and nearby deposits are the models for the Noranda-type volcanogenic massive sulphides (Sangster 1972). The mine geology has been described by Price (1948), Sinclair (1971) and Cattalani et al. (1988). The Horne deposit lies within rhyolitic rocks of Archean age in the Abitibi greenstone belt. Nearby volcanic rocks range from basalts to rhyolites. The rocks close to the deposit have been intensely hydrothermally altered. Rhyolites in both the footwall and hanging wall have undergone pervasive sericite-silica alteration, but locally intense chloritization has occurred around the massive cupriferous ores and in veinlet-type (stringer) copper ore in the footwall.

Fractionation lines were drawn from data for the volcanic rocks collected in this study and supplementary data from Ujike and Goodwin (1987). Binary plots of Al_2O_3 -Zr and TiO_2 -Zr (Fig. 3) were used to establish immobile element fractionation lines. The TiO_2 -Zr plot was preferred for use in the mass change calculations as the line fit was better, and there is a greater separation of the mine tholeiites from a calc-alkaline series also present in the district.

The majority of the altered samples plotted on the TiO_2 -Zr diagram lie between two alteration lines (radii) which intersect the fractionation line at about the limits of the field of rhyodacite-rhyolite rocks (Fig. 3). The original amounts of TiO_2 and Zr in each altered sample is obtained, as described above, by extending the alteration radii to the fractionation line (or solving the line equations for Ti and Zr). Mass change factors are calculated from either component (e.g. Zr precursor/Zr sample) and reconstructed compositions are calculated with Eq. (1). Samples plotting between the origin and the fractionation line on immobile element plots have gained mass, and those on the other side have lost mass.

Data for the mobile element contents of the precursors are calculated from the binary plots with Zr as monitor. The igneous fractionation lines are less easily located for these elements, and the positions of the altered samples are not restricted to origin-precursor alteration lines. Plots of data for SiO_2 -Zr, Fe_2O_3 -Zr and MgO -Zr are illustrated in Figs. 4, 5 and 6. The precursor contents of these and other mobile elements were calculated by projecting the precursor Zr compositions, obtained from the

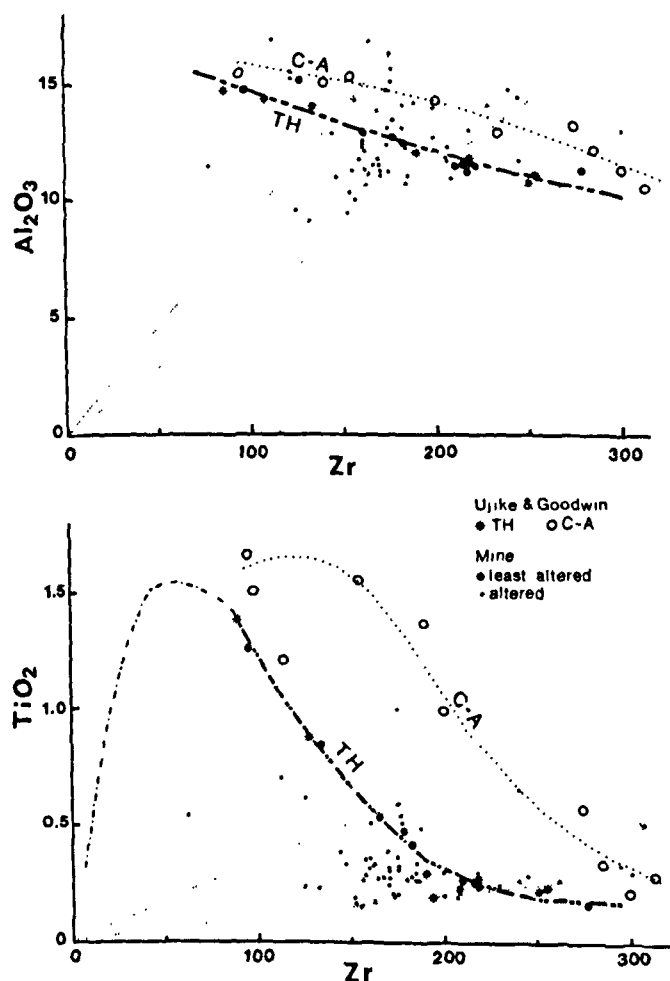


Fig. 3. a Both TiO_2 and Zr are immobile components. The dot-dash extension of the tholeiite fractionation line is inferred. The fine dotted alteration lines encompass the bulk of the altered rocks. The heavy section of the tholeiite line is expressed by the equation $y = 2.43 - 0.0149x + 0.000023x^2$. C-A, calc-alkaline; TH, tholeiite, b fractionation and alteration paths for Al_2O_3 -Zr. Separation of the tholeiite and calc-alkaline fractionation lines is difficult due to their proximity. Symbols as in Fig. 3a. Equation for the tholeiite line is $y = 18.0 - 0.0365x + 0.000035x^2$

Zr- TiO_2 diagram, to the fractionation lines or by solving the fractionation line equation for Zr in the precursor. Some fractionation lines were fitted with polynomials and others with straight-line equations.

With the above estimations of the precursor and reconstructed compositions, the loss or gain in each component and in net mass were calculated with Eq. (2). These net changes are plotted on Harker diagrams against the original SiO_2 content of the precursor in Fig. 7, and average net changes for the alteration zone have been calculated.

The chemical changes are calculated as divergences from the unaltered precursor rocks. Other components such as ore metals, gangue material and isotopes can be treated in a similar fashion.

SiO_2 . The igneous fractionation line for SiO_2 (Fig. 4) displays a near-linear SiO_2 enrichment ($D < 1$) up to rhyolite compositions, where it flattens with quartz fractionation. The maximum silica content of the precursors is

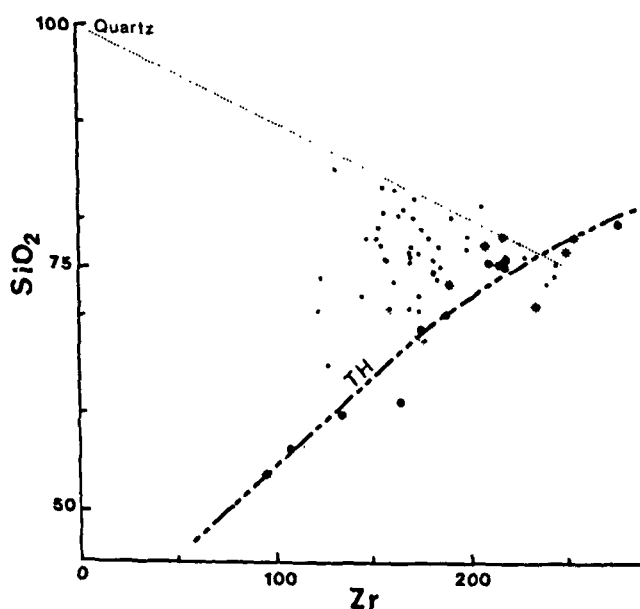


Fig. 4. Mobile SiO_2 vs immobile Zr. The fractionation path for SiO_2 approaches a straight line for basic and intermediate compositions, but becomes depleted by fractionation of quartz in the felsic members. Samples plotting between the fractionation line and quartz have either been silicified or contain quartz phenocryst accumulations. Symbols as in Fig. 3a. Equation for the line is $y = 35.0 + 0.23x - 0.00025x^2$

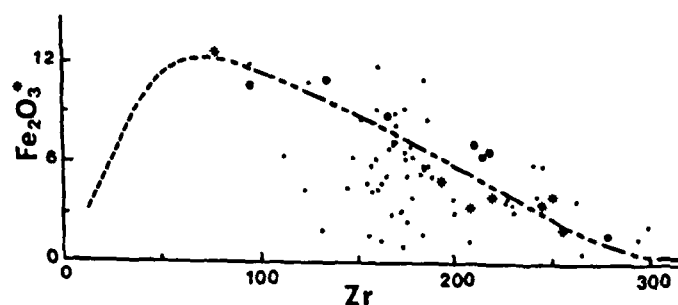


Fig. 5. Plot of Fe_2O_3^* vs immobile Zr. Symbols from Fig. 3a. Equation for line is $y = 16.5 - 0.06x + 0.000035x^2$

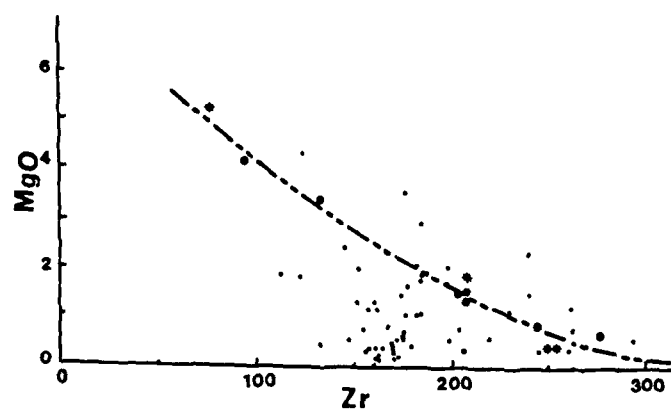


Fig. 6. Plot of MgO vs immobile Zr. Symbols as in Fig. 3a. Equation for line is $y = 8.0 - 0.044x + 0.000060x^2$

about 75 wt% SiO_2 . Most of the altered samples plot between the fractionation line and quartz, qualitatively indicating extensive hydrothermal silicification combined with a smaller effect owing to quartz phenocryst accumulation. There has been an average net addition of 13.8% SiO_2 (Fig. 7). Samples showing SiO_2 loss are heav-

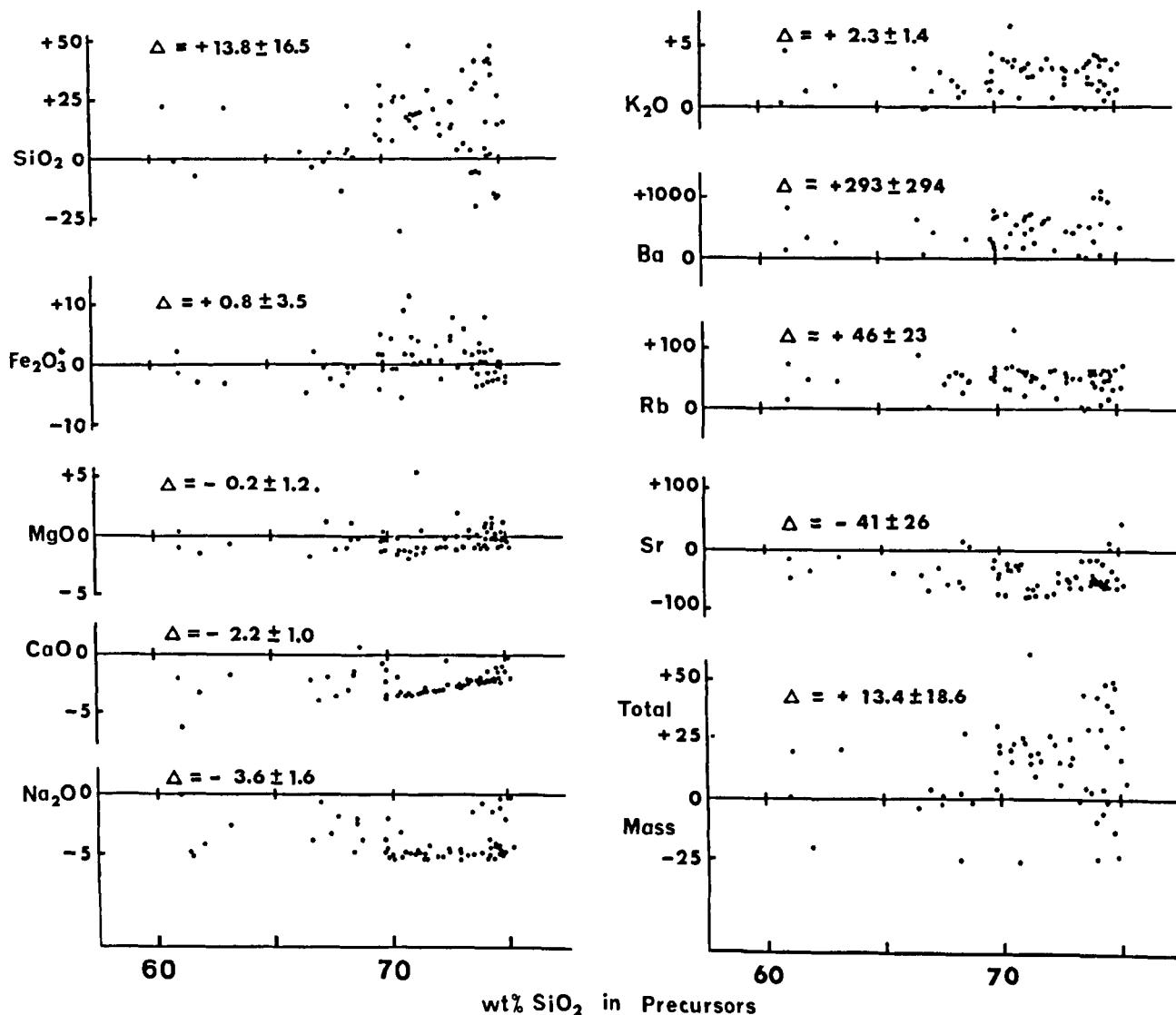


Fig. 7. Total mass and mobile component changes plotted against the calculated SiO₂ content of the precursor for each sample. The

delta values are the average gains or losses (\pm , one standard deviation) of the components

ily chloritized. Figure 7 illustrates a quantitative display of SiO₂ changes.

Al₂O₃. The Al₂O₃ fractionation line has a characteristic gentle slope to lower values in the rhyolites (Fig. 3b), and a linear equation regressed the data as well as the polynomial. Al₂O₃ is normally highly immobile in alteration zones, although it may experience mobility on the centimeter scale as evidenced by veinlet and amygdale fillings (MacLean and Kranidiotis 1987). Scatter in the Al₂O₃ data used to establish the fractionation line can largely be attributed to plagioclase phenocryst accumulation.

Fe₂O₃. The fractionation line for Fe₂O₃-Zr (Fig. 5) is similar to that for TiO₂ owing to their equivalent chemical behavior in igneous systems. More basic tholeiitic lavas would follow Fe and Ti enrichment trends at low Zr contents. Most of the altered samples fall below the fractionation line but, because of the mobility of iron, this does not confirm its loss; a sample with a combination of gains in both total mass and iron could also plot in this area. The material change plot (Fig. 7) and average

change calculation show a net addition of 0.8 wt% Fe₂O₃.

MgO. MgO forms a depletion-type ($D > 1$) igneous fractionation trend (Fig. 6). Alteration has further depleted the mine rocks by an average 0.2 wt% MgO (Fig. 7). Magnesium is fixed in chlorite at an early stage of alteration, but may be depleted by replacement of chlorite by sericite (at constant Al).

CaO, Na₂O, Sr. These components were extensively leached during alteration. Of the three, Na₂O is the most depleted (70%), followed by CaO and Sr (Fig. 6). CaO is retained in unreacted plagioclase, epidote and calcite.

K₂O, Rb, Ba. The precursor rocks contain an average of 0.34 wt% K₂O, 7 ppm Rb and 50 ppm Ba. An average of 2.3 wt% K₂O, 46 ppm Rb and 293 ppm Ba were added during alteration, mainly through the production of sericite. Additions of these elements are clearly shown on Fig. 7, in contrast to the strong depletion of Na, Ca and Sr and the mixed addition-depletion of Fe, Mg and Si.

Total mass. Total mass changes range from losses of 20% to gains of 50%, but are obviously dominated by additions (net 13.4 wt%). The changes are mostly a function of the addition of silica, but also reflect the constant losses of Ca and Na and large addition of K.

Discussion

The technique of using immobile elements and fractionation lines accurately identifies altered volcanic rock precursors and measures material changes. The calculations are straightforward and are readily adapted to spreadsheet computer programs. If the requirements of chemical continuity in the rock series and element immobility are met, the technique probably can be used to monitor other metasomatic changes. The accuracy of the calculations depends on the accuracy of the fractionation (or mixing) lines. Fractionation lines can, however, be updated as new data are obtained. Initial inhomogeneities in the monitoring elements and local deviations from mixing or fractionation trends are the main sources of calculation error.

Other methods of estimating material changes in altered rocks, particularly those of Gresens (1967), have found considerable use. Gresens formulated equations involving major oxide analyses and densities to estimate volume and mass changes. The equations contain two dependent variables (mass and volume) with no independent means to determine (or fix) one of them. The method was designed essentially for single precursor rocks (Gresens 1967; Babcock 1973). Grant (1986) rearranged the equation to calculate "isocon" (equal chemical composition) lines, but the problem of two variables remained. The mass variable can now be fixed for many altered rock systems by using the procedures of MacLean and Kranidiotis (1987) to test for immobile elements.

Volume changes can be calculated from normative mineral assemblages for precursors and altered equivalents using appropriate mineral densities. Actual volume changes in seafloor volcanics and sediments may not be large owing to void spaces that take up most silica and carbonate, and sericitization and chloritization of Al-bearing components are approximately isovolumetric processes. However, intense chloritization is invariably accompanied by extensive leaching of silica which causes large volume losses (MacLean and Kranidiotis 1987).

Where good sampling access is available, it will be possible to draw precise material change profiles through alteration zones. Besides the changes in rock-forming components, additions and losses of base and precious metals and gangue components can be accurately measured and portrayed. The precursor data also provide a basis for estimating overall changes in hydrothermal systems. For example, the sericite-silica alteration zone at the Horne mine, which originally was a low-K tholeiitic rhyolite, has a minimum volume of 5 km³ (MacLean, Ch. 6, in Cattalani et al. 1988) which has received exceptionally large additions of silica (13.8 wt%), equivalent to 0.7 km³ of quartz and 2.3 wt% K₂O.

Greenschist-facies rocks around volcanogenic massive sulphide deposits generally provide sufficient ranges

of compositions to monitor igneous fractionation trends. Ophiolites and other basalt-dominated stratigraphy will have shorter fractionation intervals, but they should not be treated as single precursor systems without proper testing.

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References

- Babcock, R.S.: Computational models of metasomatic processes. *Lithos* 6:279–290 (1973)
- Campbell, I.H., Leshner, C.M., Coad, P., Franklin, J.M., Gorton, M.P., Thurston, P.C.: Rare-earth element mobility in alteration pipes below massive Cu-Zn sulfide deposits. *Chem. Geol.* 45:181–202 (1984)
- Cattalani, S., Barrett, T.J., MacLean, W.H., Hoy, L., Hubert, C., Fox, J.S.: Metallogeny of base-metal massive sulfide deposits in the Abitibi Belt, Quebec: 1. The Horne and Quemont mines, Noranda. Mineral Exploration Research Institute, Project No. 82-058, Ministère de l'Énergie et Ressources du Québec (1988)
- Finlow-Bates, T., Stumpfl, E.F.: The behavior of the so-called immobile elements in hydrothermally altered rocks associated with volcanogenic submarine-exhalative ore deposits. *Mineral. Deposita* 16:319–328 (1981)
- Gibson, H.L., Watkinson, D.H., Comba, C.D.A.: Silicification: Hydrothermal alteration of an Archean geothermal system within the Amulet rhyolite formation, Noranda, Quebec. *Econ. Geol.* 78:954–971 (1983)
- Grant, J.A.: The Isocon diagram – a simple solution to Gresens' equation for metasomatic alteration. *Econ. Geol.* 81:1976–1982 (1986)
- Gresens, R.L.: Composition-volume relationships of metasomatism. *Chem. Geol.* 2:47–55 (1967)
- MacLean, W.H.: Rare earth elements mobility at constant inter-REE ratios in the alteration zone at the Phelps Dodge massive sulphide deposit, Matagami, Quebec. *Mineralium Deposita* 23:231–238 (1988)
- MacLean, W.H.: Geology and ore deposits of the Matagami District. *Can. Inst. Min. Met. Sp. Vol.* 34:483–495 (1984)
- MacLean, W.H., Kranidiotis, P.: Immobile elements as monitors of mass transfer in hydrothermal alteration: Phelps Dodge massive sulfide deposit, Matagami, Quebec. *Econ. Geol.* 82:951–962 (1987)
- Price, P.: Horne mine. In: *Structural Geology of Canadian Ore Deposits*. *Can. Inst. Min. Met. Jubilee Vol. I*:763–772 (1948)
- Sangster, D.F.: Precambrian volcanogenic massive sulphide deposits in Canada: a review. *Geol. Sur. Can. Pap.* 72-22:44 p (1972)
- Sinclair, W.D.: A volcanic origin for the origin of the No. 5 Zone of the Horne mine. *Econ. Geol.* 66:1225–1231 (1971)
- Ujike, O., Goodwin, A.M.: Geochemistry and origin of Archean felsic metavolcanic rocks, central Noranda area, Quebec, Canada. *Can. Jour. Earth Sci.* 24:2551–2567 (1987)
- Watson, E.B., Harrison, T.M.: Zircon saturation revisited: temperature and composition effects in a variety of crustal magma types. *Earth Planet. Sci. Lett.* 64:295–304 (1983)

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