The Behaviour of So-Called Immobile Elements in Hydrothermally Altered Rocks Associated with Volcanogenic Submarine-Exhalative Ore Deposits

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Evidence is available that some elements, notably Zr, TiO_2, Y, Sc, Ce and Nb are largely immobile during the alteration of volcanic rocks owing to metamorphism, hydrothermal events and weathering (e. g. Floyd and Winchester, 1978). However, it is shown, by reference to analyses of rocks from the environment of five volcanogenic massive sulphide bodies, that while Zr, TiO_2 (and Ce?) are mostly immobile even during intense hydrothermal alteration, Y and particularly Sc and Nb may be extremely mobile. When elements are removed by solution in a hydrothermal fluid it seems that reaction rates are such that these elements are almost totally removed from the rock. Therefore, of the so-called immobile trace elements, only Zr and TiO_2 may be used with any reliability to identify the degree of magmatic differentiation in an hydrothermally altered rock. However, if an element has been mobile it is usually readily identified as having moved.

INTRODUCTION

Many massive sulphide deposits seem to be associated with sequences of differentiated volcanic rocks. From hand specimen and thin section study it is, however, often not possible to adequately classify these rocks owing to superimposition of extreme hydrothermal alteration. The chemistry of any particular sample from close to one of these deposits may thus be a function of at least three processes

1. The original composition produced by magmatic differentiation.

2. The chemical elements added or subtracted by later reaction of the rock with hydrothermal fluids.

3. Relative dilution or concentration of the remaining elements in the rock by addition or subtraction of another component.

Determination of the original composition (1) following processes (2) and (3) can be extremely problematical.

Few areas containing volcanogenic massive sulphide bodies exhibit the sort of stratigraphic continuity that allows comparison of the chemistry of altered rocks near the deposits with the same rock type, but unaltered, some distance away.

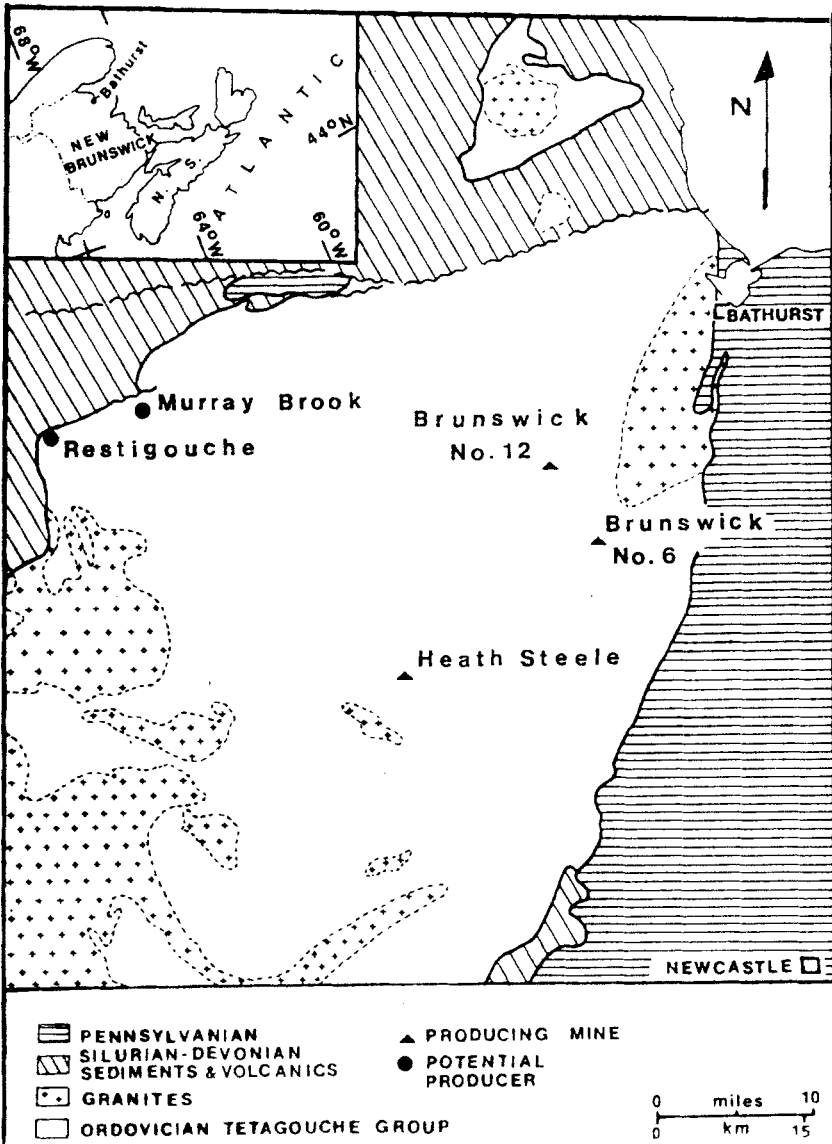*Present address: Billiton Research, Westervoortsedijk 67D, PO Box 38, 6800 LH Arnhem, Netherlands

Fig. 1. Simplified geological map of Northern New Brunswick, showing distribution of the Ordovician Tetagouche Group, and relevant ore deposits

The general problem of identifying the magmatic parentage of altered and metamorphosed igneous rocks has led to the study of distribution patterns of trace elements in igneous rocks not thought to be mobile during alteration processes. Winchester and Floyd (1977), and Floyd and Winchester (1978) have applied this approach successfully to a wide range of volcanic rock types and their altered and metamorphosed equivalents. However, few, if any of these rocks, had suffered alteration as intense as that exhibited by the volcanic tuffs and lavas associated with massive sulphide bodies. As part of a general project on volcanogenic sul-
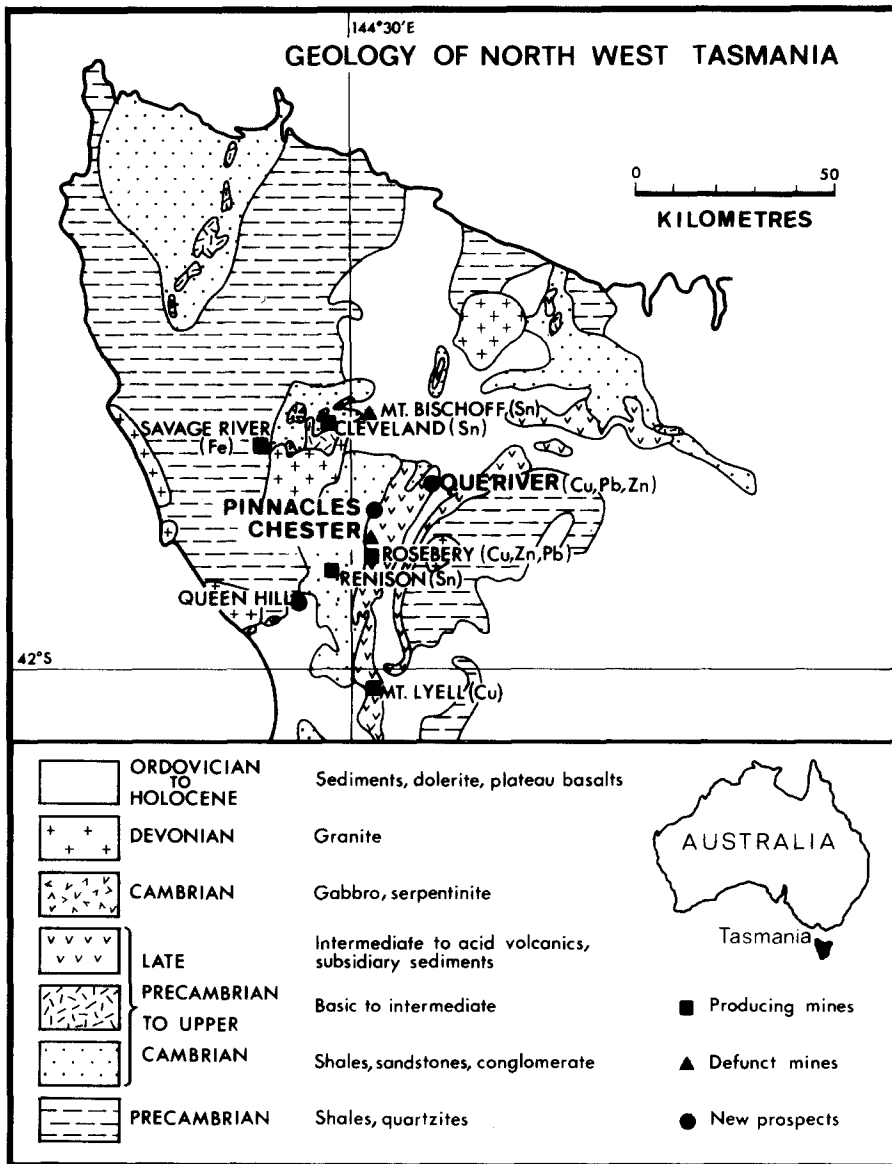
GEOLOGY OF NORTH WEST TASMANIA

144°30'E

0   50

KILOMETRES

MT. BISCHOFF (Sn)
SAVAGE RIVER
(Fe)
CLEVELAND (Sn)
QUE RIVER (Cu, Pb, Zn)
PINNACLES
CHESTER
ROSEBERY (Cu, Zn, Pb)
RENISON (Sn)
QUEEN HILL

42°S

MT. LYELL (Cu)

	ORDOVICIAN TO HOLOCENE	Sediments, dolerite, plateau basalts
	DEVONIAN	Granite
	CAMBRIAN	Gabbro, serpentinite
	LATE	Intermediate to acid volcanics, subsidiary sediments
	PRECAMBRIAN TO UPPER	Basic to intermediate
	CAMBRIAN	Shales, sandstones, conglomerate
	PRECAMBRIAN	Shales, quartzites

AUSTRALIA

Tasmania

■ Producing mines

▲ Defunct mines

● New prospects

Fig. 2. Geological sketch map of North-Western Tasmania: Regional geology, tectonic units and location of main orebodies

phide deposits, chemical analyses have been performed on a representative suite of drill core samples from the neighbourhood of five volcanogenic sulphide deposits. This paper reports the results of a study of the so-called immobile elements in these samples. The five deposits examined were: Restigouche and Murray Brook in New Brunswick (Fig. 1) and Chester Pyrite, Pinnacles and Que River (Fig. 2) in Tasmania. All occur in sequences of chlorite- and micaceous rocks that are of tuffaceous origin, or in sediments derived from volcanic sources. The Tasmanian examples form part of an arc of intermediate to acid

volcanics and pyroclastics (Mount Read Volcanics) of Cambrian age lying in a trough generated by rifting of a Precambrian basement (Solomon, 1962; Corbett et al, 1974; Reid, 1975; Burton, 1975).

The deposits of the Bathurst District, New Brunswick, occur within the 10.000m thick, strongly deformed Middle Ordovician Tetagouche Group, which forms part of the Appalachian Geosyncline. The Tetagouche Group has been intensely faulted and metamorphosed to greenschist facies grade during the Taconian (Upper Ordovician) and the Arcadian (Middle Devonian) oregenies. It can be visualised as a caldera-like depression filled with mafic and felsic igneous material.

ORIGINAL HOST ROCKS - HAND SPECIMEN AND THIN SECTION EVIDENCE

Despite the often extreme alteration, the host rocks to the orebodies considered here are all usually identified in hand specimen as acid to intermediate volcanics. There is a tendency to distinguish andesites, dacites or rhyolites on the basis of colour; green rocks being mapped as andesites and very light rocks as rhyolites. Many of these are now composed almost entirely of secondary minerals. While it is often true that the iron-richer andesites will tend to alter to green chloritic phases and the dacites and rhyolites are more likely to produce sericite rocks, this does not allow for possible major additions or subtractions of iron, alkalies and silica.

None of the rocks associated with the deposits are true lavas; some evidence of fragmental texture is present in all the volcanics. The nature of the host rocks established on hand specimen and petrographic grounds can be summarized as follows:

1) Restigouche: - sits in a sequence composed mainly of crystal and lithic tuffs, and of sediments formed by reworking of these tuffs. A few siliceous rocks, as well as sericitic samples may have been chemical and clay sediments

respectively. The crystal-bearing lithologies appear to be mainly dacitic and preferentially, although not uniformly, occur on top of the deposit.

2) Murray Brook: - is dominated by siltstone and slate lithologies composed of chloritic and sericitic material the origin of which cannot be clearly defined. Components of dominantly fragmental (acid?) volcanic origin are also present. The micaceous lithologies may be metamorphosed clay and silicate iron formation and/or metamorphosed devitrified glasses.

3) Chester: - occurs in a heavily altered unit of vitric crystal tuffs. Minor fragmental lithic tuffs and reworked tuffaceous sediments have also been recorded. Much of the glassy material appears to have a "collapsed pumice" texture; this point is taken by many people to indicate shallow water and terrestrial conditions. Occasional dykes cut the sequence. Exploration geologists have mapped the volcanics as andesitic and the dykes as dacitic.

4) Pinnacles: - has similar host rocks to the Chester deposit; the addition of some lithic pyroclastic material and fine sediments constitutes a minor point of difference.

5) Que River: - is set in a sequence dominated by lithic crystal tuffs. A limited amount of glassy texture is present in fragments contained in the minor sedimentary facies in close association with the ore. Typical dacitic textures are more common in rocks from the hanging wall of the ore deposit; by default the remaining darker coloured rocks might be classified as andesites.

DIFFERENTIATION AND ALTERATION

Mineralogical zonation due to alteration is not demonstrable for volcanogenic submarine exhalative ores to the extent that is possible for porphyry copper deposits. The dominant systematic trend on approaching a deposit is the disappearance of feldspar with formation of sericite

and/or carbonate, expressed as a zone of low sodium contents. A difference in susceptibility to alteration of phenocrysts as opposed to matrix material is frequently noticeable, too. Phenocrysts of feldspar persist into zones where the matrix has been totally altered to mica. This is probably a function of the highly reactive nature of a primary glassy matrix.

In all the deposits examined sericitization is the most prevalent mineralogical change that has occurred. In the Canadian deposits chlorite is very abundant in some samples and in the Chester host rocks carbonate (often kutnahorite) is important. Silicification is notably variable.

Massive additions of SiO_2 have been observed in some samples from the deposits yet in other cases formation of sericite has occurred in a silica undersaturated system and quartz phenocrysts have been replaced at their margins by sericite. The variation in silica values within the deposits studied exceeds by far what would be expected for the typical intermediate to acid volcanic rocks indicated by petrographic study. For example, in the Que River samples SiO_2 values range from 21 to 87 per cent. The silica deficient samples tend also to be the very heavily chloritized and/or sulphide bearing. Additions or subtractions of major amounts of such minerals will have led to dilution or concentration of other components. Thus it is impossible to identify the nature of the primary rock types on the basis of absolute values of elements obtained from chemical analysis. To try and overcome this problem Winchester and Floyd (1977) and Floyd and Winchester (1979) have investigated the ratios of so-called "immobile" elements in igneous rocks. They showed that the elements Ti, Zr, Y, Nb, Ce, Sc, Ga can be used to identify the rock type instead of using the main elements. Hence in metamorphosed and altered rocks the ratios of some of these elements can (if it is accepted that they are truly immobile) be used to identify the primary rock.

Figures 3-7 are Zr/TiO_2 vs. Nb/Y diagrams for the deposits constructed

after the method of Winchester and Floyd (1977). They indicate that all the deposits are dominantly in rock sequences of calc-alkaline affinity. The spread of data for Nb/Y is very large compared to that for Zr/TiO_2 and suggests some of the rocks are of more alkaline parentage. However, some of the individual analyses gave zero ppm for Nb and Y (set arbitrarily at 1 ppm for ratio calculation) suggesting they have been mobile. Of the Zr and TiO_2 analyses only three TiO_2 analyses gave a zero figure. The question arises if three samples have exhibited total mobility of one of these elements, how can one be sure that both Zr and TiO_2 have not been at least partially mobile?

If Zr and TiO_2 are truly both immobile and also indicative of the stage of differentiation of magma, then theoretically they should be usable to show the extent of differentiation and alteration. A magma at A (Fig. 8) could differentiate to form other rock types with TiO_2 and Zr values at B. Dilution or concentration of TiO_2 and Zr owing to net addition or subtraction of other components will cause the parent rock composition to "spread" along the lines X-Y. Graphs of TiO_2 and Zr for all the examined deposits show this form (Fig. 9-13). Groupings that do not exhibit the extreme X-Y spread (eg. dacites at Que River and andesites at Chester) have thus not suffered major volume changes. This suggests that partial mobility of Zr and TiO_2 does not occur. Either the elements remain as a guide to the original rock type and degree of addition or subtraction of other components or if it becomes mobile, TiO_2 is totally extracted. No evidence was found for Zr dissolution.

The shape of the line A-B will probably not be linear but the resulting diagram after alteration will differ little from Figure 8 if A-B-C is a simple curve.

This interpretation contrasts with that of MacGeehan and Maclean (1980). They argued that systematic addition of SiO_2, Zr (and also Na, Y and Rare Earths) was accompanied by systematic depletion
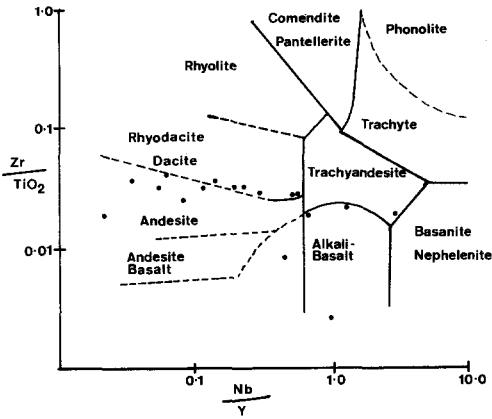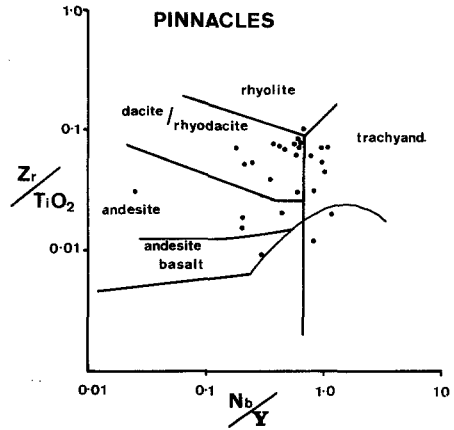
RESTIGOUCHE
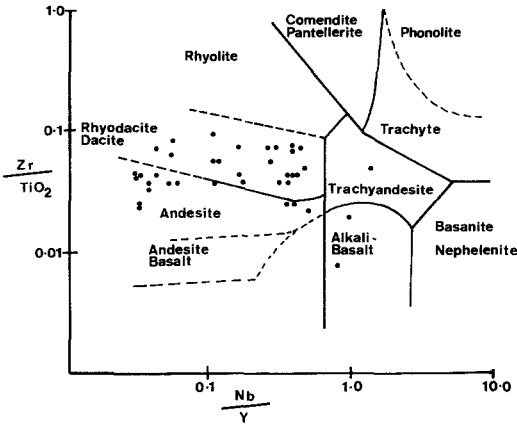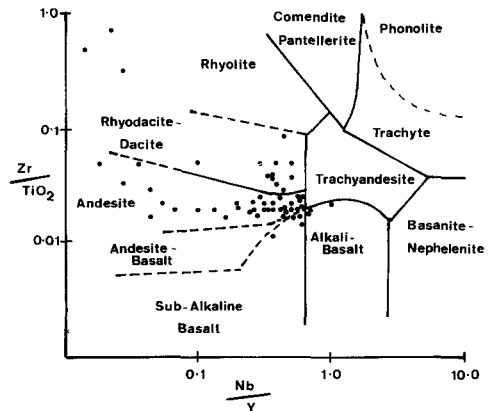
CHESTER PYRITE DEPOSIT
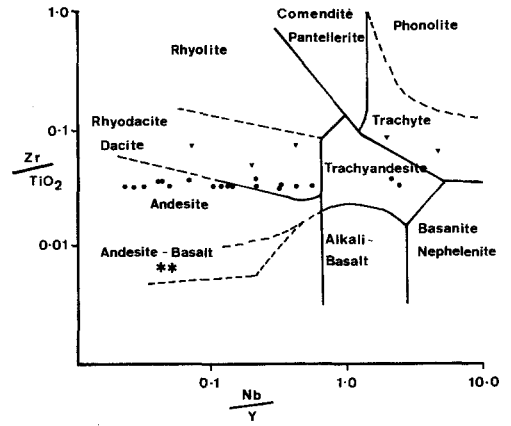
MURRAY BROOK

PINNACLES

QUE RIVER

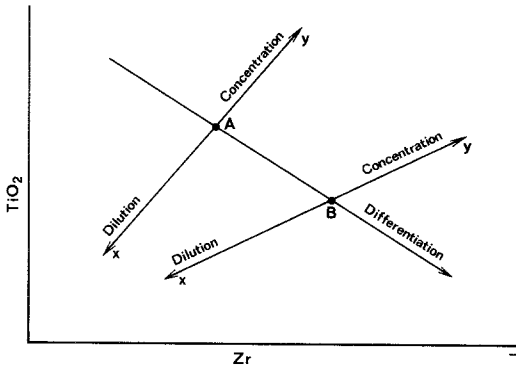Figs. 3-7. Diagrams of Zr/TiO_2 vs. Nb/Y following the scheme of Winchester and Floyd (1977)

Fig. 8. Hypothetical diagram to show the effect of differentiation on two "immobile" elements with differing behaviour and the effect of removing or adding other components. If a magma differentiates and produces two compoents that are erupted with compositions at A and B then addition of a third component, for instance SiO_2, during hydrothermal alteration will cause the Zr/TiO_2 ratios to follow lines towards the origin. Removal of a component will cause concentration and Zr/TiO_2 to follow direction Y.
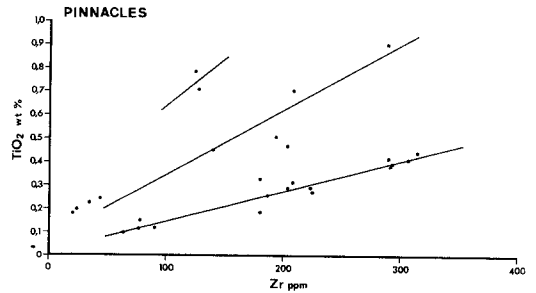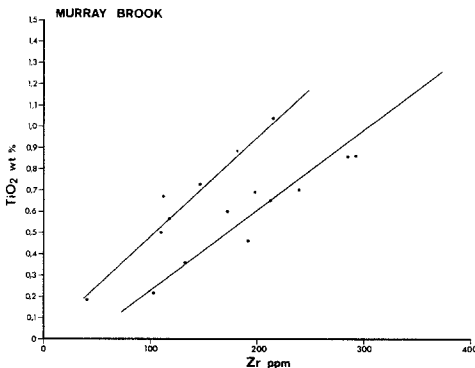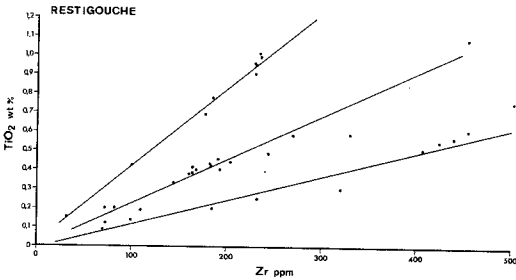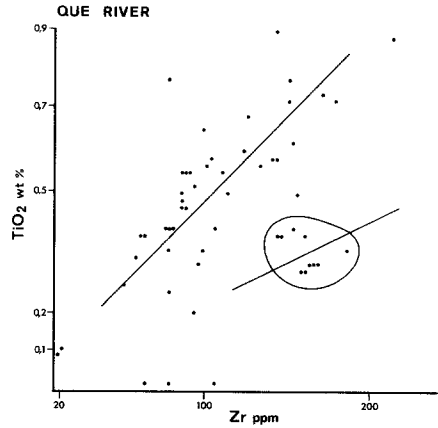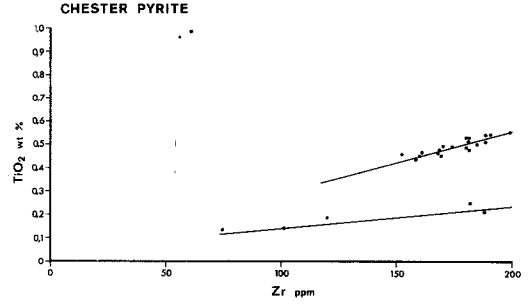
Figs. 9-13. TiO_2 vs. Zr for each of the deposits studied. The form of these diagrams is similar to Fig. 8

(actual dissolution) in Fe, Mg, Ca, Ti, Mn, P, V, Cr, Co, Ni, Cu, Zn during alteration of a basaltic rock. Fundamental to their argument was the suggestion that the Al_2O_3 content remained constant and thus these changes were constant volume processes. It does, however, seem coincidental that these changes duplicate in direction those exhibited by differentiation. The limited change in Al_2O_3 content is also typical for differentiation processes (eg. Willcox, 1979).

The difference between the effects of alteration and differentiation is readily apparent when the data from Que River are considered. Visual examination of the chemical analyses of the host rocks to the Que River deposits suggested they could be divided into three groups. Discriminant analysis confirmed the reality of these groupings. The andesite and dacites of group 1 all lie stratigraphically above the orebody. Samples of group 2

are from close to and within the ore lenses. Group 3 rocks come from areas laterally distant and stratigraphically below the deposit. The group 2 and group 3 rocks are almost all andesitic in terms of Zr/TiO_2 ratios. Variations in some other elements are readily explained as a function of the differentiation process. The high Ce of group 1 are explainable in terms of magmatic differentiation (Figs. 14, 15). Yet La does not closely follow the Ce trend in a few of the highly altered, sulphide-rich samples of group 2 It seems reasonable to argue that the fluid responsible for depositing the sulphide extracted the La yet left untouched the chemically very similar Ce. The diagrams of Floyd and Winchester (1978) using Ce do, however, use the absolute analytical value for the element and thus are not valid for rocks with such movements of major components. Chromium and vanadium, in addition to exhibiting the depletion expected in the dacitic sam-
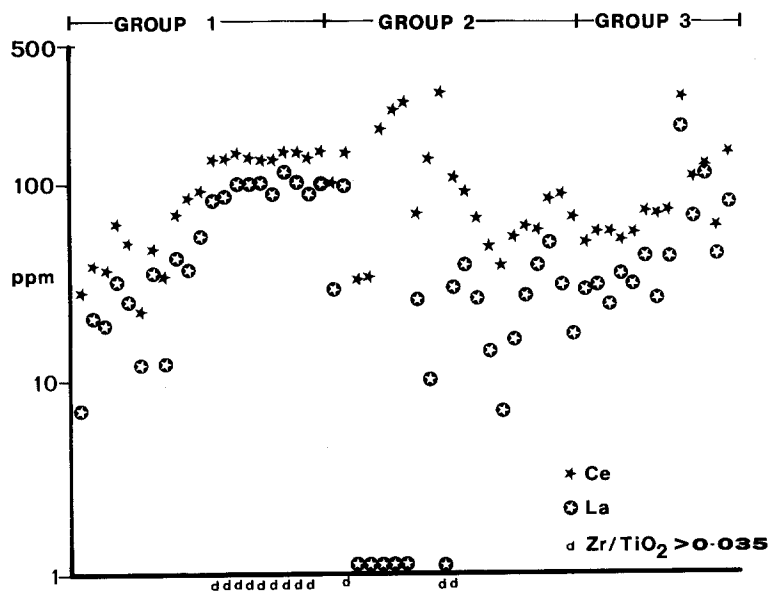

Fig. 14. Relative changes in Ce and La contents for samples from the Que River deposit. The expected parallel behaviour for these two elements due to differentiation is quite clear but in the sulphidized Cu, Pb, Zn-enriched samples (Group 2) La has suffered extensive removal. The X-axis consists merely of the samples arranged next to each other. The positions of the samples within a Group have been determined by visual inspection of the data and placing what appeared to be chemically similar samples next to each other
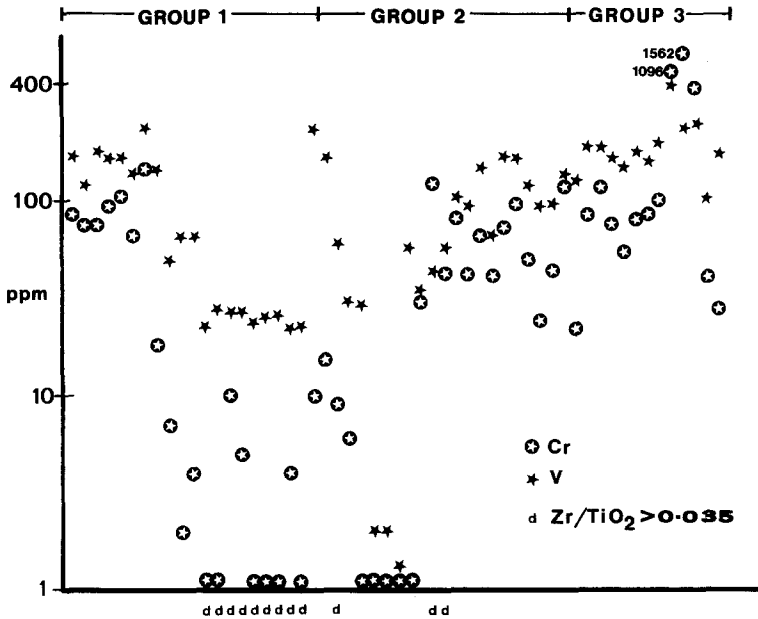
Fig. 15. Relative changes in Cr and V contents for the samples (X-axis) from Que River. The removal of Cr from the Group 1 dacites (differentiation) and the Group 2 mineralized tuffs (hydrothermal dissolution) is quite obvious. A few samples in Group 3 have been enriched in Cr. The trends for V are similar to but not as obvious as for Cr. Sample positions on the X-axis are identical to those in Fig. 14

ples, have also been removed entirely from many of the specimens that have lost La (Fig. 15). Chromium and vanadium are both markedly enriched in three of the group 3 samples and such material may represent the site of later deposition of the removed material.

A number of elements show this tendency to total removal in all the deposits studied. Scandium values were typically quite low but in the samples exhibiting intense alteration and sulphidization zero values were common. Although no regular pattern could be discerned the elements Cr, Cu, Nb, Pb, Sc, Sr, Th, Y and V are all prone to extraction during alteration.

REFERENCES

Burton C C T (1975) Rosebery zinc-lead-copper orebody: In K. Knight (ed) - Economic Geology of Australia and Papua New Guinea 1. Austral Inst Min Metal 619-627

Corbett K D, Reid K O, Corbett E. B, Green G R, Wells K, Sheppard N W (1974) The Mount Read Volcanics and Cambrian-Ordovician relationships at Queenstown, Tasmania. J Geol Soc Aust 21: 173-186

Floyd P A, Winchester J A (1978) Identification and discrimination of altered and metamorphosed volcanic rocks using immobile elements. Chem Geol 21: 291-306

MacGeehan P T, MacLean W H (1980) An Archean sub-seafloor geothermal system, 'calc-alkali' trends, and massive sulphide genesis. Nature 286: 767-771

Reid K O (1975) Mount Lyell copper deposits. In: Knight K (ed) Economic geology of Australia and Papua New Guinea 1. Austral Inst Min Metall 604-619

Solomon M (1962) Tectonic history of Tasmania; In: Geology of Tasmania Spry A M, Banks M R (eds) J Geol Soc Aust 9:311-339

Wilcox R E (1979) The liquid line of descent and variation diagrams; In: Yoder H S (ed) The evolution if igneous rocks. Princeton University Press, Princeton, 205-232

Winchester T A, Floyd P A (1977) Geochemical discrimination of different magma series and their differentiation products using immobile elements. Chem Geo 20: 325-347

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