BUCHANS, NEWFOUNDLAND: A CASE STUDY OF RARE EARTH ELEMENT PATTERNS

by

D.F. Strong[1]

Introduction

In recent years, there has been a rapid increase in the application of rare earth elements (REE) to the study of mineral deposits, and there are indications that such studies may have applications in mineral exploration. Taylor and Fryer (1983) recently completed a comprehensive review of such studies on granophile deposits. Thurston (1980, 1981) was the first to recognize that Archean felsic volcanic rocks of the Canadian Shield which host massive sulfide deposits are characterized by 'flat' REE patterns, while associated nonmineralized units have steeper negative-sloping REE patterns. Campbell et al. (1981, 1982) confirmed these observations, and the patterns discussed by them are summarized in Figure 1. The very high grade polymetallic sulfide deposits in Ordovician-Silurian volcanic rocks at Buchans, Newfoundland provide an ideal opportunity to test the applicability of the findings from the Archean volcanic rocks.

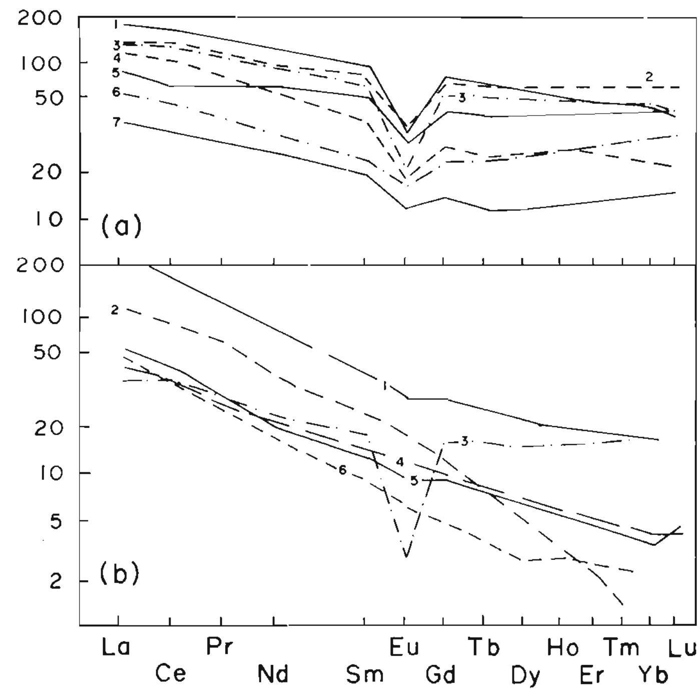

Figure 1: *Chondrite-normalized REE patterns for seven ore-bearing (a) and six barren (b) felsic volcanic rocks given by Campbell et al. (1982).*

Geological Setting

A comprehensive description of the geological setting and the mining history of the Buchans deposits was published in 1981 as a special paper of the Geological Association of Canada (Swanson et al., 1981). Some revisions to the details of the geological setting have resulted from recent work, for example, by Binney (1984).

Production at Buchans started in 1928. Just over 16 million tonnes of ore had been mined to the end of 1983. The orebodies have been spectacularly high grade, averaging 14.62% Zn, 7.60% Pb, 1.34% Cu, 226.5 g/t Ag, and 1.474 g/t Au (Thurlow and Swanson, 1981).

Thurlow et al. (1975) first described these polymetallic deposits as similar to the volcanogenic Kuroko-type of Japan. The recognition of thrust faults within the volcanic sequence has resulted in a revision of the stratigraphy described by Thurlow, as shown in Figure 2 and described in Table 1. The samples used in this study were taken from Thurlow's original collection, but they have been reassigned to the stratigraphic units shown in Figure 2.

Analytical Methods

Fifty-seven samples were selected from a collection of rock powders which were chemically analyzed by Thurlow (1980); the full chemical data are given by him. Samples were chosen representing each of the stratigraphic units in the volcanic sequences which host the Buchans orebodies, and some dike samples were included to represent possible late-stage magmatism.

Contribution to the Canada-Newfoundland co-operative minerals program 1982-84. Project financed by the Newfoundland Department of Mines and Energy and NSERC.

[1] Department of Earth Sciences, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X5

The REE concentrations were determined at Memorial University (MUN) using the thin-film X-ray fluorescence technique of Fryer (1977), the same method used by Thurston (1980, 1981) and subsequently supported by Campbell et al. (1981, 1982) using instrumental neutron activation analysis. The data are available from the author on request. Sample number JGT-160B, a rhyolite flow from the Skidder area, was analyzed with three separate analytical batches. These duplicate analyses provide an indication of the precision (Figure 3a) which agrees with numerous estimates of precision and accuracy at ± 15% or better made during routine analysis at MUN (B.J. Fryer, personal communication and manuscript in preparation). The REE patterns plotted in Figures 3 and 4 are normalized to the chondrite values given by Taylor and Gorton (1977).

Rare Earth Element Data

The samples are grouped into 'felsic' and 'mafic' types, but there are 'intermediate' compositions which may fall into either group. To facilitate comparison, the SiO_2 concentrations are written on the summary diagrams, along with concentrations of Na_2O, K_2O, LOI, and Ba. These components give some indication of the degree of alteration. The REE patterns are sequentially arranged in Figures 3 and 4 with the stratigraphically lowest units at the top. The following discussion proceeds from oldest to youngest.

Felsic Rocks

Figure 3a shows that felsic rocks from the lowest units, the Footwall dacite and the Skidder rhyolite, have relatively flat

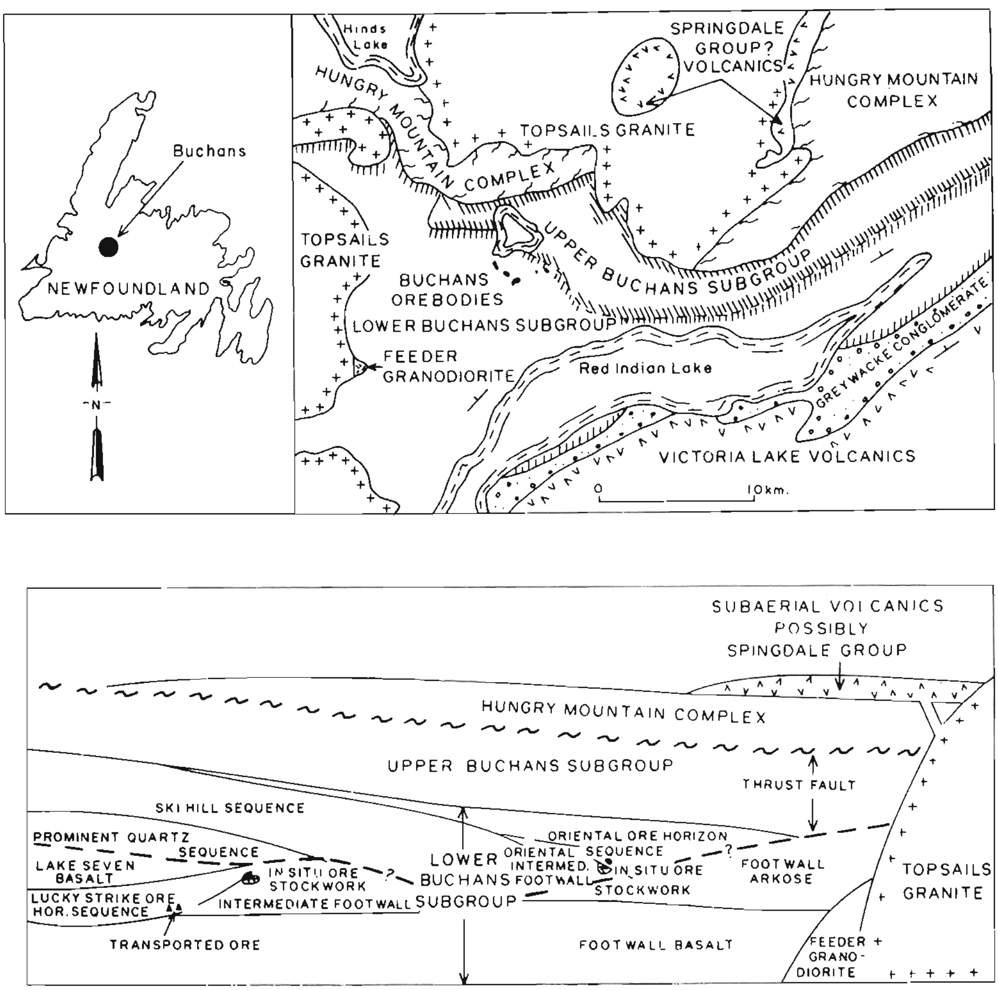

Figure 2: *Simplified geological map (a) and schematic stratigraphy (b) of the Buchans area (after Thurlow and Swanson, 1981). See Table 1 for lithological descriptions.*

TABLE 1: STRATIGRAPHY OF THE BUCHANS GROUP*

Unit (Maximum thickness)	Lithologies	Mineralization
Upper Buchans Subgroup (2000 m (?))	Mafic to felsic pyroclastics and breccias with lesser flows, minor volcanic sediment. Includes a basal member (Upper Arkose) of resedimented conglomerate.	Little Sandy Prospect (Cu) and several areas of weakly to heavily disseminated pyrite, and traces of chalcopyrite.
Lower Buchans Subgroup		
Oriental Ore Horizon Sequence (400 m)	Dacitic tuff, rhyolite breccia domes, pyritic siltstone and wacke, pyroclastic breccia, polyvolcanic breccia-conglomerate, "granite conglomerate".	High grade massive sulfide orebodies; Oriental #1 and #2. Old Buchans Conglomerate and possibly Old Buchans East and West. Sandfill and Middle Branch Prospects.
Oriental Intermediate Sequence (300 m)	Pumiceous felsic pyroclastics and pyroclastic breccias, local altered intermediate and mafic flows, pyroclastics and breccias.	Minor ore grade stockwork mineralization with larger areas of subeconomic epigenetic Pb-Zn-Cu.
Ski Hill Sequence (1000 m)	Mainly andesitic pyroclastics and breccias; minor basaltic flows, dacitic tuff.	Local isolated black ore clasts.
Prominent Quartz Sequence (2000 m)	Mainly dacitic pyroclastics, pyroclastic breccias and related tuffaceous sediments, lesser rhyolite. Interbedded basaltic and andesitic units, jasper chert.	Local disseminated pyrite, Pb-Zn and traces of Pb-Zn veining.
Lake Seven Basalt (350 m)	Basaltic pillow lava, pillow breccia and lesser pyroclastics.	Barren.
Lucky Strike Ore Horizon Sequence (600 m)	Dacitic tuff, massive rhyolite, pyritic siltstone and wacke, pyroclastic breccia, polylithic volcanic breccia-conglomerate, "granitic conglomerate", local basaltic and andesitic horizons.	High grade massive sulfide orebodies; Lucky Strike, North, Two Level, Rothermere #1 and #2, MacLean, Clementine Prospect. Subeconomic trains and isolated occurrences of sulfide clasts.
Intermediate Footwall (250 m)	Complexly interbedded and altered mafic to felsic flows, pyroclastics and breccias, related tuffaceous pyritic siltstone and wacke.	Localized ore grade pyritic stockwork Zn-Pb-Cu mineralization. Small, stratiform, high grade, polymetallic massive sulfides. Larger areas of subeconomic disseminated and veinlet mineralization.
Footwall Arkose (2500 m)	Mainly lithic arkose; lesser arkosic conglomerate, siliceous graywacke; minor siltstone, mudstone, chert. Contains felsic pyroclastics several kilometres east of Buchans.	Connel Option: very small bedded pyritic Pb-Zn occurrence; otherwise barren.
Footwall Basalt (2000 m (?))	Basaltic pillow lava, pillow breccia, lesser pyroclastics, massive flows, interbedded chert. Very minor felsic pyroclastics.	Skidder Brook pyritic massive sulfide deposit (Cu-Zn).

* After Thurlow and Swanson (1981)

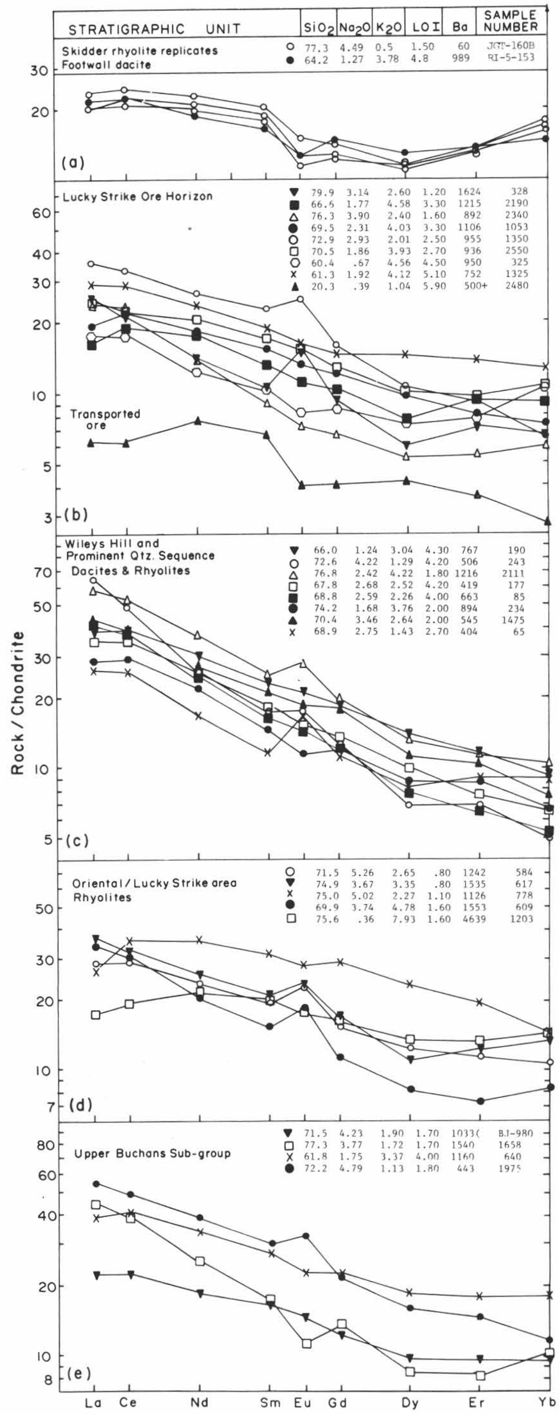

Figure 3: *Rare earth element patterns, normalized to chondrite data given by Taylor and Gorton (1977), for 'felsic' volcanic rocks of the Buchans area. Additional chemical data are given in weight percent. In Figure 3(c), samples 85, 234, 1475 and 65 are from the Prominent Quartz Sequence.*

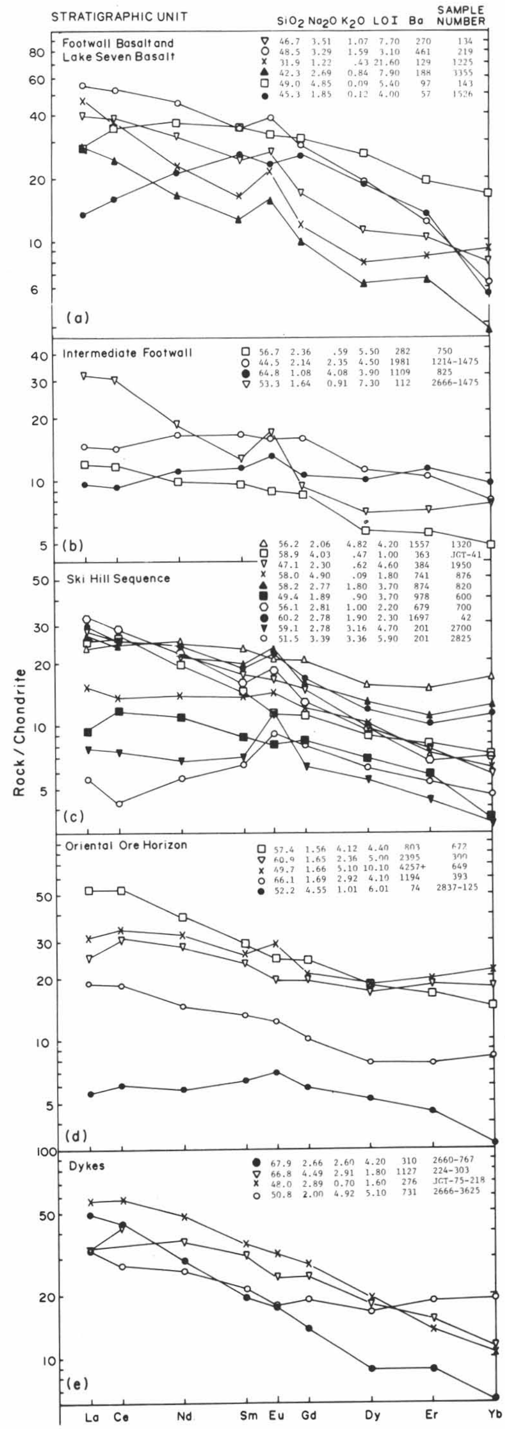

Figure 4: *Rare earth patterns for the 'mafic' volcanic rocks of the Buchans area. In Figure 4(a), samples 143 and 1526 are from the Lake Seven Basalt.*

patterns with a slight depletion of Eu and enrichment of Er and Yb. There is no significant difference between the rhyolite and the dacite REE patterns, despite their differences in most other elements, and their apparent differences in alteration, as indicated by variations in LOI, Na/K, etc.. The flat patterns are comparable to those shown in Figure 1 for Archean mineralized rocks at Golden Grove, Western Australia (sample 6), and the mid-Miocene Kuroko district of Japan (sample 7), although the absolute abundances as shown by the chondrite ratios (indicated henceforth by *) of the latter are much higher. This similarity is noteworthy in that the Footwall sequences are shown by Thurlow (1980, *his Figure 3-1)* to form only a basement to the mineralized volcanic sequences, and not to have significant mineralization themselves (Figure 2).

REE patterns for silicic volcanic rocks from the Lucky Strike and Oriental ore horizons are shown in Figures 3b and 3d. The patterns for the two horizons are similar, but the total REE concentrations (TREE*) are generally lower in the Lucky Strike horizon. All have generally negative slopes, although not as steep as those for the unmineralized samples shown in Figure 3c. Also, they show a slight enrichment of Yb* (i.e. higher Yb/Gd*) relative to the patterns in Figure 3c. Likewise, the TREE* concentrations are generally lower, with La* less than 36 and Yb* less than 15. The only ore sample analyzed in this study, number 2480 (transported ore, Figure 3b), shows much lower TREE*, similar to that determined by Graf (1977) for massive sulfides in the Bathurst, New Brunswick area. There are no significant Eu* depletion anomalies in these mineralized samples, although there are several positive Eu* anomalies. These do not correspond to any obvious indication of feldspar enrichment, either through albitization (higher Na_2O) or plagioclase accumulation (higher CaO or Na_2O), although plagioclase phenocrysts are common in most of the Buchans volcanic rocks. Likewise, the TREE* are not enriched, providing no evidence for significant differentiation of the magmas from which they were derived.

Figure 3c shows the REE patterns from two units apparently unrelated to ore, i.e. the Wileys Hill Sequence at some distance from and stratigraphically lower than ore, and its possible stratigraphic equivalent, the Prominent Quartz Sequence. There is no significant difference between the two groups, both showing slight positive Eu* anomalies like those in the mineralized units, and slightly more negative slopes, with La* between 65 and 26, and Yb* between 9.36 and 4.92. One exception is sample 65, dacitic tuff from the Prominent Quartz Sequence, which shows a flatter pattern than the others. There is no obvious indication from the other elements that alteration might explain this difference and there is no correlation between alteration and REE patterns of the other rocks. These patterns conform to what would be expected for unmineralized Archean volcanics (Figure 1), i.e. calc-alkaline REE patterns with negative slopes, although the TREE* of the Buchans rocks are significantly lower.

Similar negative slopes are observed for two of the felsic volcanic rocks of the Upper Buchans Subgroup (Figure 3e), but there is a slight relative enrichment of the HREE (higher Yb/Gd*) in three samples. These rocks also have higher average Ba concentrations than those of Figure 3c, although the Upper Buchans Subgroup is shown by Thurlow (1980, *his Figure 3-1)* to overlie the mineralization (Figure 2).

Mafic Rocks

REE patterns for the Footwall Basalts and Lake Seven Basalts, both unmineralized, are shown in Figure 4a. The former have generally negative slopes which are unaffected by alteration. Sample 1225, which contains more than 20% CO_2 (and 27.4% CaO), differs from the others only by a slight enrichment in Er and Yb, as would be expected from the effects of CO_3-complexes as agents of HREE transport and deposition (Taylor and Fryer, 1983). Samples 143 and 1526, from below the Prominent Quartz Sequence, show flatter patterns with lower LREE* and higher HREE* than the Footwall Basalts. This may reflect a loss of LREE from originally similar rocks, e.g. by feldspar fractionation, but there is no Eu-enrichment anomaly to support such a suggestion. Instead, the difference may be an original magmatic feature, i.e. these rocks may be genetically different, possibly somewhat fractionated tholeiites instead of calc-alkaline basalts. However, it is equally possible that the LREE were lost during greenschist facies alteration.

REE patterns for unmineralized mafic fragmental rocks from the Intermediate Footwall and the Prominent Quartz Sequence are shown in Figure 4b. Except for sample 2666-1475 from the Prominent Quartz Sequence, the patterns have substantially lower LREE* values than those of the Footwall Basalts but their HREE* are similar. The two samples with lowest TREE* have contrasting K_2O and Ba, and both are more siliceous than the other samples.

Unmineralized mafic rocks from the Ski Hill Sequence are also different from most of the Footwall Basalts, having higher silica and Ba concentrations; most can be described as andesites. They also have different TREE*, generally with La* below 33 compared to values above 40 in the former, but they are like the Footwall Basalts in having slightly positive to insignificant Eu* anomalies. Four of the samples are substantially depleted in LREE* relative to most of the Ski Hill Sequence, and have flat patterns, with TREE* lower than even those of the Intermediate Footwall samples. Although there may be two genetically different magma types represented in this assemblage, this is not indicated by any other trace elements, so an alteration control must be considered.

REE patterns for mafic to intermediate rocks from the mineralized Oriental Ore Horizon Sequence are shown in Figure 4d, and for dikes in Figure 4e. They are similar to those of the Ski Hill Sequence, having similar negative slopes and lack of Eu anomalies. One sample of mafic tuff, sample 2837-125, is strongly depleted in TREE*, and has a flat pattern like some of those in the Ski Hill Sequence or Intermediate Footwall. Mineralized sample 1872-649 shows no difference in REE pattern from those of any unmineralized samples.

Discussion

From the above observations, it must be said that, while there are suggestions of changes in REE distribution patterns accompanying mineralization which merit further detailed study, they are not consistent enough for routine application. The recognition of distinct differences in REE patterns between Archean mineralized and unmineralized felsic volcanics, and parallel differences for associated sills, raised two exciting possibilities, one for mineral exploration and the other for genetic understanding. The exploration implications are obvious from the possibility of clearly recognizing mineralized felsic volcanics by their flat REE patterns, a purely empirical tool which could be empirically tested.

Secondly, the similarity in REE patterns of mineralized volcanics and associated sills seems to imply a magmatic link with ore genesis. Thurston (1981) interpreted the flat REE patterns as reflecting the activity of mineralizing fluids, and subsequently (Thurston and Fryer, 1983) invoked petrogenetic processes reflecting contamination by older sialic crust and compositionally zoned magma chambers. Campbell et al. (1982) used the consistent presence of negative europium anomalies in their data to suggest that plagioclase fractionation was important to the mineralization process. Indeed, Campbell et al. (1981, page 45) had as an underlying theme to their interpretations that "we can be confident that [REE patterns] are governed by fundamental partial melting and fractionation processes", essentially those obeying the Rayleigh-type rules of crystal/liquid equilibria as outlined by Gast (1968) and Shaw (1970). However, there is abundant evidence of the profound effects of fluids at all stages, from magma crystallization to hydrothermal alteration (e.g. the review by Taylor and Fryer, 1983). Campbell et al. (1981) did not find any evidence of REE mobility in the pervasive low grade alteration envelopes surrounding the orebodies, but their later work (1983) has shown significant depletion of light and middle REE in the sub-ore alteration pipes. Nevertheless, Eu-depletion anomalies can be produced by feldspar-destructive alteration, even in low grade zones, and this may have caused the observed anomalies. Flat REE patterns have also been documented as alteration effects in a number of geological environments, and interpreted as resulting from LREE-leaching by chloride-bearing fluids, in line with the experimental results of Flynn and Burnham (1977). HREE enrichment can also be caused by the action of either F- or CO_2-bearing fluids (Taylor and Fryer, 1983). Thus, it cannot be assumed that either of the characteristics which Campbell et al. (1981) mention, *viz.* the flat patterns or Eu* anomalies, are primary features of the magmas or, similarly, that the mineralization had any primary magmatic cause.

Cu, Pb and Zn can be readily leached from footwall rocks. Indeed, such leaching is inherent to most genetic interpretations of volcanogenic massive sulfide deposits. Campbell et al. (1981, page 52) also suggested that Cu, Zn and Pb might behave as incompatible elements during silicate fractionation and concentrate in residual liquids, ultimately giving rise to ore deposits. If such processes resulted in the deposition of the large tonnages of these elements at Buchans, one might expect the effects on REEs and other trace elements to be equally large. Because such effects are absent from the Buchans volcanic and associated intrusive rocks, crystal fractionation could not have been an important factor in the formation of the Buchans orebodies. Therefore, the observed variations in REE patterns probably represent a range from the original igneous patterns to those modified as the result of leaching, transport and deposition by Cl-bearing aqueous fluids, according to earlier models suggested for such Kuroko-type deposits, e.g. by Sato (1971). The stable isotope data for S, O, and H suggest that such fluids were mainly seawater (Kowalik et al., 1981), although there may have been some magmatic input of ore metals (Sawkins and Kowalik, 1981).

While the distinctive REE patterns of Archean mineralized felsic volcanic rocks appear to be encouraging as an exploration tool, they do not appear to be universally applicable. This study strengthens the conclusion of Campbell et al. (1982) that "although all of the ore-bearing felsic volcanic rocks studied [by them] show the same distinctive flat REE pattern, it does not follow that all ore-bearing felsic volcanic rocks will have this type of REE geochemistry. Further testing is needed to clarify this point." It is probable that REE patterns of mineralized volcanic rocks will have to be explained in terms of multistage processes and controls, for example, differences in source regions, magmatic sources and processes, magmatic-hydrothermal processes and seawater convection. As with most other geochemical techniques, caution will be necessary in applying the results from one area to the rocks of another.

Acknowledgements

I am grateful to J.G. Thurlow for permission to use his samples for this study, and his guidance in reassignment of them to the latest version of the evolving stratigraphy of the Buchans Group. I thank J. Tuach and P. Davis for the REE analyses, and I.H. Campbell, J.M. Franklin, B.J. Fryer and P.C. Thurston for unpublished information and for criticism of the manuscript. The study was financed by the Newfoundland Department of Mines and Energy and the Natural Sciences and Engineering Research Council of Canada operating grant No. A7975.

References

Binney, W.P.
1984: Estimation of physical parameters of Maclean channel sulfide-bearing debris flows, Buchans, Newfoundland. *In* Current Research, Part A, Geological Survey of Canada, Paper 84-1A, pages 495-498.

Campbell, I.H., Coad, P., Franklin, J.M., Gorton, M.P., Scott, S.D., Sowa, J. and Thurston, P.C.
1981: Rare earth elements in felsic volcanic rocks associated with Cu-Zn massive sulphide mineralization. Ontario Geological Survey, Miscellaneous Paper 98, pages 45-53.

1982: Rare earth elements in volcanic rocks associated with Cu-Zn massive sulphide mineralization: a preliminary report. Canadian Journal of Earth Sciences, Volume 19, pages 619-623.

Campbell, I.H., Lesher, C.M., Coad, P., Franklin, J.M., Gorton, M.P. and Thurston, P.C.
1983: Rare earth element mobility in alteration pipes below massive Cu-Zn sulfide deposits. (Unpublished manuscript.)

Flynn, R.T. and Burnham, C.W.
1977: An experimental determination of rare earth partition coefficients between a chloride-containing vapour phase and silicate melts. *In* Experimental Trace Element Geochemisatry, Pergamon, Oxford, pages 685-701.

Fryer, B.J.
1977: Rare earth evidence in iron formations for changing Precambrian oxidation states. Geochimica et Cosmochimica Acta, Volume 41, pages 361-367.

Gast, P.W.
1968: Trace element fractionation and the origin of tholeiitic and calc-alkaline magma types. Geochimica et Cosmochimica Acta, Volume 32, pages 1057-1086.

Graf, J.L.
1977: Rare earth elements as hydrothermal tracers during the formation of massive sulphide deposits in volcanic rocks. Economic Geology, Volume 72, pages 527-548.

Kowalik, J., Rye, R. and Sawkins, F.J.
1981: Stable isotope study of the Buchans polymetallic sulphide deposits. Geological Association of Canada, Special Paper 22, pages 229-254.

Sato, T.
1971: Physicochemical environment of Kuroko mineralization at Uchinotai deposit of Kosaka Mine, Akita Prefecture. Society of Mining Geologists of Japan, Special Issue 2, pages 137-144.

Sawkins, F.J. and Kowalik, J.
1981: The source of ore metals at Buchans: magmatic versus leaching models. Geological Association of Canada, Special Paper 22, pages 255-268.

Shaw, D.M.
1970: Trace element fractionation during anatexis. Geochimica et Cosmochimica Acta, Volume 34, pages 237-243.

Swanson, E.W., Strong, D.F. and Thurlow, J.G.
1981: The Buchans Orebodies: Fifty Years of Geology and Mining. Geological Association of Canada Special Paper 22, Part 1 (Text), 350 pages.

Taylor, R.P. and Fryer, B.J.
1983: Rare earth element lithogeochemistry of granitoid mineral deposits. CIM Bulletin, Volume 76, pages 74-84.

Taylor, S.R. and Gorton, M.P.
1977: Geochemical application of spark source mass spectrography. III. Element sensitivity, precision and accuracy. Geochimica et Cosmochimica Acta, Volume 41, pages 1375-1380.

Thurlow, J.G.
1980: Geology, ore deposits, and applied rock geochemistry of the Buchans Group. Ph.D. thesis, Memorial University of Newfoundland, 314 pages.

Thurlow, J.G. and Swanson, E.A.
1981: Geology and ore deposits of the Buchans area, central Newfoundland. Geological Association of Canada, Special Paper 22, pages 113-142.

Thurlow, J.G., Swanson, E.A. and Strong, D.F.
1975: Geology and lithogeochemistry of the Buchans polymetallic sulphide deposits, Newfoundland. Economic Geology, Volume 70, pages 130-144.

Thurston, P.C.
1980: The volcanology and trace element geochemistry of cyclical volcanism in the Archean Confederation Lake Area, Northwestern Ontario. Ph.D. thesis, University of Western Ontario, 553 pages.

1981: Economic evaluation of Archean volcanic rocks using REE geochemistry. Geological Society of Australia, Special Publication 7, pages 439-450.

Thurston, P.C. and Fryer, B.J.
1983: The geochemistry of repetitive cyclical volcanism from basalt through rhyolite in the Uchi-Confederation greenstone belt, Canada. (Unpublished manuscript.)