RARE EARTH ELEMENTS IN PROTEROZOIC METABASALTS AND ASSOCIATED VOLCANOGENIC SULPHIDE ORE FROM HAVERI, SOUTHWESTERN FINLAND

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REE data on two tholeiitic metabasalts and a metalava breccia from the Haveri formation display a coherent distribution pattern from La 28 to Lu 7 times that of chondrite. Such contents and LREE enrichment have been observed in some tholeiitic basalts from marginal basins, Archean greenstone belts, and calc-alkaline basalts from island arcs. REE distribution in a submassive sulphide ore overlying metalava breccia is from La 6 to Lu 2 times that of chondrite. A positive Eu anomaly is recorded in both the epidotized metalava breccia and the genetically related sulphide ore. It is suggested that Eu could be used as a pathfinder in the exploration of volcanic exhalative ore deposits.

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Introduction

The purpose of this study is to give fresh information on the contents and distribution of rare earth elements (REE) in Finnish metabasalts and associated volcanogenic sulphide ores, to compare these rocks with basalts from various environments and ages, and to discuss the behaviour of REE in volcanogenic ore-forming processes.

One of the authors (KM) supervised exploration drilling for Outokumpu Oy in the environment of the exhausted Haveri mine in 1977. The four samples studied are from these drill holes.

General geology

The Haveri mine is located at Viljakkala, roughly 35 km NW of Tampere. The drill holes mentioned above are 0.3—1.0 km south of the mine. The pyrrhotite-dominated gold-copper ore deposits in and around the mine are closely associated with tholeiitic metabasalts, metalava breccias and related rocks; the whole sequence is known as the Haveri formation (Mäkelä 1980). The ore-forming metals originate from metalava breccias through leaching by hydrothermal fluids (heated sea-water), and the sulphur originates from contemporaneous sea-water. The massive sulphides (mainly pyrrhotite with some chalcopyrite and minor pyrite) deposited under hydrothermal (volcanic exhalative) conditions. The sulphides commonly display banded structures indicating deposition on the sea-floor. The conditions during the main ore-forming stage have been estimated at: temperature 250°C, pH 5, oxygen fugacity 10^{-40} atm., and minimum pressure 40 bar (Mäkelä op. cit.).

The geology, geochemistry and origin of the metabasaltic rocks and associated ore deposits from Haveri have been described and thoroughly discussed by Stigzelius (1944) and Mäkelä (1980). It was suggested that the original geotectonic setting of the Haveri formation was an initial-stage Svecofennidic island-arc. The massive sulphide deposits within it were correlated with those of the Cyprus type. The regional metamorphic conditions in the Haveri district were estimated at c. 550°C temperature and 2.5 kbar pressure (Mäkelä 1980).

Description of samples

The samples studied are typical of the Haveri formation. The following is a brief description of each of them.

Sample 1 is a dark green metabasalt that, except for some green/grey-mottled breccia-like features, is fairly homogenous by structure. Microscopic examination shows that the rock is composed of dark green hornblende and plagioclase (An_{40}) with quartz, opaques, biotite and sphene as main accessory minerals. The grain size varies from 0.05 to 0.1 mm, and the texture is granoblastic.

Sample 2 is a dark green, massive intersection of a metabasalt or, partly at least, of a feeder dyke. The rock is composed of pale green amphibole often with crystal accumulations pseudomorphic after pyroxene (c. 30 vol-% of rock), and of plagioclase (An_{30}). Biotite and sooty, pigmenting opaques are associated with the amphibole. The size of the pyroxene pseudomorphs is 1 mm, and the grain size of the plagioclase 0.05 mm.

Sample 3 is a dark green/white-mottled metalava breccia originating from broken-pillow breccia structures. The constituent minerals are bluish green hornblende, epidote, quartz and sphene. No plagioclase is present. The accessory minerals include opaque and carbonate. The grain size averages 0.1 mm, and the texture is granoblastic.

Sample 4 is a »massive sulphide» intersection, stratigraphically overlying and genetically related to the metalava breccia. The sample contains c. 40 vol-% pyrrhotite and some chalcopyrite, occurring as the matrix in a dark green metalava breccia. The rock is composed of bluish green hornblende, epidote, quartz and opaques. The opaque minerals include pyrrhotite and some chalcopyrite with accessory magnetite, pyrite and cobaltite. The grain size varies from 0.05 mm to 0.1 mm, and the texture is granoblastic.

Results

Table 1 gives the chemical compositions, and Fig. 1 the chondrite-normalized REE distribution patterns of the four samples analyzed. The analytical methods are those referred to in Table 1. The following features are observed in the REE distribution patterns.

All the samples are enriched in light REE (LREE) in comparison with heavy REE (HREE), and their normalized distribution patterns resemble each other (except for Eu).

Samples 3 and 4 display clear positive Eu anomalies. The positive Eu anomalies displayed by samples 1 and 2 are weak and, considering the trends from La to Lu, insignificant.

The REE contents in sample 4 are c. 5 times lower than those in the other samples ana-

Table 1. Chemical analyses of the Haveri formation rock samples 1—4 discussed in the text.

	1	2	3	4
SiO_2	48.82	49.39	47.70	37.70
TiO_2	1.91	1.77	1.68	0.46
Al_2O_3	13.55	12.45	9.98	5.04
FeO*	15.15	15.49	21.96	13.63
MnO	0.29	0.19	0.26	0.04
MgO	4.51	4.49	3.27	2.75
CaO	10.33	11.47	11.20	7.10
Na_2O	2.16	3.13	0.83	0.39
K_2O	0.83	0.59	0.89	0.26
P_2O_5	0.39	0.44	0.46	0.09
FeS	0.96	1.37	2.14	35.10
Total	98.90	100.78	100.37	102.56
Co	25	23	65	690
Ni	26	42	27	99
Cu	183	401	684	2310
Zn	30	20	30	30
Pb	10	12	23	33
Ag	2	2	2	3
Au	0.2	$<$ 0.2	0.4	$<$ 0.2
La	11	9.9	10	2.2
Ce	22	23	27	4.5
Nd	22	16	12	$<$ 3
Sm	4.0	3.0	3.6	0.91
Eu	1.5	1.4	3.6	0.59
Tb	0.78	0.65	0.78	0.17
Dy	4.4	3.0	4.5	0.73
Yb	3.0	2.4	2.8	0.54
Lu	0.28	0.26	0.32	0.09
La : Yb	3.67	4.13	3.57	4.07
Eu : Eu*	1.08	1.29	2.77	1.87

1. Metalava. Diamond drill hole Hvr-5, depth 111.00—114.00 m.
2. Metalava. D.d. hole Hvr-8, depth 174.00—182.30 m.
3. Metalava breccia. D.d. hole Hvr-9, depth 31.80—34.10 m.
4. Ore. D.d. hole Hvr-9, depth 29.30—31.80 m.

The whole rock XRF, sulphide phase AAS, and sulphur analyses are routine analyses of Outokumpu Oy, Exploration. REE analyses were made at the Reactor Laboratory, Technical Research Centre of Finland (Rosenberg and Wiik 1971, and Rosenberg 1977).

Major elements are expressed in wt-%, minor elements in ppm. FeS = S expressed as FeS. FeO* = $(Fe_{total} - Fe_{FeS})O$. Eu* was obtained by interpolation between Sm and Tb.

lyzed, probably owing to the dilution of metalava breccia by sulphides. However, generally speaking, its chondrite-normalized pattern (LREE enrichment) resembles those of samples 1—3 reflecting the lodging of REE mainly in silicates.

Comparison with various basalt types

REE are considered as a rather immobile group of elements (e.g. Condie 1976). They have therefore been used as a means of comparing volcanic rocks from different environments and ages (e.g. Jahn et al. 1974).

A feature typical of the tholeiitic metabasalts of the Haveri formation is their consistent LREE enrichment (La : Yb = 3.6—4.1 vs. c. 1.6 in chondrites). La : Yb ratios of this magnitude are common in various basalts as will be shown in what follows.

Young basalts with tholeiitic affinities are found in oceanic and continental environments (mid-ocean ridges, deep ocean floors, marginal or back-arc basins, oceanic islands, island arcs, continental plateau basalts). Bryan et al. (1976) recognize two groups of basalts on the ocean floors. Group I, »normal» to mid-ocean ridges and ocean floors, is characterized by LREE depletion (La : Yb $<$ 1.1) whereas group II is heterogeneous and commonly LREE enriched (La : Yb ratios generally $>$ 2). Note that group II basalts have been found in nearly every oceanic environment, including mid-ocean ridges. Basalts from marginal or back-arc basins are generally tholeiitic. The La : Yb ratios of such basalts range from 0.3 to 7, typically from 1 to 4 (see data in Hart et al. 1972; Gill 1976; Hawkesworth et al. 1977; Saunders and Tarney 1979; Saunders et al. 1979; Stern 1979; Weaver et al. 1979).

The La : Yb ratios in the rocks of the island-arc tholeiitic series range from 1 to 2 (Jakeš and Gill 1970). The ratio for basalts of the island-arc calc-alkaline series is typically 3.5 (Jakeš and White 1972). La : Yb ratios of this magnitude are found in calc-

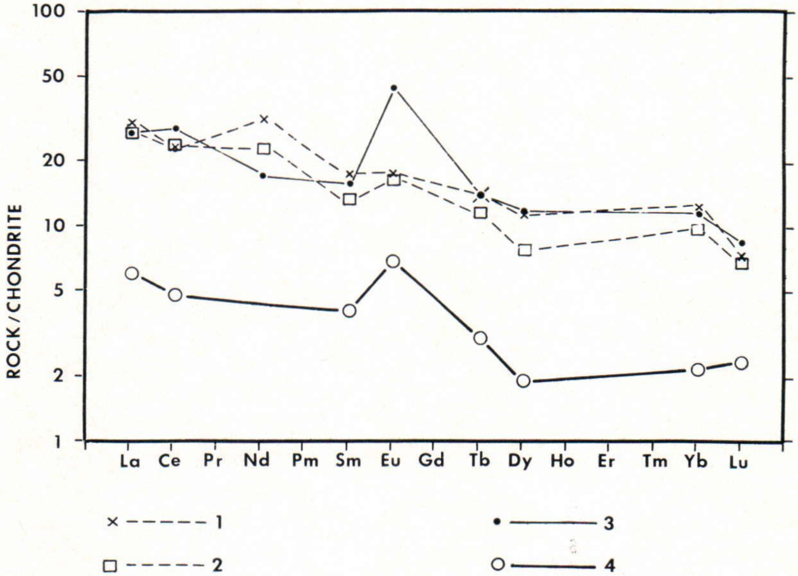

Fig. 1. Normalized REE distributions in the Haveri formation rock types (Leedey chondrite, Masuda et al. 1973; Koljonen and Rosenberg 1975). 1. and 2. metalavas, 3. metalava breccia, 4. sulphide ore.

alkaline basalts in some active parts of continental margins (Lopez-Escobar et al. 1977).

The data given by Schilling and Winchester (1969) and Herrmann (1970) indicate that the La : Yb ratios in tholeiites from oceanic islands range from 4 to 10, and in tholeiitic continental plateau basalts from 3 to 10.

On the basis of averages given by Condie (1976) the La : Yb ratios of metabasalts from Archean greenstone belts range from 1.5 to 5. The tholeiitic metabasalts from the Tipasjärvi greenstone belt display La : Yb ratios from 3 to 5 (Blais et al. 1978, Fig. 9).

The LREE enrichment in the tholeiitic metabasalts from Haveri (La : Yb $\sim$ 4) indicates that they differ from normal (but not all) mid-ocean ridge and ocean floor basalts. For the same reason they also differ from typical basalts of the island arc tholeiitic series. On the basis of their La : Yb ratios the Haveri metabasalts resemble some tholeiitic basalts from marginal basins and oceanic islands, some tholeiitic continental plateau basalts, calc-alkaline basalts from island arcs and some continental margins, and some Archean tholeiitic metabasalts.

REE in volcanic ore-forming processes

Conspicuous features of Fig. 1 are the positive Eu anomalies in samples 3 and 4. Several events may give rise to positive Eu anomalies in rocks: (1) cumulation of plagioclase, into which Eu has become relatively enriched, will produce a positive Eu anomaly; (2) during the precipitation of chemical sediments Eu could preferably enter precipitating phases; (3) Eu can become relatively enriched into hydrothermal fluids; (4) Eu is sometimes relatively enriched during epidotization processes; (5) Eu could be enriched by metamorphic differentiation (Koljonen and Rosenberg 1974; Condie et al. 1977; Graf 1977; Hellmann et al. 1979; Kerrich and Fryer 1979).

Samples 3 and 4 are successive samples from the same drill core; both display a positive Eu anomaly of equal magnitude. Therefore, and because similar anomalies are lacking from the metalavas, the positive Eu anomalies probably have a common origin.

Samples 3 and 4 are rich in epidote and therefore differ from samples 1 and 2. Hence, the origin of the positive Eu anomalies is attributed to the circulation of ore-forming hydrothermal fluids in the metalava breccia. These fluids are thought to have caused for the transportation of Eu, epidotization, and the leaching and transportation of ore-forming elements (cf. Mäkelä 1980).

According to the data by Condie et al. (1977) and Hellmann et al. (1979), Eu : Eu* ratios in intensely epidotized rocks (60—80 vol-% epidote) are c. 1.5. This value is lower than those for sample 4 and, especially, sample 3 (in which the quantity of epidote is c. 30 vol-% and Eu : Eu* is 2.8). This indicates that the hydrothermal fluid contributing to the epidotization and ore-forming process was relatively enriched in Eu.

Conclusions

The results of the present study indicate that in the Haveri formation the LREE contents of the tholeiitic metabasalts are 20 to 30 times and the HREE contents 6 to 12 times higher than those of chondrites. Such a LREE-enrichment pattern is found in tholeiitic basalts of various environments and ages including young marginal basins, oceanic islands, continental plateau basalts, some Archean metabasalts, and some island-arc and active continental margin calc-alkaline basalts.

The metalava breccia produced a REE distribution pattern identical to those of metalavas except for a positive Eu anomaly. A genetically related sulphide ore sample shows a similar pattern at a lower REE concentration level, including a positive Eu anomaly.

Positive Eu anomalies have been reported by Graf (1977) from Ordovician volcanogenic massive sulfide deposits and associated rocks. Kerrich and Fryer (1979) found positive Eu anomalies in Archean auriferous carbonate-chert sediments, hydrothermal quartz veins and host rocks. The results of the above and the present study suggest that a positive Eu anomaly in a volcanic rock unit implies of hydrothermal fluid circulation within the unit. Consequently, if we keep in mind the formation mechanism of volcanic exhalative ore deposits (leaching and transportation of metals by hydrothermal fluid, and subsequent deposition on the sea floor), such an anomaly might indicate the existence of a volcanic exhalative ore deposit in the environment. However, more studies on REE in volcanic rocks, related ore deposits, and minerals are required to asses the value of Eu as a pathfinder in the exploration of volcanogenic ore deposits.

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