RARE EARTH ELEMENTS IN MIDDLE PRECAMBRIAN VOLCANIC ROCKS OF FINLAND, WITH A DISCUSSION OF THE ORIGIN OF THE ROCKS

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The contents of rare earth elements (REE) have been determined in five Svecofennian metamorphosed volcanic rocks and are compared with those found in the Karelian zone and Recent tholeiites. In the Svecofennian zone, REE contents in low silica volcanic rocks are like those in the calc-alkalic series and in continental tholeiites, whereas in the Karelian zone they are like those in island arc tholeiites. It is argued that in the Karelian zone, where magmatism initiated, tholeiitic basalts originated in the upper mantle; as shown in normalized form, the light REE are depleted, reflecting the distribution pattern found, for example, in rocks of pyrrolite composition. As orogeny advanced, more and more crustal material — basement and geosynclinal sediments — was recycled and the REE distribution pattern changed to that found in the synorogenic calc — alkalic rocks (1.8—1.95 Ga), reflecting the REE pattern present in sediments.
The chemical composition of the magmatic rock series formed during Svecokarelian folding is quite like that observed in island arc systems.

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Introduction

On the basis of REE distribution, tholeiitic basalts can be classified as of the oceanic or island arc types or the continental type (Frey *et al.* 1968; Herrmann 1968, 1970; Jakeš & Gill 1970; Nakamura & Masuda 1971; Schilling & Winchester 1969). On the whole, the total REE content in tholeiites is lower than in alkali- and silica-rich rocks and higher than in olivine- and pyroxene-rich mafic rocks. Oceanic and island arc tholeiites contain less REE than continental tholeiites or gabbroic calc—alkalic rocks, and the La/Yb ratio is about unity, whereas for the latter it is about ten (*cf.* Jakeš & Gill 1970). The REE pattern found in oceanic types is attributed to differentiation within the upper mantle — *e.g.*, in the low velocity zone — the chemical composition of which is similar to that of chondrites (*e.g.* Green 1970; Green & Ringwood 1967; Masuda & Matsui 1966). In Precambrian and Recent volcanic rocks the trace as well as the major element compositions are the same. The content and distribution patterns of elements such as REE, U, and Th, which are unable to substitute to any appreciable extent in the major minerals of the upper mantle (olivine, aluminous pyroxene, *etc.*), have not changed in basalts with time. Yet, olivine-pyroxene rock itself, which is similar to chondrites, cannot give rise to magmas having constant composition through all geologic time. To explain the constant chemical composition of those parts of the Earth where magmas have formed, Jahn, Shih, and Murthy (1974), among others, have proposed that either the trace elements have been repeatedly and fully recycled within a restricted and closed system of the crust and the upper mantle during the last three gigayears (recycled mantle), or the trace elements have been replenished from the lower part of the mantle (replenished mantle).

Since REE as a group offer much petrogenetic information, we have studied their content and distribution patterns in some Middle Precambrian metamorphic volcanic rocks found in Finland.

Experimental and the normalization of REE contents

REE have been determined by instrumental activation analysis as described earlier (Rosenberg & Wiik 1971; Rosenberg 1972). Major elements have been analyzed by the conventinal wet method and alkalis by atomic absorption spectrometry.

REE contents are presented normalized against chondrites, as proposed by Masuda and Coryell; in the figures they are normalized against Leedey (L/6) chondrite (Masuda *et al.* 1973; Koljonen & Rosenberg 1974). The total REE contents in tables have been calculated from the graphs.

General geology

The regional distribution of volcanogenic rocks in Finland is displayed in Fig. 1. Volcanic rocks and their plutonic differentiates belonging to the Svecokarelian folding are grouped with the Karelian and Svecofennian rocks (*cf.* Eskola 1963).

The Karelian metasediments belong to epicontinental facies and are deposited along the northeastern boundary of the Svecokarelian fold belt in the neighborhood of an old craton. In the Karelian zone, basic extrusives and intrusives are mostly found in Jatulian sedimentary rocks, which have deposited on Prekarelian gneisses. Basic volcanic rocks usually occur in quartzites, but they are also found in shales and dolomites, and in places they cut the basement. The texture is often ophitic and, in the largest dykes, gabbroid. Most of them represent low-temperature mineral facies — greenschist, or the epidote-amphibolite facies, and near granites also amphibolite facies. Albite-rich spilitic rocks are also typical of the Karelian zone (*cf.* Piirainen & Rouhunkoski 1974). Basic volcanic rocks are not met with in the topmost, the Kalevian medasediments of geosynclinal facies (*cf.* also Eskola 1925; Gaál & Rauhamäki 1971; Härme 1949; Laajoki 1973; Meriläinen 1961; Mikkola 1949; Nykänen 1971; Piispanen 1972; Väyrynen 1928).

The Svecofennian metasediments belong mostly to geosynclinal facies. Situated in southern and southwestern Finland, they form an arc in W—E and SE—NW direction, south of the silica-rich plutonic rocks of central Finland. These plutonic rocks separate the medasediments of the Karelian and Svecofennian zones. The Svecofennian supracrustal sequence has sedimented in a basin whose base in unknown (Simonen 1953). The metasediments from bottom to top are phyllites, graywackes, and graded shales. Lying over them are arkoses, graywackes, and conglomerates, with interbeds of acid and basic volcanic rocks, and the basic volcanic rocks overlie the sediments. South of the schist belt, basic and

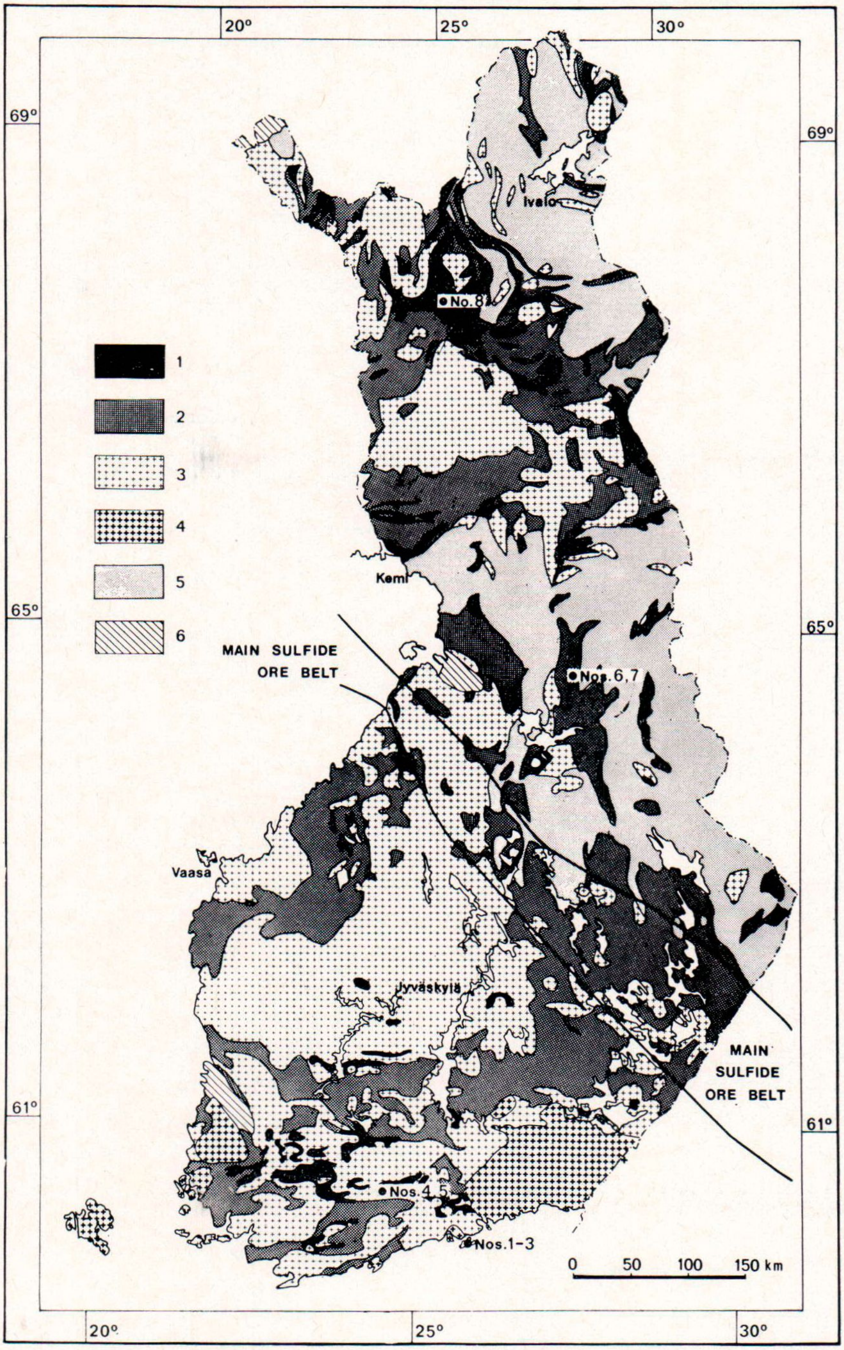


Fig. 1. Sites of samples studied presented on a generalized geological map of Finland (Simonen 1960 a). 1. Volcanic rocks; 2. schists (including quartzite); 3. silicic plutonic rocks; 4. rapakivi intrusions; 5. Presvecokarelian basement (schist, paragneiss, granulite, orthogneiss); 6. Jotnian and Caledonian sedimentary rocks.

TABLE 1

Petrography of investigated Svecofennian samples

No.	Rock type	Texture	Mineral assemblage	Location
1	Metabasalt (gabbroid)	Blastoporphyritic with granoblastic and hypidiomorphic features	Plagioclase (An_{55-60}), hornblende, hypersthene, augite, biotite; accessory magnetite, serpentine	Porvoo, Suur-Pellinki, Nyttisholmen
2	Uralite porphyry (pillow lava)	Somewhat foliated. Matrix is granoblastic and plagioclase is cumulophyric	Plagioclase (An_{50}), hornblende; accessory sphene, sericite, apatite, zircon, calcite, magnetite	Porvoo, Suur-Pellinki
3	Metavolcanite	Blastoporphyritic, fine-grained	Hornblende, plagioclase (An_{30-40}); accessory quartz, biotite, chlorite, epidote	Porvoo, Suur-Pellinki, Ednäs
4	Uralite gabbro	Hypidiomorphic	Plagioclase (An_{55-60}), hornblende, uralite, augite, biotite; accessory apatite, tremolite, chlorite, magnetite, quartz, calcite	Hyvinkää, Kytäjä
5	Metavolcanite	Stratified, fine-grained	Plagioclase (An_{10-15}), chlorite, quartz, potassium feldspar; accessory magnetite, epidote, calcite, apatite, zircon, biotite	Hyvinkää, Kytäjä

acid (leptite) volcanogenic intercalations in schists are found. The metamorphic grade in the Svecofennian zone is higher than in the Karelian zone and the rocks are mostly of amphibolite and granulite facies. Plutonic rocks cut the schists, and migmatitic rocks are very common in southern Finland. Rapakivigranites (1.6 Ga) form a separate group, which became emplaced after the main phase of Svecokarelian folding (*cf.* also Sederholm 1897, 1907, 1923, 1926, 1934; Seitsaari 1951; Simonen 1960 b; Tuominen 1958, 1966).

Geology of the studied areas

Petrography, and major element and REE contents of the Svecofennian volcanogenic rocks studied are displayed in Tables 1, 3, and 4.

The volcanic rocks in Pellinki (Nos. 1—3) form a uniform area where primary structures are well preserved (Laitala 1973). They are mostly pyroclastic and are formed from tuffs and agglomerates which later, in folding, underwent metamorphism. Basic tuffs predominate but also intermediate and acid ones are found. With the pyroclastic rocks there are also metamorphosed lava beds, which are mostly basic uralite porphyries and contain variants resembling plutonic rocks. In a few places, lavas rich in silica are also found (*cf.* also Laitala 1964, 1965; Sederholm 1923, 1926).

In Hyvinkää (Nos. 4 and 5) basic volcanic rocks surround a belt of plutonic rocks (Härme 1953, 1954). Basic and intermediate banded tuffites are common and lenses of agglomerate occur on both sides of the gabbro. The banded volcanic rocks are, in part, pyroclastic and in places are sedimentary in character with intercalations of mica schist. The volcanic rocks are

TABLE 2

Rocks and references to the normalized REE analyses displayed in Figs. 2 and 3

No.	Rock type	Location	Total REE ppm	La/Yb	References
6	Basic tuffite	Puolanka, Finland	28	0.25	Laajoki 1975
7	Metadiabase	Puolanka, Finland	18	1.3	Laajoki 1975
8	Greenschist	Kittilä, Finland	23	2.9	Sahama 1945
9	Oceanic tholeiites (average of 11 tholeiites and olivine tholeiites)	Kohala Mt., Hawaii, Mid-Atlantic Ridge, East Pacific Rise	83	1.3	Frey *et al.* 1968
10	Continental tholeiites (average of 163 samples)	Siberian Platform, Noril'sk region, USSR	82	6.5	Herrman 1970 (Balashov & Nesterenko 1966)
11	Deccan traps (average of 10 tholeiites)	Mahabaleshwar region, India	106	4.0	Nakamura & Masuda 1971
12	Continental tholeiite	Columbia Plateau, USA	182	6.5	Schmitt *et al.* 1964
13	Precambrian shales (average of 36 samples)		108	12.0	Wildeman & Haskin 1973
14	Average of Svecofennian volcanic rocks (TABLE 1, Nos. 1—5)	Finland	76	8.2	
15	Synorogenic Precambrian granites (average of 5 samples)	Finland	196	18.0	Koljonen & Rosenberg 1974
16	Average of volcanic rocks and synorogenic granites (Nos. 14—15)	Finland	137	11.6	

penetrated by dykes of gabbro, diorite, granodiorite, and microcline granite (Simonen 1948, 1960 b). Gabbro is accompanied by fine-grained marginal varieties that grade into the volcanic rocks, the latter representing an extrusion of early orogenic phase, the gabbros being intrusives. It seems that the other plutonic rocks, ex-cluding microcline granites are comagmatic products of differentiation. The granites, which penetrate all rocks, belong to the late-kinematic phase (*cf.* also Tenhola 1971).

REE distribution in the investigated areas

Compared with chondrites, the light REE are enriched in both the rock series investigated (Figs. 2 a, b), and the distribution patterns resemble those found in continental tholeiites (Table 2, Fig. 2 d, Nos. 10—12). In the pillow lava (Table 1, No. 2) major element content (*e.g.* sodium) has altered after deposition, but the REE content has not changed either through weathering or by metamorphism. REE do not

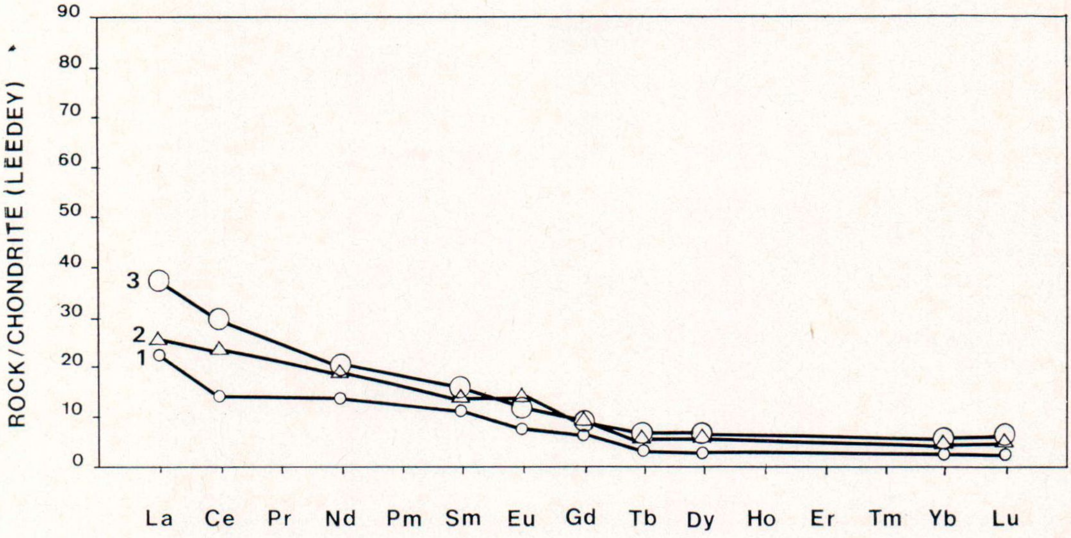
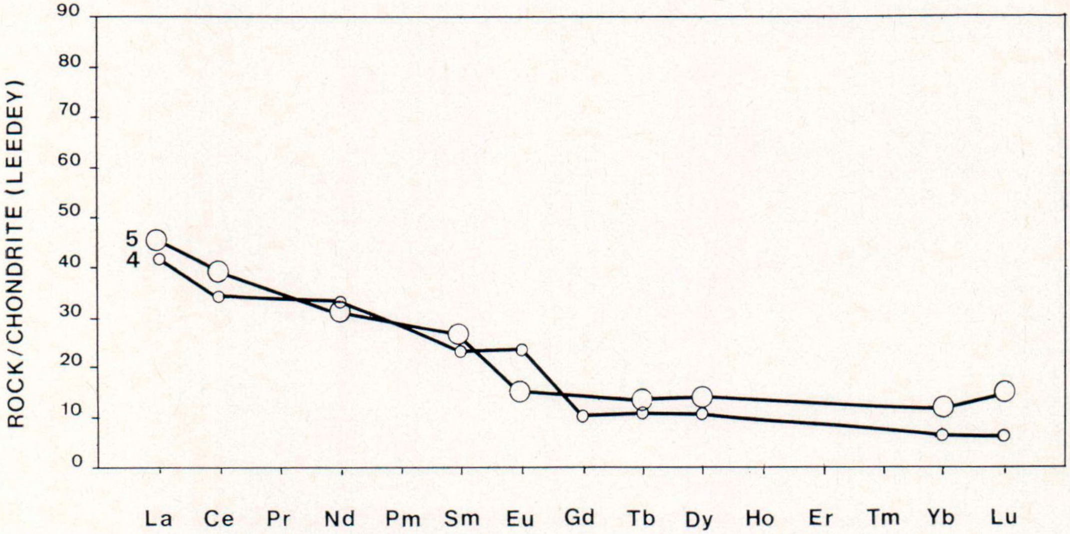


Fig. 2. REE contents normalized against chondrite (Leedey, Masuda *et al.* 1973). The numbers on the graphs indicate the analyses shown in Tables 1 and 2.

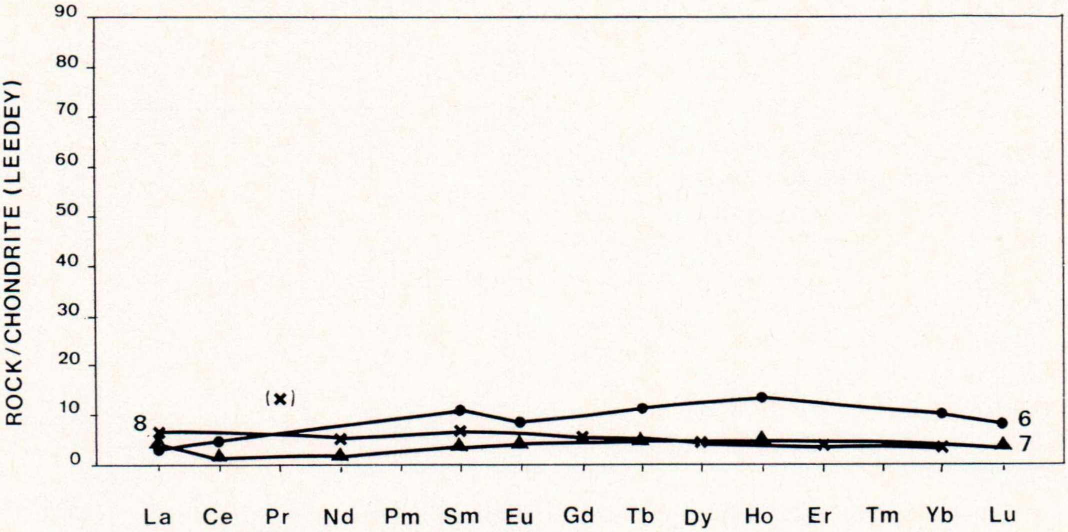
a) Volcanic rocks from Pellinki (Nos. 1—3). Svecofennian zone.



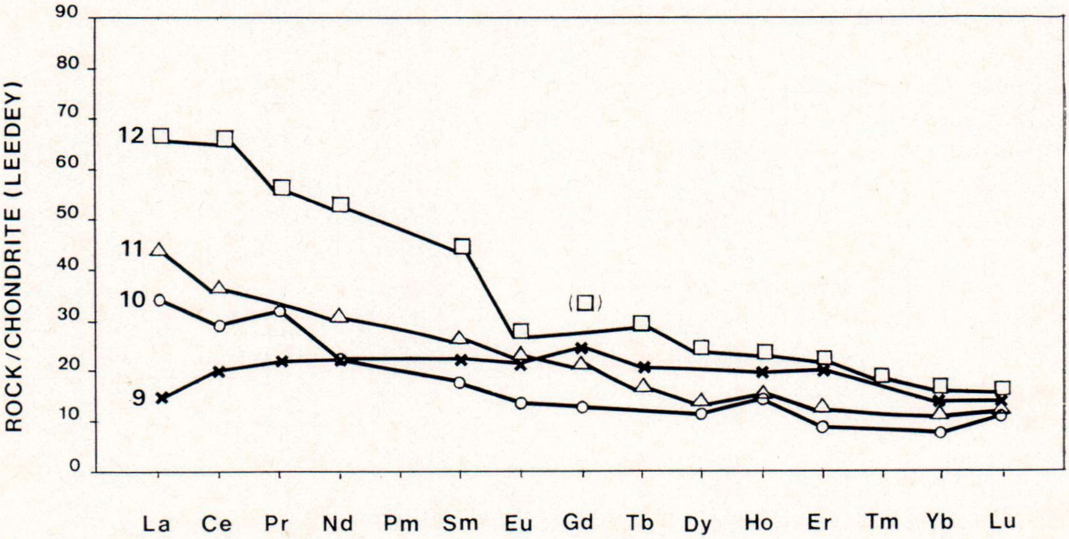
b) Gabbro (No. 4) and metavolcanite (No. 5) from Hyvinkää. Svecofennian zone.

migrate before high metamorphic conditions are established (Koljonen & Rosenberg 1974).

Most REE are found in silica-rich differentiates. Similar distribution patterns in the two groups indicate that each of them forms a co-magmatic series, and the gabbro (No. 4) in Hyvinkää has differentiated from magma which earlier brought about the adjacent volcanic rocks. The Eu anomaly is positive because in gabbro Eu is incorporated into plagioclase in place of Ca, and through crystal accumulation of plagioclase is concentrated into the gabbro fraction. The



c) Basic tuffite (No. 6), metadiabase (No. 7), and greenschist (No. 8). Karelian zone.



d) Oceanic tholeiites (No. 9), continental tholeiites from Siberia (No. 10), Deccan traps (No. 11), and a continental tholeiite from Columbia Plateau (No. 12).

remaining melt, on the other hand, was enriched in silica during the process and is depleted of Eu. The enrichment of Eu in the early differentiates is, to a lesser degree, also observed in the Pellinki area (Nos. 2 and 3).

The REE distribution patterns are quite similar, demonstrating that, although total contents differ, the magmas have originated in the same manner during the Svecokarelian folding, and that the volcanic rocks in southern Finland are genetically related to the synorogenic calc — alkalic plutonic rocks.

Discussion

The contents and distribution patterns found in Precambrian volcanic rocks in Finland are quite like those of the Recent period, and the REE distribution in upper mantle and crust seems to be formed through the recycling of the elements in a closed system in the Earth. Although the mineralogy and chemistry are still under study, on the basis mostly of REE distribution there would seem to be a fundamental difference between Karelian and Svecofennian volcanic rocks, reflecting their different origins. This has also a great influence on the chemical composition of ores formed (*e.g.* oxide or sulfide). In the Karelian sequence (Table 2, Fig. 2 c) the REE are like those in island arc (or abyssal) tholeiites (Table 2, Fig. 2 d, No. 9), and in the Svecofennian sequence like those in calc—alkalic rocks. The boundary between these types is not sharp because areas where magmas are formed shift during orogeny, and silica-rich synorogenic plutonic rocks also are found in the Karelian zone. Also possible is the mixing of magmas formed at different depths, and the lateral separation of magmas is dependent on the dip of the active fault planes (Benioff seismic zone).

In the most prominent shear zone in Finland (Kahma 1974; Mikkola & Niini 1968; Tuominen *et al.* 1973), which seems to separate calc—alkalic and tholeiitic magma series, is situated the main sulfide ore belt (Fig. 1). Probably sulfides mobilized and migrated from metasediments to this belt and accumulated before the orogenic plutonic rocks were emplaced (Koljonen 1974, 1975). Also it is possible, and even probable, that early volcanism introduced elements found in ores to the sediments in the first place (*cf.* Piirainen 1974). The high content of selenium and low S/Se ratio support this hypothesis because Se is a common element in high-temperature volcanic emanations.

Since REE contents and distribution patterns in the Karelian volcanic rocks (Fig. 2 c) are

TABLE 3

Chemical compositions and norms of Svecofennian volcanic rocks.
The numbers indicate samples in TABLE 1

No.	1	2	3	4	5
SiO_2 ..	46.96	50.44	57.43	50.09	61.40
Al_2O_3	17.28	17.88	15.64	15.68	13.91
Fe_2O_3	5.98	4.27	4.03	4.64	4.95
FeO ..	6.95	6.64	5.31	6.34	2.22
MnO .	0.16	0.09	0.06	0.16	0.08
MgO .	7.30	2.91	3.83	6.31	2.21
CaO .	10.12	10.40	7.43	9.76	6.49
Na_2O .	3.60	4.33	2.62	3.46	2.26
K_2O ..	0.51	0.83	1.80	1.03	4.85
H_2O+	0.67	0.26	0.91	0.49	0.92
H_2O-	0.16	0.08	0.02	0.11	0.20
TiO_2 .	0.69	1.03	0.95	1.53	0.80
P_2O_5 .	0.23	0.32	0.27	0.35	0.18
Total	100.61	99.48	100.30	99.95	100.47
CIPW norms					
qz ...	—	—	14.22	—	16.79
or ...	3.01	4.90	10.64	6.09	28.66
ab ...	26.27	35.21	22.17	29.28	19.12
an ...	29.48	26.90	25.60	24.21	13.49
ne ...	2.27	0.78	—	—	—
di	15.45	18.70	7.71	17.59	11.87
wo ...	—	—	—	—	0.95
hy ...	—	—	10.77	8.88	—
ol	12.78	3.77	—	2.85	—
mt ...	8.67	6.19	5.84	6.73	5.09
il	1.31	1.96	1.80	2.91	1.52
he ...	—	—	—	—	1.44
ap ...	0.53	0.74	0.63	0.81	0.42
H_2O ..	0.83	0.34	0.93	0.60	1.12

TABLE 4

REE contents of Svecofennian volcanic rocks.
The numbers indicate samples in TABLE 1
The values in parentheses are estimates

No.	1	2	3	4	5	Leedey
La	8.6	10	14.4	15.7	17	0.378
Ce	15	23	29	33	38	0.976
Pr ...	—	—	—	—	—	(0.138)
Nd ...	11	14	14.5	23	22	0.716
Sm ...	2.8	3.4	3.8	5.4	6.1	0.230
Eu ...	0.70	1.10	1.07	2.02	1.25	0.0866
Gd ...	2.5	2.7	—	3.1	—	0.311
Tb ...	0.31	0.40	0.45	0.58	0.78	(0.0568)
Dy ...	1.4	2.1	3.1	4.1	5.6	0.390
Ho ...	—	—	—	—	—	(0.0868)
Er	—	—	—	—	—	0.255
Tm ..	—	—	—	—	—	(0.0399)
Yb ...	1.0	1.22	1.48	1.82	3.0	0.249
Lu ...	0.21	0.22	0.28	0.29	0.57	0.0387
~ΣREE	47	49	77	97	109	3.95
La/Yb	8.6	8.2	9.7	8.6	5.7	1.5

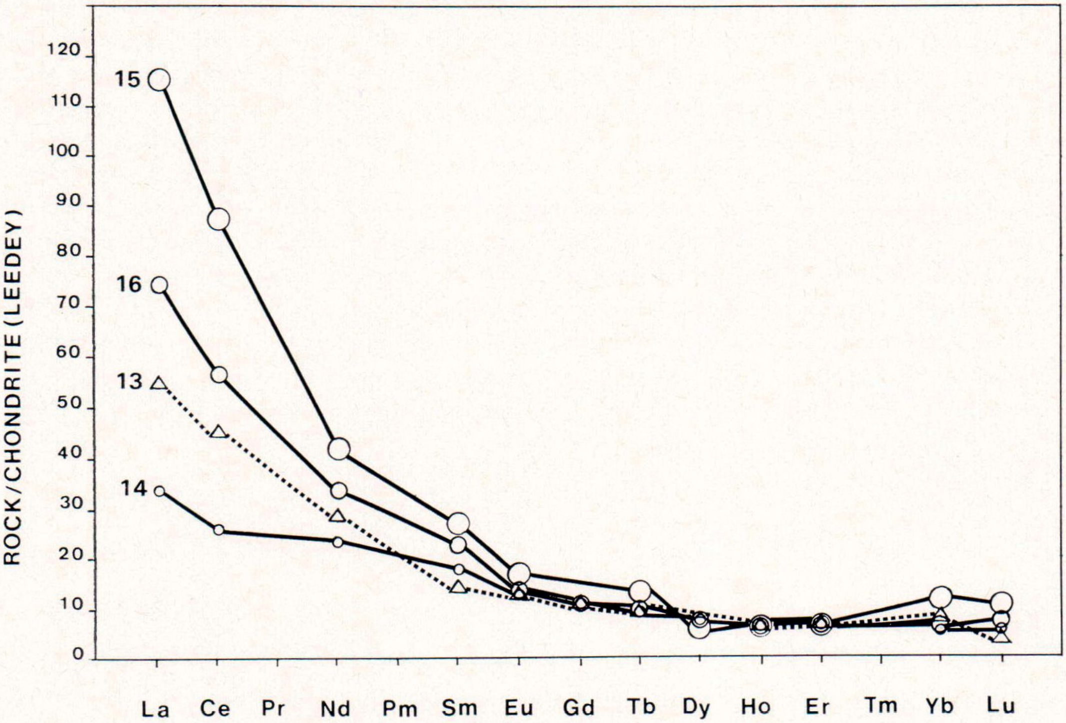


Fig. 3. REE in Precambrian sediments (No. 13), Svecofennian volcanic rocks (No. 14, average of Nos. 1—5), Finnish synorogenic granites (No. 15), and the mean of Nos. 14 and 15 (No. 16).

similar to those found in island arc tholeiitic basalts and in high-temperature peridotites in which light REE are depleted as indicated by normalized graphs (*cf.* Frey 1969), it would seem that magmas were genereted in the low parts of crust or in the upper mantle (*e.g.* in the low-velocity zone) during the early phases of orogeny. As the orogeny advanced, the geosynclinal sediments of the lithosphere were resorbed, and the chemical composition of tholeiitic magmas changed as more and more crustal material was assimilated to that of the calc — alkalic series.

The temporal variation of magmatic rocks similar to those formed during Svecokarelian folding — tholeiitic and calc—alkalic rocks — has been observed in island arcs by Kuno (1950, 1959, 1968) and Tilley (1950), and the presence of tholeiitic rocks prior to the eruption of calc — alkalic and alkalic rocks has been emphasized by Baker (1968), Donnelly *et al.* (1971), Gill (1970) and Jakeš & White (1969).

From the REE distribution pattern, volcanic and plutonic rocks belonging to the calc—alkalic series seem to have formed through the melting of crustal material, and the REE pattern is thus a fossil remanent of that in basement and sediments (*cf.* Green & Ringwood 1968). Under selective anatexis the sediments with their contained REE separated into silica-rich and silica-poor fractions, but the fractions in many places were almost certainly not in magmatic form contemporaneously. The generalized distribution patterns of REE following the separation of the two fractions are similar to those displayed in Fig. 3 (Table 2). The distribution pattern of the average (No. 16) of granites (No. 15) and basic volcanic rocks (No. 14) is similar to that found in Precambrian sediments (No. 13). Because no sedimentation basement has been found in the Svecofennian area, it would seem that, over a wide area, it has melted with the geosynclinal sediments to form anatectic magmas (Simonen 1960, p. 95).

The total REE content in magmas formed from sediments through anatexis is higher than that in magmas formed in the mantle, because REE are enriched into the upper crust and into the silica-rich differentiates in it. Every recycling process seems to increase the content of light REE, and the content is accordingly greatest in the latest-formed alkali-rich differentiates. It seems, nevertheless, that REE are enriched only in silicic magmas formed under high-temperature conditions; for low-temperature late differentiates are depleted of them(Koljonen & Rosenberg1974).

The total content of Eu and heavy REE does not change much during recycling because they can be incorporated into calcic plagioclase (Eu), and into pyroxenes and olivine (Dy—Lu) more readily than can the light elements. This difference is indicated by the La/Yb ratio, which in the calc—alkalic series is high ($\sim$ 10) and in island arc and abyssal tholeiites low ($\sim$ 1).

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