

RARE-EARTH ELEMENTS IN PRECAMBRIAN IRON FORMATIONS IN VÄYRYLÄNKYLÄ, SOUTH PUOLANKA AREA, FINLAND

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Partial rare-earth element (REE) and ore analyses of 19 samples of oxide-, carbonate-, silicate-, and sulphide-facies rocks from the Superior-type Precambrian (Karelian) iron formations and associated rocks (pelitic metasediments, dolomite, basic tuffite and metadiabase) are given. For comparison one analysis of an Archean (Prekarelidic) iron formation of the Algoma type is also included.

The Karelian iron formations are relatively rich in REE and their REE distribution patterns show depletion of Ce. This is due to the regularly occurring apatite, in which these features are multiplied as is indicated by the analysis of the apatite-rich band. This stratum is interpreted as a marine phosphorite interband and, consequently, the apatite in the iron formations as of marine origin.

With the exception of Ce, the REE distribution patterns in iron formations and associated pelitic metasediments and dolomite are relatively similar. All these rocks show a clear trend towards relative depletion of the lighter REE and Yb and Lu in comparison with the North American shale (NAS). Metadiabase and basic tuffite are poor in REE and depleted in the lighter REE in the same way as are tholeiitic basalts.

Archean iron formations seem to have a greater Eu:Sm ratio than the younger iron formations. More REE data from geologically wellknown iron formations are needed, however, before any definitive conclusions can be drawn.

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Introduction

Few studies have been published concerning rare-earth element (REE) distribution in iron formations. Classical works in this respect are those of Landergren (1936, 1948) from Sweden. From the Soviet Union REE data are available

from the Imandra region (Balashov & Goryainov 1966) and from Krivoy Rog (Tugarinov *et al.* 1973). Wildeman and Haskin (1973) have given two REE analyses of American iron formations. There are two comprehensive studies from Canada, which cover REE distribution in Algoma- (Fryer 1971 a) and Superior-type iron

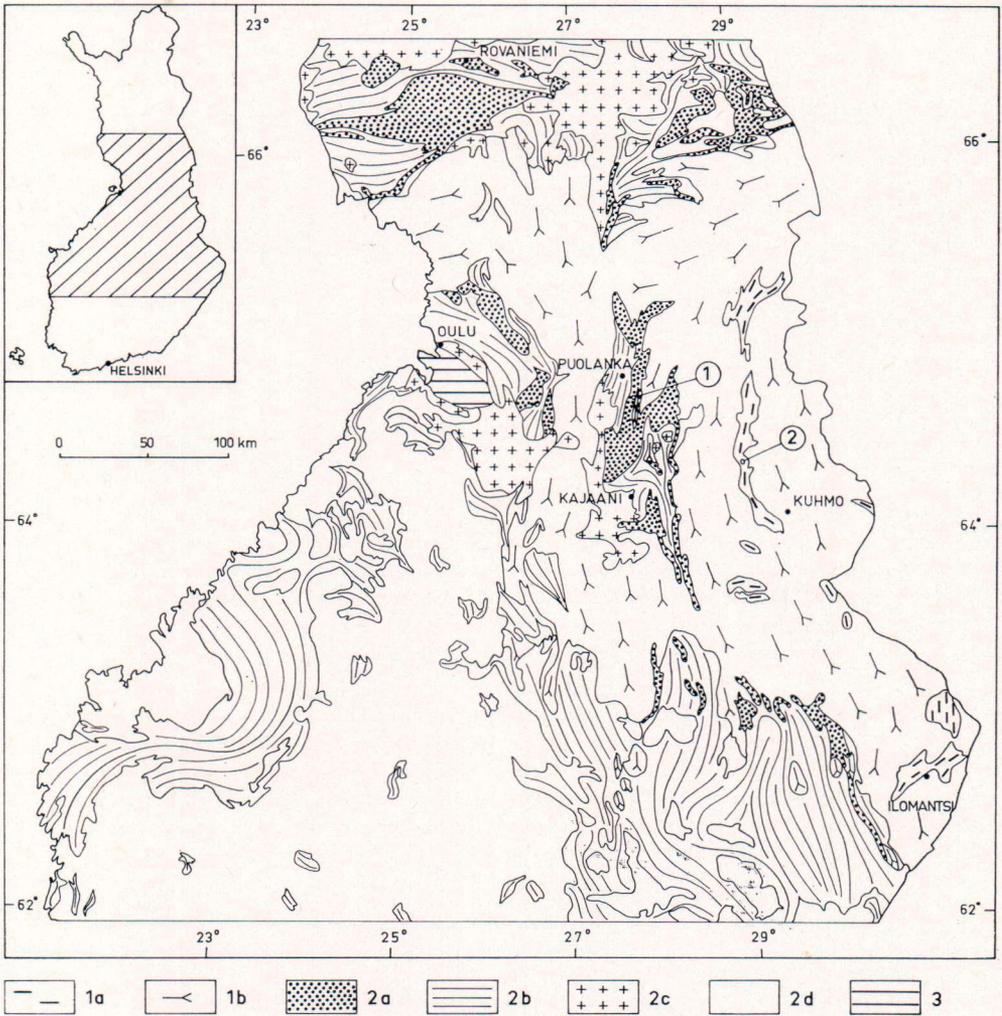


Fig. 1. The sites of the Värylänkylä iron formations (1) in Puolanka and the Härmänjoki iron formation (2) in Kuhmo presented on the simplified geological map of Finland (Simonen 1960). 1) Prekarelidic basement: a) schists and paragneisses, b) orthogneisses (granite gneiss). 2) Karelidic and Svecofennidic rocks: a) Karelian (Jatulian) quartzites, b) Karelidic and Svecofennidic schists, gneisses, migmatites, metabasalts and amphibolites, c) Karelidic granite, d) other (mainly silica-rich) orogenic plutonic rocks. 3) Jotnian sedimentary rocks (siltstone). The Kainuan schist belt consists of Karelian quartzites and schists trending from Kajaani to Puolanka.

formations (Fryer 1971 b). Partly on the basis of REE distribution Parák (1973 a, b) has recently proposed that the Kiruna ores are of exhalative-sedimentary origin.

In 1973 the Geological Survey of Finland carried out prospecting on the small iron-formation occurrences in Värylänkylä, South

Puolanka area, NE Finland (Fig. 1), during which the REE distribution in the iron formations and associated rocks was studied. The purpose of this paper is to give the REE data and to discuss their stratigraphical and genetical significance. The paper constitutes the first part of the author's studies of Finnish iron formations.

Experimental

The REE analyses were performed by Mrs. Riitta Zilliacus, M.Sc., in the Reactor Laboratory of the Technical Research Center of Finland. The instrumental activation technique used has been described in other publications (Rosenberg & Wiik 1971; Rosenberg 1972; Koljonen & Rosenberg 1974). The other elements given in Table 2 were analysed in the Ore Laboratory of the Geological Survey of Finland using routine ore-analysis methods.

General geological setting

The study area belongs to the part of the Karelidic belt known as the Kainuan schist belt (Fig. 1). This NNW trending schist belt is characterized by the Jatulian at its eastern margin and by the Kalevian in its middle and western parts. The Jatulian is an epicontinental lithosome composed mainly of quartzites with minor basal arkosites. The Kalevian is a flysch lithosome with phyllites and mica schists. Between these two units a minor lithosome occurs that is known as the Marine Jatulian, and which contains phyllites, black schists, dolomites, quartzites and iron formations. Thus, the iron formations in Kainuu are of the Superior type. Karelidic rocks are intruded by metadiabases of the early Karelidic magmatism and by Karelidic granite.

The general geology of the South Puolanka area has recently been studied by the author (Laajoki 1973). In Väyrylänkylä the iron formations occur in the synclinorium known as the Salmijärvi basin and are met with in the Dolomite-Phyllite Formation of the Marine Jatulian. The geological setting of the two main iron formations, Pääkkö and Iso Vuorijärvi, is shown in Fig. 2. The stratigraphy and the facies changes within the iron formations in different sections of the Salmijärvi basin are given in Fig. 3. The eastern parts of the iron-formation horizon (Pääkkö section) consist of silicate-bearing

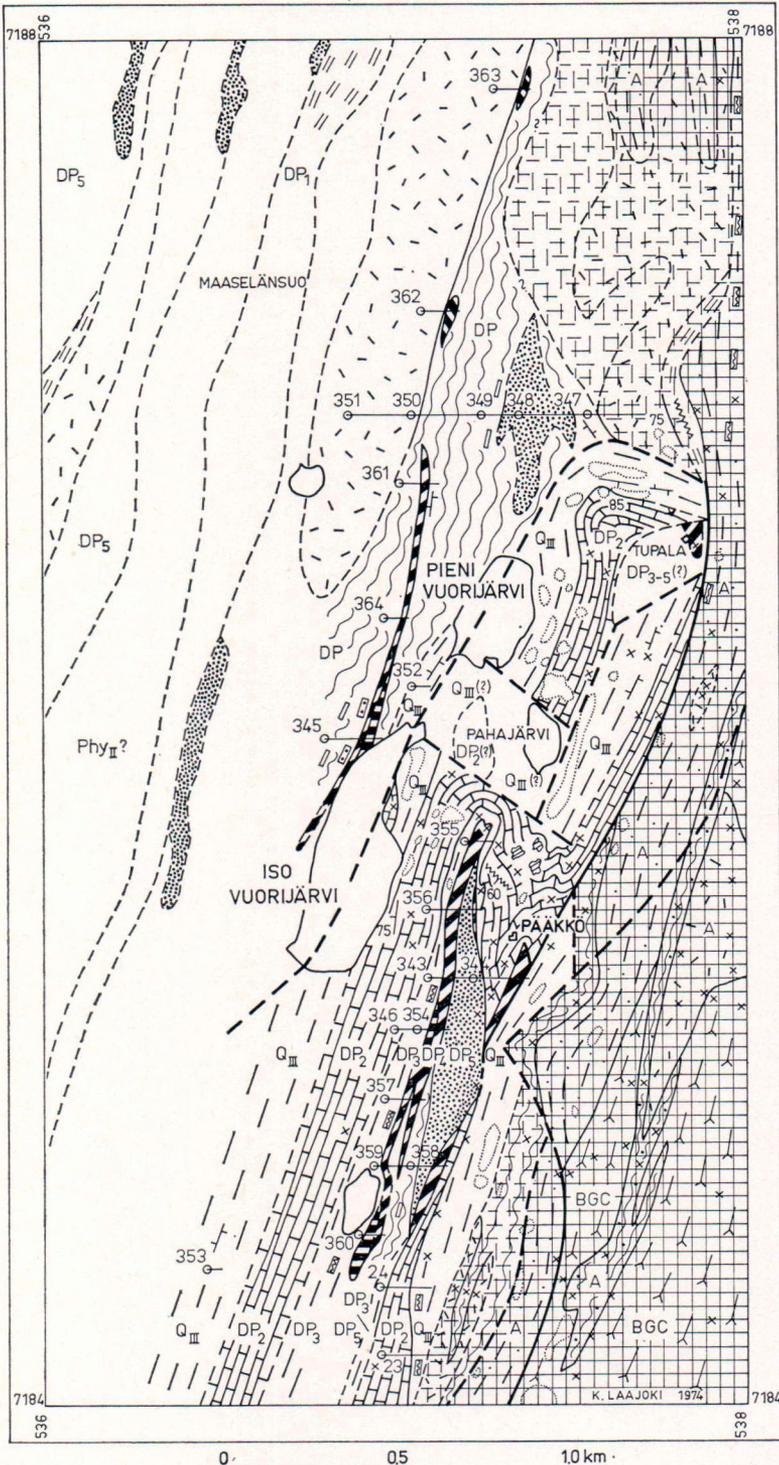
quartz-magnetite-banded rock of the oxide facies. Quartz-siderite-banded rocks of the carbonate facies together with quartz-magnetite-banded rocks and iron-rich black schists of the sulphide facies are encountered in the middle parts (Iso Vuorijärvi section). The two northernmost occurrences of the Iso Vuorijärvi iron formation are mainly composed of iron-silicate-magnetite rock of the silicate facies. In the westernmost parts, about 3 km west of the Pääkkö farm (outside the map area in Fig. 2), iron-rich black schists of the sulphide facies are predominant (Seppola section). The latter rocks are manganiferous. They are considered to represent the iron formation deposited in the deepest parts of the Salmijärvi basin. The oxide and carbonate facies seem to have deposited in a subtidal environment. Some 5 km south of the Pääkkö section, in the Kōrölä area, small iron formations occur that consist mainly of quartz-magnetite-banded rocks.

The whole rock Pb—Pb isochrone age of the Pääkkö iron formation is $2\ 080 \pm 45$ Ma (Sakko & Laajoki 1975).

Owing to their small dimensions and poor grade ($Fe_{tot} \sim 26\%$) the iron formations in Väyrylänkylä are uneconomic. Another detrimental factor is their exceptionally high P content ($P \sim 1.2\%$) (Geological Survey of Finland 1974). The partial ore analyses of the iron-formation samples (Table 1) dealt with in this study are given in Table 2.

Sample description

The names, rock-stratigraphic units and codes of the samples analysed are tabulated in Table 1. The locations of the core samples collected from the map area in Fig. 2 can be determined with the aid of the drill hole numbers and depth intervals included in the sample codes. Samples Nos. 1—5 represent the dominant rock, quartz-magnetite-banded rock of the oxide facies, from different iron formations in Väyrylänkylä. In



SYMBOLS

- 1 [Symbol: Horizontal lines with small triangles pointing right]
- 2 [Symbol: Wavy lines]
- 3 [Symbol: Horizontal lines with small triangles pointing right]
- 4 [Symbol: Horizontal lines with small triangles pointing right]
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- 7 [Symbol: Wavy lines]
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- 9 [Symbol: Horizontal lines with small triangles pointing right]
- 10 [Symbol: Horizontal lines with small triangles pointing right]
- 11 [Symbol: Horizontal lines with small triangles pointing right]
- 12 [Symbol: Dashed line]
- 13 [Symbol: Solid line]
- 14 [Symbol: Line with a 70-degree angle and a dip symbol]
- 15 [Symbol: Wavy line with a 60-degree angle and a dip symbol]
- 16 [Symbol: Circle with an 'x' inside]
- 17 [Symbol: Circle with a dot inside]
- 18 [Symbol: Grid pattern]

Fig. 2. Stratigraphic-lithologic map of the surroundings of the Pääkkö iron formation (in the middle lower part) and the Iso Vuorijärvi iron formation (in the middle). Lithologic symbols: 1) Prekarelidic basement gneiss. 2) Conglomeratic mica schist. 3) Arkosite and feldspar-and/or sericite-bearing quartzite. 4) Quartzite-orthoquartzite/the same as intercalations. 5) Tectonic inclusions of quartzite. 6) Dolomite/the same as intercalations. 7) Phyllite/the same as intercalations. 8) Black schist/the same as intercalations. 9) Iron formation: a) oxide facies, b) silicate facies, c) carbonate facies. 10) Basic tuffite. 11) Metadiabase and/or -volcanics. 12) Stratigraphic-lithologic contact. 13) Fault or tectonic contact. 14) Bedding and dip. 15) Approximate strike and dip of shear-folded beds. 16) Outcrop. 17) Drill hole and number. 18) Allochthonous formations. Stratigraphic units: BGC) Basement Gneiss Complex. A) Arkosite Formation. Q_{III}) Quartzite Formation III. DP) Dolomite-Phyllite Formation: DP₁) Seppola Tuffite Member. DP₂) Salmijärvi Dolomite Member. DP₃) Pääkkö Quartzite Member. DP₄) Pääkkö Iron-Formation Member. DP₅) Salmijärvi Phyllite Member. Phy_{II}) Phyllite Formation II.

TABLE 1

Rock-stratigraphic positions and codes of the samples of the iron formations and associated rocks. The rock-stratigraphic abbreviations refer to Figs. 2 and 3. In sample codes the number of the REE-analysis and the map sheet are given first. These are followed by the number of the drill hole and the depth interval of the core samples analysed or the observation number of the outcrop samples (Nos. 18 and 20)

Sample number and name	Rock-stratigraphic unit	Sample code
1. Quartz-magnetite-banded rock	Pääkkö Iron-Formation Member (DP ₄)	1/3441/R343/ 82.00— 83.00 m
2. » » » »	» » » » (DP ₄)	4/3441/R344/151.55—152.55 m
3. » » » »	Iso Vuorijärvi iron formation	10/3441/R345/114.70—115.70 m
4. » » » »	Körölä iron formation	15/3441/R5 / 75.00— 77.00 m
5. » » » »	Pääkkö Iron-Formation Member (DP ₄)	13/3441/R356/ 76.00— 77.00 m
6. Quartz-magnetite-limonite-banded rock	» » » » (DP ₄)	3/3441/R355/ 46.00— 47.00 m
7. Fe-silicate-magnetite rock	Iso Vuorijärvi iron formation	9/3441/R362/104.30—105.30 m
8. Apatite-rich band	Pääkkö Iron-Formation Member (DP ₄)	16/3441/R360/ 51.40 m
9. Quartz-siderite banded rock	» » » » (DP ₄)	2/3441/R360/ 39.50— 40.50 m
10. » » » »	Iso Vuorijärvi iron formation	11/3441/R345/136.00—137.00 m
11. Dolomite	Salmijärvi Dolomite Member (DP ₂)	5/3441/R356/ 13.10— 13.20 m
12. Iron-rich black schist	Iso Vuorijärvi iron formation	17/3441/R345/129.40—130.20 m
13. Manganiferous iron-rich black schist	Seppola iron formation	18/3441/R337/ 61.00— 63.00 m
14. Black schist	Salmijärvi Phyllite Member (DP ₅)	6/3441/R343/103.40—104.40 m
15. Phyllite	Pääkkö Quartzite Member (DP ₃)	7/3441/R343/ 49.75— 49.85 m
16. Amphibole-bearing phyllite	Schists east of Iso Vuorijärvi iron formation (DP ₃ ?)	14/3441/R350/110.00—111.00 m
17. Amphibole-biotite-garnet rock	Schist wedge in the southern end of the Pääkkö iron formation	8/3441/R359/ 57.35— 57.45 m
18. Basic tuffite	Seppola Tuffite Member (DP ₅ ?)	19/3441/118-PE-65
19. Metadiabase	Liejeenjoki metadiabase (Phy _{II} ?)	12/3441/R351/167.80—168.00 m
20. Quartz-amphibole-magnetite-banded rock	Härmäjoki iron formation (Prekarelic schists of Kuhmo)	20/4412/3-VH-71

Co-ordinates of the drill holes and outcrops outside the map area in Fig. 2 are; 4) x = 7 179.400, y = 535.870; 13) x = 7 185.550, y = 534.370; 18) x = 7 184.540, y = 534.140; 20) x = 7 145.280, y = 453.780.

places Preglacial weathering has caused weak secondary enrichment of iron in this kind of rock (Laajoki 1975), in which case the rock contains limonite bands (No. 6) in addition to quartz and magnetite bands. Sample No. 7 is a rust-coloured iron-silicate-magnetite rock, which is considered to be weathered silicate-facies rock. The rocks of the carbonate facies are represented by samples Nos. 9 and 10. The rocks of the oxide, silicate and carbonate facies are almost pure chemical sediments and they are considered as the *iron formations proper*. Sample No. 8 is from an apatite-rich band about 0.5 cm thick. The presence of apatite was verified by X-ray diffraction studies made by P. Kallio. According to the P content (Table 2) the band contains approximately 70 % apatite. Bands like these are especially characteristic of the rocks of the

carbonate facies in the Pääkkö iron formation. In addition to apatite, they also contain quartz, sheet silicates, carbonates and carbonaceous, probably organogenic material. Some of them show faint pelletal features. The rocks of the sulphide facies (Nos. 12 and 13) seem to be a mixture of both clastic and nonclastic material. Samples Nos. 11, 14, 15 and 16 represent typical Marine Jatulian metasediments. Sample No. 17 is somewhat exceptional. Its iron content is so high that, according to the general definition by Gross (1965), the rock should be included in the iron formations. Its main constituents are amphiboles, biotite, garnet and clastic quartz. Moreover it contains accessory zircon and is relatively rich in Ti and poor in P (Table 2). Thus, it is a more or less clastic metasediment. Sample No. 18 is from a basic tuffitic metasediment. Meta-

TABLE 2

REE concentrations (ppm) and P, Fe_{tot}, FeHCl, S, Mn and Ti contents (Wt-%) in iron formations and associated Laboratory of the Technical Research Center of Finland. The other elements were analysed in the Ore Laboratory

No.	La	Ce	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Tm
1....	15.4	21.0	18.8	3.9	1.1	3.5	0.78	4.5	1.1*)	0.62
2....	17.5	13.0	26.0	4.4	1.3	n.d.	0.85	n.d.	1.2*)	n.d.
3....	18.9	12.2	26.3	3.8	1.2	n.d.	0.75	n.d.	0.9*)	n.d.
4....	17.1	15.5	18.6	3.3	1.2	n.d.	0.69	n.d.	1.0	n.d.
A	17.2	15.4	22.4	3.9	1.2	(3.5)	0.77	(4.5)	(1.1)	(0.62)
5....	13.0	22.5	12.5	3.2	1.2	3.5	0.64	3.4	9.97	0.62
6....	18.1	30.3	13.4	4.3	1.3	n.d.	0.80	n.d.	1.1*)	n.d.
7....	25.8	17.1	31.9	5.4	1.5	n.d.	1.0	n.d.	1.5	n.d.
8....	104	81.9	146	27.9	9.9	n.d.	5.3	n.d.	8.9	n.d.
9....	16.0	13.3	5.1	4.2	1.5	1.9	0.82	4.3	1.1*)	0.66
10....	18.4	15.2	13.5	3.4	0.83	n.d.	0.55	n.d.	<0.5	n.d.
11....	5.4	12.4	6.3	1.7	0.47	n.d.	0.30	n.d.	0.4*)	n.d.
12....	37.3	45.8	42.8	8.7	2.7	n.d.	1.7	n.d.	2.3*)	n.d.
13....	25.9	49.9	38.5	6.6	1.9	n.d.	1.2	n.d.	1.0	n.d.
B	31.6	47.9	40.7	7.7	2.3		1.5		(1.7)	
14....	21.3	40.9	28.4	7.1	1.3	n.d.	0.9	n.d.	1.5	n.d.
15....	20.0	41.9	23.1	4.7	0.99	n.d.	0.78	n.d.	0.97	n.d.
C	20.7	41.4	25.8	5.9	1.1		0.84		1.2	
16....	14.3	39.6	17.0	3.6	1.0	n.d.	0.81	n.d.	0.94	n.d.
17....	7.9	23.1	22.6	3.2	0.79	n.d.	0.55	n.d.	0.81	n.d.
18....	0.63	5.9	<1.0	2.4	0.75	n.d.	0.65	n.d.	1.1	n.d.
19....	1.4	1.9	1.3	0.71	0.40	n.d.	0.37	n.d.	0.51	n.d.
20....	3.4	6.4	3.9	0.72	0.45	n.d.	0.18	n.d.	0.24	n.d.

n.d. = not determined. *) estimated from the distribution pattern. y) analysed by Risto Saikkonen. Σ REE =

diabases of the early Karelidic magmatism are represented by sample No. 19.

For comparison one sample (No. 20) from the Prekarelidic iron formation of Kuhmo is included. The iron formations of Kuhmo are closely associated with basic volcanics (Hyppönen 1973) and thus belong to the Algoma type.

Results and discussion

The analytical data are given in Table 2. REE contents normalized to the composite of 40 North American shales (NAS), mostly Paleozoic in age, (Haskin *et al.* 1968, Table 2), are presented graphically in Figs. 4—9. For the normalization

of Dy the estimated value 5.0 ppm for NAS was used (Wildeman & Haskin 1973).

REE in iron formations proper: If the REE contents of the iron formations proper in Väyrylänkylä (Table 2) are compared with those available in the literature (Balashov & Goryainov 1966; Fryer 1971 a, b; Tugarinov *et al.* 1973; Wildeman & Haskin 1973) and with the Kuhmo iron formation (No. 20) the exceptional abundance in REE of the Väyrylänkylä deposits becomes evident: their total REE content is about four times greater than that in Sokoman and Krivoy Rog. In Väyrylänkylä the REE content seems to be more or less directly proportional to the P content of the rock (Fig. 10 and the ratio Σ REE/P $\times 10^{-3}$ in Table 2). This de-

rocks. Sample descriptions are given in TABLE 1. REE analyses were performed by Riitta Zilliacus in the Reactor of the Chemistry Department, Geological Survey of Finland

Yb	Lu	Eu/Sm	Σ REE	P %	$\frac{\Sigma \text{ REE}}{\text{Px}10^{-3}}$	Fe _{HCl} %	Fe _{tot} %	S %	Mn %	Ti %
2.3	0.30	0.28	64.68	1.16	56	22.1	31.9	0.78	0.06	0.06
1.7	0.30	0.30	66.25	1.45	46	23.9	34.4	0.82	0.02	0.02
2.7	0.30	0.32	67.05	0.83	81	21.2	28.6	1.46	0.03	0.02
1.4	0.25	0.36	59.04	1.44	41	16.3	24.0	0.68	0.08	0.07
2.0	0.29	0.31	64.26							
2.2	0.21	0.38	56.42	1.15	49	23.4	31.0	0.83	0.09	0.04
1.2	0.25	0.30	70.75	1.15	62	26.8	30.0	1.06	0.01	0.03
3.0	0.36	0.28	87.56	2.00	44	32.9	35.6	0.39	0.01	0.00
11.5	1.11	0.35	396.51	12.8y)	31	n.d.	n.d.	n.d.	n.d.	n.d.
2.7	0.29	0.36	45.01	1.44	31	26.6	28.0	1.03	0.02	0.02
0.99	0.20	0.24	<53.57	0.89	60	22.8	22.9	0.42	0.05	0.03
0.54	0.10	0.28	27.61	0.14	197	1.92	2.06	0.18	0.12	0.11
6.3	0.98	0.31	148.58	0.50	297	20.3	20.3	9.65	0.03	0.33
3.3	0.44	0.29	128.74	0.38	339	19.9	20.5	10.9	1.63	0.14
4.8	0.71	0.30	138.91							
2.4	0.47	0.18	104.27	0.14	745	7.17	8.13	4.57	0.06	0.43
2.0	0.32	0.21	94.76	0.11	861	7.24	7.28	0.27	0.02	0.69
2.2	0.40	0.19	99.54							
1.4	0.23	0.28	78.88	0.18	438	10.1	10.5	0.21	0.12	0.68
1.5	0.26	0.25	60.71	0.16	379	12.6	21.8	0.20	0.04	0.54
2.5	0.33	0.31	<15.26	0.09	170	7.98	9.99	0.12	0.14	0.72
1.1	0.21	0.56	7.90	0.10	123	5.00	8.02	0.32	0.15	0.30
0.57	0.13	0.63	15.99	0.09	178	21.9	25.5	0.57	0.25	0.02

Σ (La, Ce, Nd, Sm, Eu, Tb, Ho, Yb, Lu). A) Average of 1—4. B) Average of 12—13. C) Average of 14—15.

pendence is especially marked when the apatite-rich band (No. 8) is compared with the other iron-formation samples (Nos. 1—7, 9, and 10).

Ce is depleted in the REE distribution patterns (Figs. 4 a, 5 a, 7, and 9 a). The REE content and distribution pattern of the apatite-rich band in Pääkkö is of the same type as those in the apatites from Florida, in the pelletal phosphorites from Queensland and in the metalliferous sediments from the Pacific Ocean (Fig. 9). The marked depletion of Ce and the relatively low average total REE content in the apatites from the Bone Valley Formation of Florida, the Phosphoria Formation and the Moroccan deposits, are ascribed to the fact that they were formed in a marine environment (Altschuler *et al.* 1967;

Fleischer & Altschuler 1969). The pelletal phosphorites of Queensland are considered to have been formed under shallow marine conditions (Cook 1972). The REE patterns of the sediments from the Pacific Ocean imply either that the REE were coprecipitated from sea water with iron-manganese hydroxyoxides, or that they are incorporated in the phosphatic fish debris found in all samples (Dymond *et al.* 1973; *cf.* also Bender *et al.* 1971). Thus, the apatite-rich band in Pääkkö seems to be a marine phosphorite interband. Consequently, the apatite in the Väyrynkylä iron formations is of marine origin. The Ce-depleted REE patterns of the oxide, silicate and carbonate facies are due to the REE incorporated in this apatite.

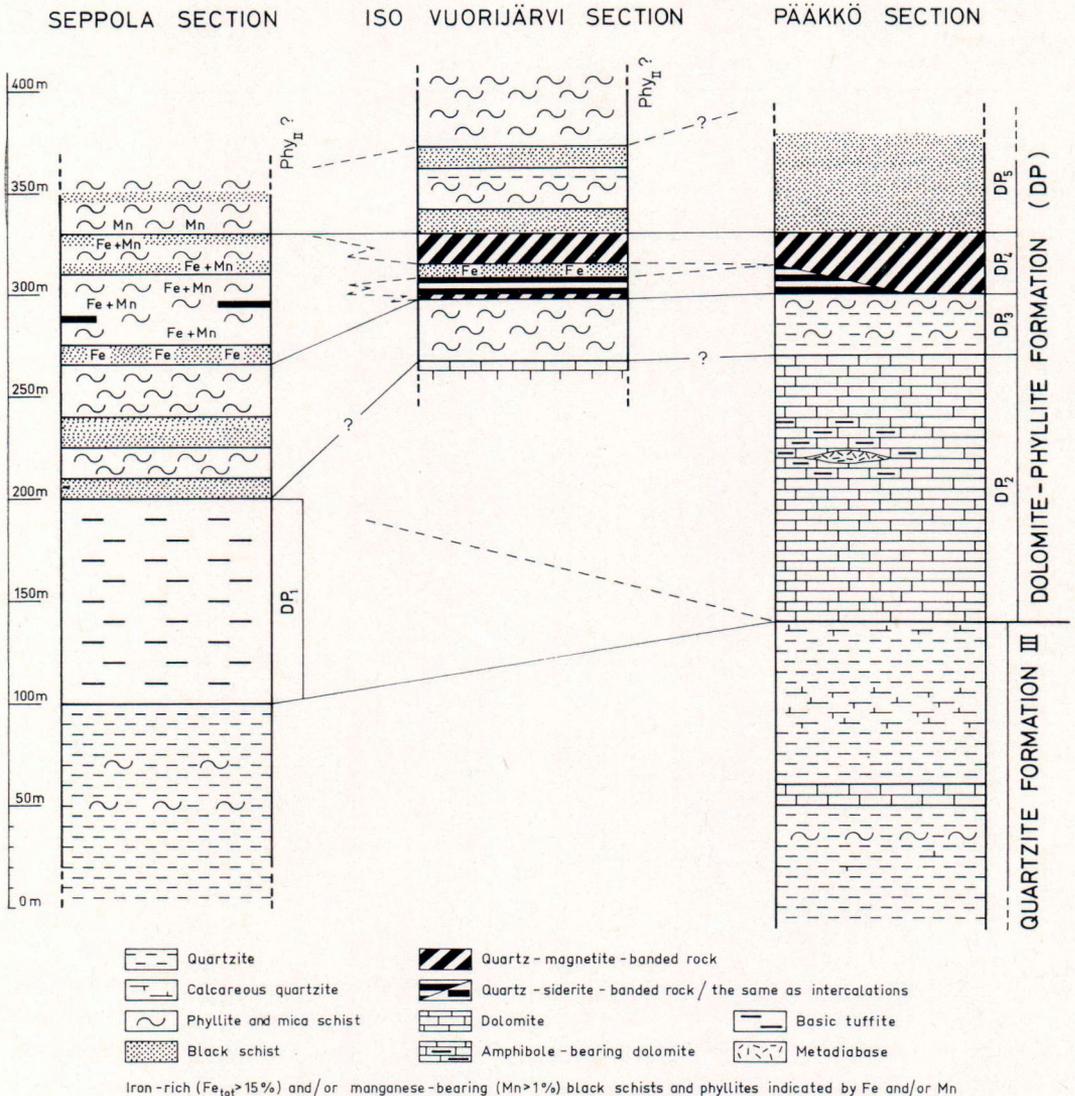


Fig. 3. Stratigraphic columns from the different sections in the Salmijärvi basin.

In general the REE contents and distribution patterns of the oxide, silicate and carbonate facies are similar (Fig. 7). They all show clear trend towards relative depletion of the lighter REE and Yb and Lu in comparison with the NAS. The REE contents and distributions in the quartz-magnetite-banded rocks from Pääkkö, Iso Vuorijärvi and Körölä are almost identical (Fig.

4 a), which indicates a structural-stratigraphic interpretation in the light of which these deposits belong to the same metasedimentary horizon.

The effects of surface weathering on the REE distribution pattern can be seen in sample No. 6 (Fig. 4 b). The rock seems to be more enriched in Ce and more depleted in Nd than do the

fresh rocks. Thus, Ce is only slightly depleted in this sample. These observations indicate that samples Nos. 5 and 9 and probably No. 1, too, are all somewhat affected by weathering. In Sokoman Fryer (1971 b) detected that »altered» oxide facies rocks show relative enrichment in heavy REE. However, the REE distribution pattern of the weathered silicate-facies rock (Fig. 7, No. 7) is normal. This rock does not contain

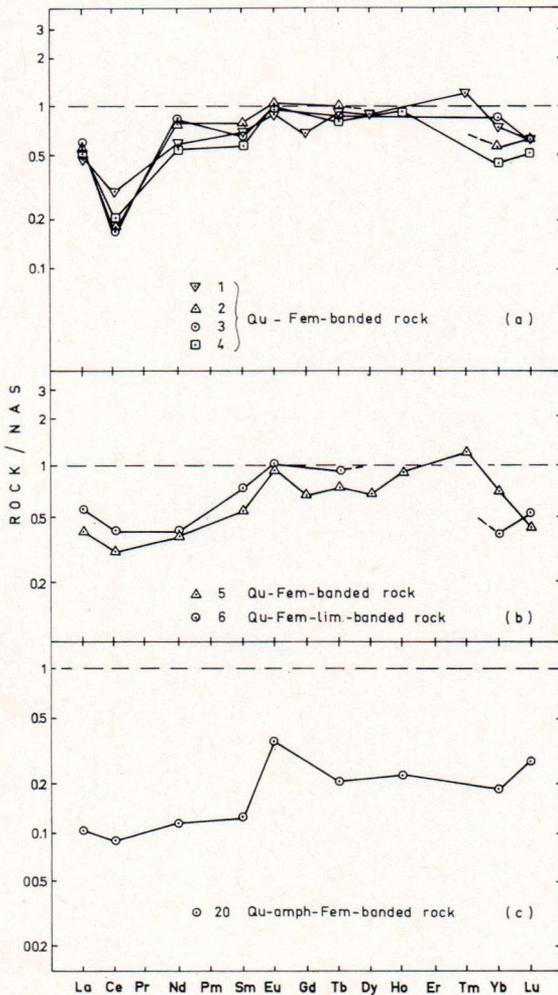


Fig. 4. NAS-normalized REE distribution patterns for (a) oxide facies and (b) altered oxide facies of the Väyrynkylä iron formations and for (c) iron formation of Kuhmo. Mineral abbreviations used in Figs. 4–11 are as follows: qu = quartz, Fem = magnetite, si = siderite, lim = limonite, amph = amphibole, bi = biotite.

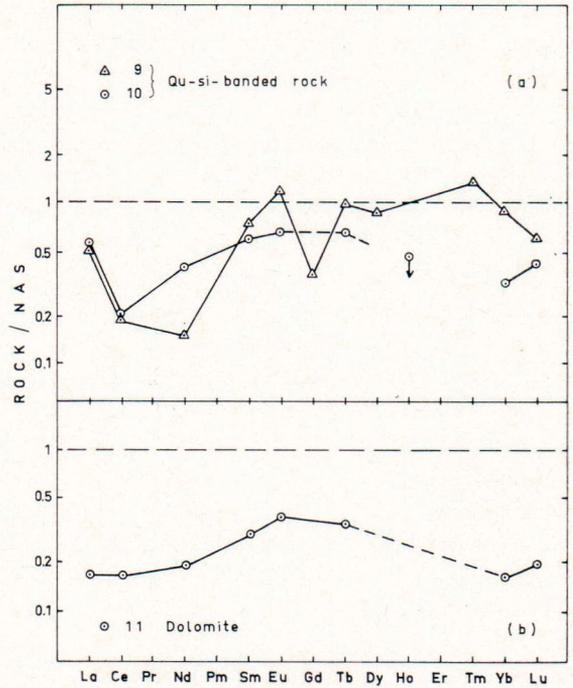


Fig. 5. NAS-normalized REE distribution patterns for (a) carbonate facies of the Pääkkö and Iso Vuorijärvi iron formations and for (b) Salmijärvi dolomite.

limonite, and hence, the effects described are probably due to the formation of limonite.

REE in sulphide-facies rocks: The REE content and distribution pattern of the sulphide facies deviates from those of other iron-formation facies in that its Ce depletion is less pronounced and it is richer in REE (Fig. 7). In this respect the sulphide-facies rocks resemble normal clastic metasediments, black schist and phyllites (Fig. 6). They evidently contain REE incorporated both in marine apatite, the amount of which is markedly lower than that in the iron formations proper as indicated by P contents (Table 2), and in clastic material (Fig. 10). The composite nature of this iron-formation facies is thus also apparent in the REE. There does not seem to be any marked difference between the REE in the manganeseiferous (No. 13) and the ordinary iron-rich black schist (No. 12). The more obvious

depletion of Ce in the latter rock is to be ascribed to the higher P (apatite) content (Table 2).

REE in associated rocks: Marine Jatulian pelitic metasediments (Nos. 14–16) have lower total REE contents and show a clear trend towards depletion of the lighter REE and Yb and Lu compared with the NAS (Fig. 6). The average REE distribution of the black schist and phyllite (Table 2, B) is, however, very close to that of the clays and shales of the geosynclines (Ronov *et al.* 1974; Table 6) and shows only a slight depletion of La and Ce. Their REE distributions also exhibit similarities with schists from southern Lapland (Sahama 1945), and with the Karelian black schist from Outokumpu (Wildeman & Haskin 1973, Table 2). With the exception of Ce, the iron formations and Marine Jatulian pelitic metasediments have similar REE distribution patterns. This is especially obvious between the quartz-magnetite-banded rock and the amphibole-bearing phyllite (Table 2, A and No. 16).

The Salmijärvi dolomite (No. 11) has an REE pattern close to the average of the carbonates in the geosynclines (Ronov *et al.* 1974; Table 6). Compared with the quartz-siderite-banded rock (Table 2, No. 10) it is depleted in La by a factor of 0.29, in Ce by a factor of 0.82, and in Nd, Sm, Eu, Tb, Yb, Lu by a factor of 0.47–0.57. For comparison between the dolomite and pelitic metasediments (Table 2, B), the depletion factor is 0.24–0.36 for La, Ce, Nd, Sm, Tb, Yb and Lu. For Eu, however, it is markedly greater, being 0.43. Thus, the REE distribution pattern in the dolomite is closer to that in pelitic rocks than that in the carbonate-facies rock of the iron formations. This suggests that the REE are mainly incorporated in the clastic material of the dolomite (*cf.* Fryer 1971 b, p. 102).

The REE content and distribution in the Liejeenjoki metadiabase (No. 19) resemble those detected by Sahama (1945) in the gabbros and metadiabases in southern Lapland. Both the Liejeenjoki metadiabase and Seppola tuffite (No. 18) show a clear relative depletion of lighter REE (Fig. 8). The amphibole-biotite-garnet rock

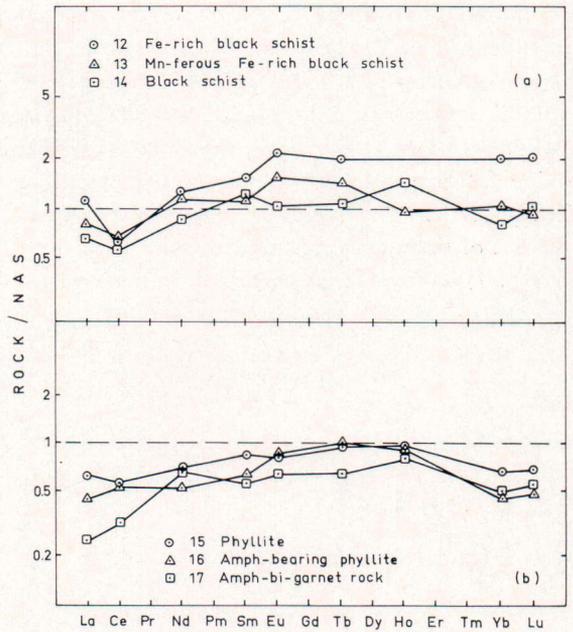


Fig. 6. NAS-normalized REE distribution patterns for (a) black schists and (b) phyllites and amphibole-biotite-garnet rock of the Salmijärvi basin.

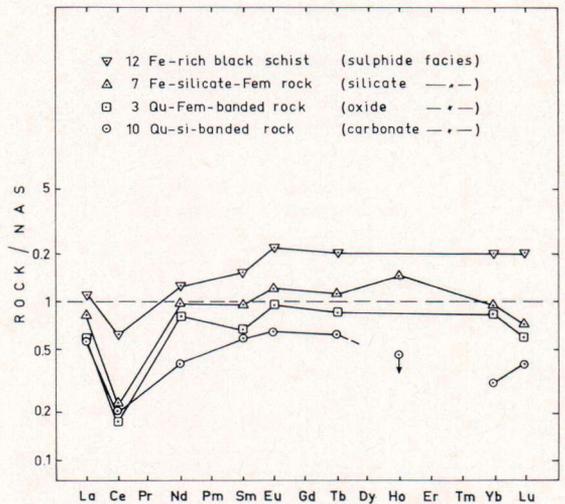


Fig. 7. NAS-normalized REE distribution patterns for the different facies of the Iso Vuorijärvi iron formation.

(No. 17) is more depleted in lighter REE than the pelitic rocks (Fig. 6). This may indicate that it contains relatively more tuffaceous material or material derived from basic rocks. On the other

TABLE 3

Eu: Sm ratio in Precambrian iron formations and in metalliferous Pacific sediments

Occurrence	Type	Age (Ma)	Eu: Sm			
			Analyses	Average	Range	References
Michipicoten	Algoma	2 750—2 700 ¹⁾	2	0.91	1.11—0.71	Fryer 1971 a
Timagami	»	> 2 450 ²⁾	2	0.70	0.51—0.89	» »
Kuhmo	»	> 2 740 ³⁾	1	0.63		This study
Mary River	»	Archean? ⁴⁾	6	0.57	0.36—0.82	Fryer 1971 a
Wyoming	Algoma?	> 2 687 ⁵⁾	1	0.44		Wildeman & Haskin 1973
Olenogorsk	Algoma	> 2 700 ⁶⁾	1	0.40		Balashov & Goryainov 1966
Biwabik	Superior	2 200—1 900 ⁷⁾	1	0.43		Wildeman & Haskin 1973
Sokoman (oxide facies)	»	1 870 ⁸⁾	8	0.34	0.23—0.42	Fryer 1971 b
Sokoman (carbonate facies) ..	»	1 870 ⁸⁾	6	0.33	0.20—0.55	» »
Krivoy Rog	»	2 000—1 800 ⁹⁾	11	0.33	0.25—0.45	Tugarinov <i>et al.</i> 1973
Väyrylänkylä	»	2 080 ¹⁰⁾	11	0.31	0.28—0.38	This study
Pacific Ocean		60— 30 ¹¹⁾	6	0.30	0.28—0.36	Dymond <i>et al.</i> 1973

¹⁾ Goldich 1973. ²⁾ Fryer 1971 a. ³⁾ Geological Survey of Finland 1973, p. 16. ⁴⁾ Fryer 1971 a. ⁵⁾ Naylor *et al.* 1970. ⁶⁾ Lazarev, oral report 1974. ⁷⁾ Goldich 1973. ⁸⁾ Fryer 1972. ⁹⁾ Semenenko 1973. ¹⁰⁾ Sakko & Laajoki 1975. ¹¹⁾ Dymond *et al.* 1973.

hand its high iron content (Table 2) and close association with the Pääkkö iron formation suggest that it was more probably originated from the iron-formation material through reworking, during which process the phosphatic material and to it bounded REE were leached out.

General discussion: Quartz-amphibole-magnetite-banded rock from the Archean iron formation of Kuhmo (No. 20) is low in total REE and shows a much greater positive Eu-anomaly than do the Superior-type iron formations in Väyrylänkylä (Fig. 4). Moreover it is relatively more enriched in heavy REE, especially Yb and Lu. In Table 3 the Eu: Sm ratios in iron formations of different ages are compared. The older rocks seem to be relatively more enriched in Eu. The relative growth in Eu content and the increase in the amount of heavy lanthanides

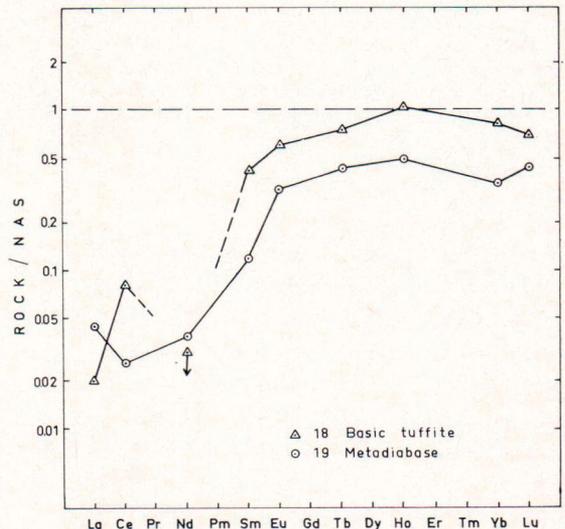


Fig. 8. NAS-normalized REE distribution patterns for Seppola tuffite and Liejeenjoki metadiabase.

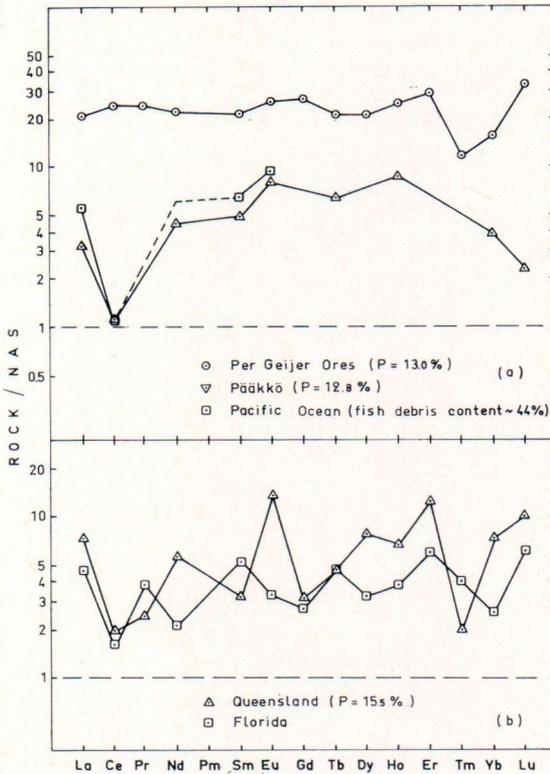


Fig. 9. NAS-normalized REE distribution patterns for (a) the average of the apatite concentrates of Per Geijer ores (Kiruna) (Parák 1973 a, Table 1, Nos. 6—16), apatite-rich band in the Pääkkö iron formation (sample No. 8 in this study), and the average of three metalliferous sediments rich in fish debris from the Pacific Ocean (Dymond *et al.* 1973, Table 2, Nos. 38-5-3, 39-2-3, 39-2-6), and for (b) the average of three pelletal phosphorites from Queensland (Cook 1972, Table 4, No. 11), and the average of three apatite concentrates from Florida (Altschuler *et al.* 1967, Table 1.)

through geological time have been discussed by several authors (Balashov & Goryainov 1966; Fryer 1971 a, b; Wildeman & Haskin 1973; Ronov *et al.* 1974). The observations by Fryer (1974, written personal communication), which have not revealed any positive Eu anomaly in iron formations younger than 2 000 Ma, further confirm the secular changes in Eu in iron formations. The similarity in the Eu: Sm ratio between the iron formations in Krivoy Rog, Sokoman and in Puolanka is striking. However, Piper

(1974) and Cullers *et al.* (1974) have shown that REE distribution patterns can be strongly dependent on depositional environments, as is indicated by the positive correlation between Algoma-type iron formations and the high Eu: Sm ratio in Table 3. In spite of their great age difference (c. 2 000 Ma) both the Värylänkylä iron formations and the Pacific metalliferous sediments have almost identical Eu: Sm ratios (Table 3). More REE data are needed before any definitive conclusion can be drawn about the time dependence of the Eu: Sm ratio in iron formations.

REE in different types of phosphorus-bearing iron-rich rocks are compared in Fig. 9 a¹). The relatively low REE contents and the Ce depletion in the Pääkkö iron formation and in the metalliferous sediments from the Pacific Ocean indicate similar depositional environments (marine). The totally different REE pattern for the Per Geijer ores suggests a different (nonmarine?) origin for

¹) It should be born in mind that the samples compared in this figure are of different types: some are apatite concentrates, some sediments and one is a metasedimentary interband (see discussion in Altschuler *et al.* 1967, p. B3).

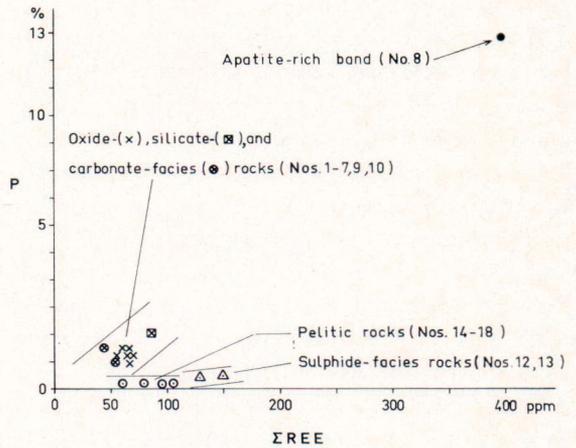


Fig. 10. Phosphorus concentration versus Σ REE in oxide-, carbonate-, and sulphide-facies rocks and apatite-rich band in Värylänkylä iron formations and in associated pelitic rocks.

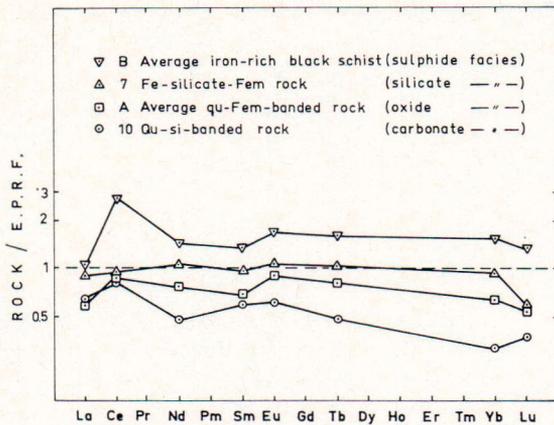


Fig. 11. REE distribution patterns for the oxide-, silicate-, carbonate-, and sulphide-facies rocks from the Väyrylänkylä iron formations normalized to the average flank sediments from the East Pacific Rise (E.P.R.F.) (Piper & Graef 1974).

the apatite in Kiruna-type ores (*cf.* concepts in Parák 1973 b; Frietsch 1973, 1974; Geijer & Ödman 1974).

After this manuscript was compiled a comprehensive paper concerning REE in sediments from the East Pacific Rise has been published (Piper & Graef 1974). Here too, a seawater source for REE seems unequivocal. The REE distribution and content in the flank sediments from this Rise are very similar to those in the oxide-facies rocks and, in particular, to those in the silicate-facies rock of the Väyrylänkylä iron formations (Fig. 11). In this comparison the composite nature of the sulphide-facies rocks is revealed by a positive Ce anomaly. The slight relative enrichment of the lighter REE of the carbonate-facies rock may indicate that this rock contains somewhat more clastic material than do other rocks of the iron formations proper. Thus, in the Väyrylänkylä iron formations the REE distribution in phosphorus-rich rock (apatite-rich band, Fig. 9 a) is close to those in the Pacific sediments relatively rich in fish debris (Dymond *et al.* 1973), whereas the REE distributions in the rocks relatively poor in phosphorus (oxide-, silicate-, and carbonate-facies rocks, Fig. 11)

are similar to those in the Pacific sediments poor in fish debris (Piper & Graef 1974).

Conclusions

1) The comparatively high REE content and depletion of Ce in the Precambrian iron formations in Väyrylänkylä are due to the presence of marine apatite.

2) The similar REE contents and distributions in the prevailing quartz-magnetite-banded rocks from the Pääkkö, Iso Vuorijärvi, and Körölä iron formations reinforce the opinion that they represent the same stratigraphic horizon.

3) The sulphide-facies rocks contain REE incorporated in both marine apatite and clastic material.

4) With the exception of Ce, the REE distribution patterns in both iron-formation rocks and pelitic metasediments are relatively similar.

5) The REE distribution pattern in dolomite is closer to that in pelitic rocks than that in carbonate-facies rocks of iron formations, which suggests that the REE are incorporated mainly in the clastic material of the dolomite.

6) The Eu: Sm ratio in the Precambrian iron formations seems to be time-bound, but more REE data from geologically well-known deposits are needed before any definitive conclusions can be drawn in this respect.

7) The REE content and distribution of apatite in different kinds of iron-rich rocks elucidates the genesis of these deposits.

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