CASE STUDY OF A MANGANESE AND IRON PRECIPITATE IN A GROUND-WATER DISCHARGE IN SOMERO, SOUTHWESTERN FINLAND

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A study was made of the mineral and chemical composition of a concentric precipitate formed around a ground-water discharge, where manganese had precipitated before iron. Birnessite was identified in the Mn-rich precipitate and goethite and lepidocrocite in the Fe-rich precipitate. Lepidocrocite is typically crystallized in hydromorphic soils where Fe is reduced. Ti and Cr are enriched more in the Fe-rich than in the Mn-rich precipitate, while the reverse is true for Ni and Cu. The K/Rb ratio is higher (790—3000) than in common rock types (160—300). This indicates the incorporation of K into the minerals formed, whereas Rb is withheld in the precipitate by adsorption. The total content of REE is increased in the precipitate studied but is lower than in oceanic Mn nodules. The La/Yb ratio is higher than usual in continental rock types, which indicates slower migration of the light REE (La — Sm) than of the heavy (Gd — Lu). Compared with the other REE, Ce is enriched in many continental oxidates, though not in the young oxidates studied here. Probably because Ce is oxidized to valence 4 +, it is chemically and through adsorption bound more strongly to precipitates than the other REE with valence 3 + and enriched upon partial dissolution. This suggests that the trace element composition of Mn and Fe precipitates largely comes about through the partial dissolution of the original precipitate.

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Introduction

This paper is a part of a comprehensive investigation designed to elucidate the exogenic geochemical cycle of manganese and iron in northern Europe. A concentric Mn, Fe precipitate formed around a ground-water discharge as cement in glaciofluvial sand is described and its mineral and chemical composition is presented and discussed. A study of the iron minerals and the trace element and especially the rare earth element (REE)

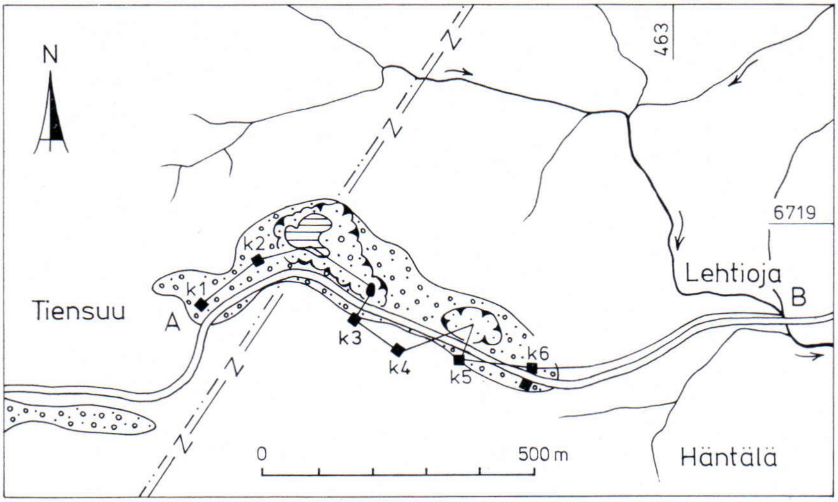

Fig. 1. Location of the gravel pit with Mn, Fe precipitate. Symbols as in Fig. 2.

contents is Fennoscandian oxidate sediments is presently underway.

The principles of precipitation of manganese and iron in Fennoscandia are discussed by Carlson *et al.* (in press), and case histories of precipitation in glaciofluvial material are presented by Låg (1960), Vasari *et al.* (1972), Alhonen *et al.* (1975), and Koljonen *et al.* (1976). The last paper also lists the most common morphological types of precipitates.

Description of the surroundings

The studied manganese and iron precipitate lies at the bottom of a gravel pit in Häntälä esker, 12 km S.W. of Somero, S.W. Finland (Fig. 1). The area is characterized by a flat clay terrain interrupted by partly till-covered rocky hills and 20—35 m-deep erosional creek and river valleys (*e.g.,* Lehtioja Creek, Figs. 1 and 2). The esker is typically longitudinal and in many places broken or covered by clay deposits.

Häntälä esker is composed of glaciofluvial sand and gravel, the deeper parts usually being coarser than the mantle and skirts. Although the esker chain is often covered with clay, in some places there is hydraulic continuity for several kilometers, with the ground water flowing in the east-northeast direction of the esker towards the valley of Lehtioja Creek. Its position as levelled via dug wells and some ground-water outcrops is presented in the longitudinal profile C — D (Fig. 2).

The studied Mn, Fe precipitate is formed in a place where the ground-water table is some twenty or thirty centimeters below the surface of the gravel pit and where it abruptly descends, forming an underground »waterfall» (Fig. 2, Profile C — D). The peculiar, more or less circular form of the precipitate (Fig. 3) is a result of piping caused by discharging ground water at the bottom of the gravel pit. The same kind of continuous piping without precipitation often occurs in sand and fine sand at the bottom of natural springs. The circles diminish in size downwards to give a funnel-like structure.

The material is somewhat finer inside the funnel than outside (see Fig. 3). Inside it is sorted concentric, the material of finest grain

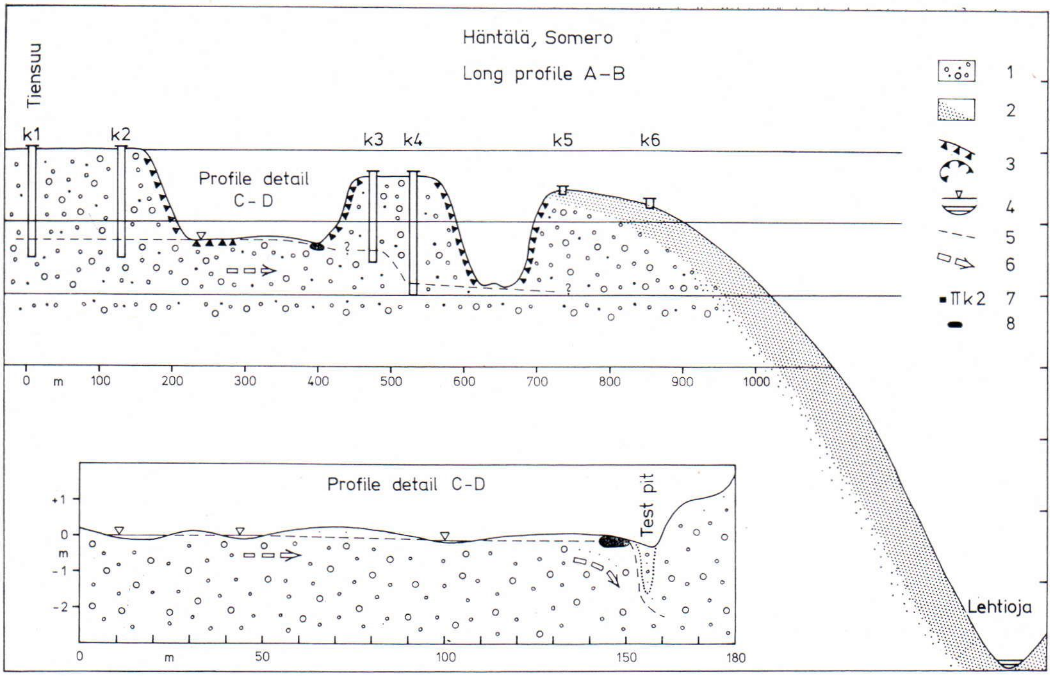

Fig. 2. Long profile through the Häntälä esker and a profile detail through the gravel pit with Mn, Fe precipitate (*cf.*, Fig. 1). (1) Gravel and sand; (2) Silt and clay; (3) Slope; (4) Recently outcropping ground-water table; (5) Ground-water table; (6) Direction of ground-water flow; (7) Dug well (levelled ground-water table); (8) Mn, Fe precipitate.

Fig. 3. The circular Mn, Fe precipitate (horizontal section). The diameter of the smaller circle is 14 cm.

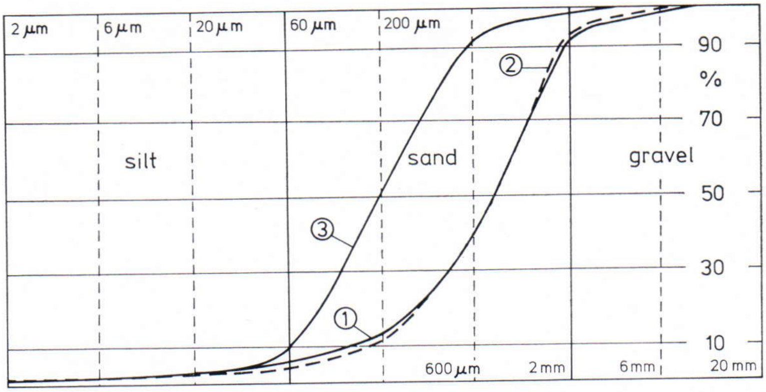

Fig. 4. Grain-size distribution of esker material. (1) Sand with Mn-rich precipitate (2 samples); (2) Sand with Fe-rich precipitate (broken line, 3 samples); (3) Sand without precipitate (2 samples).

size being sometimes in the centre and sometimes in the outer parts in the form of distinct haloes. Differences in the texture of esker material favor the selective precipitation of Mn and Fe, Mn usually being precipitated in more coarse-grained material than Fe (Koljonen *et al.* 1976). In the precipitate studied, however, there is no distinct difference in texture between material with Mn and material with Fe precipitate (Fig. 4, curves 1 and 2). Material without any cement is finer (curve 3).

The precipitate has been formed in a recently opened gravel pit, and cannot be more than about 10—15 years old.

Samples for analysis of the precipitate were collected from the innermost part of the Mn-rich cement, just outside the funnel (Table 3, No. 1), and from differently colored parts of the Fe-rich cement 1 m (No. 2) and 2 m (No. 3) from sample No. 1. Water samples were collected from the bottom of the gravel pit (No. 4).

Ground water in the Häntälä esker close to the precipitate is slightly acidic to neutral (arithmetic mean of pH values 6.9, 5 analyses) and contains small amounts of dissolved electrolytes (specific conductivity 61 μS/cm, 5 analyses, and total hardness 1.9° dH, 4 analyses). The Mn and Fe content varies considerably (Table 3, No. 4) and is especially low where the ground-water table outcrops. The Mn/Fe ratio varies between 0.007 and 0.03 (5 analyses).

Methods

The precipitates were concentrated and minerals in unheated and heated samples identified by the X-ray diffraction method as described in Koljonen *et al.* (1976). A Philips diffractometer operating with FeK_α radiation was used. The recrystallization at elevated temperatures was further studied by analysing the samples both thermally (DTA) and thermogravimetrically (TG) with a Rigaku Denki high temperature apparatus. The heating rate was 5°C/min.

The color of the precipitates was measured by comparison of the air-dried concentrated samples with Munsell Soil Color Charts (1975).

For chemical analysis the concentrated precipitates were dissolved in HNO_3 and H_2O_2. Mn was determined colorimetrically, Fe by titration with K_2CrO_7, and Al, Mg, Ca, K, Na, Ti, Sn, Pb, Cr, Ni, Co, Zn, Cu, Cd, Rb, and Li by AAS (Perkin Elmer 404).

Table 1. Some data for the analysis of REE.

Irradiation time	Decay time	Detector	Measurement time	Elements determined
5 min	0.5 h—4 h	small	10 min—20 min	Dy
7 h—30 h	4 d—7 d	large	0.5 h—2 h	La, Sm, Lu
7 h—30 h	ca. 6 weeks	small	2 h—4 h	Ce, Nd, Eu, Gd, Tb, Yb

The method of instrumental neutron activation analysis of ten REE is briefly as follows (see Rosenberg 1977): Standards are prepared by dissolution of oxides in HNO_3, and in the case of CeO_2, in a mixture of HNO_3 and H_2O_2. The stock solutions are then mixed to give a composite standard comprising all the REE studied, in concentrations approximately the same as in basalt.

Homogenized and pulverized samples (100 mg — 300 mg) and standards are weighed in 0.5 ml polyethylene capsules for the analysis of Dy and in 70 mm x Ø 6 mm quartz ampoules for the determination of the other REE. The samples, together with the standards, are irradiated, left to decay, and their γ-spectra measured (see Table 1). The irradiation of 5 min is performed in a thermal neutron flux of 1.2×10^{12} $cm^{-2}s^{-1}$ and the irradiation of 7 h — 30 h in a thermal neutron flux of 10^{13} $cm^{-2}s^{-1}$. The γ-spectra are measured with a γ-spectrometer equipped with one of two detectors, a sample changer, and a Nuclear Data 4410 pulse height analyser. The detectors are a small Ortec 5 mm x Ø 10 mm Ge(Li)-detector with a resolution of 550 eV FWHM at 122 keV and a large Ortec Ge(Li)-detector with a relative efficiency of 10 % and a resolution of 2 keV FWHM at 1332 keV. The measured spectra are punched on paper tape and analysed with a computer program written for a UNIVAC 1108 computer. The program calculates the elemental concentrations in the samples.

The isotopes and the corresponding γ-energies used for the calculation are shown in Table 2. In some cases interfering activ-

Table 2. Half-lives of the isotopes, γ-rays used, interfering activities, and detection limits of the elements determined.

Isotope	Half-life	γ-energy (keV)	Subtracted interference	Detection limit (ppm)
^{140}La	40.27 h	1595.4		0.5
^{141}Ce	32.5 d	145.4		2
^{147}Nd	11.1 d	91.4		5
^{153}Sm	47.1 h	103.2		0.06
^{152}Eu	12.2 a	121.8		0.05
^{153}Gd	236 d	103.2	^{233}Pa 103.8 keV	4
^{160}Tb	73 d	86.8	^{233}Pa 87 keV	0.05
^{165}Dy	2.36 h	94.6		0.3
^{169}Yb	30.6 d	63.1		0.07
^{208}Lu	6.75 d	208.4		0.2

ities had to be subtracted. The detection limits indicated in Table 2 are valid for basaltic rock type and as an order of magnitude for the other common rock types. Because the sensitivity of the method depends on the concentrations of certain other elements in the sample, the detection limits for different samples vary considerably. Thus the detection limit for Dy is inversely proportional to the concentration of Mn and the detection limits of Tb and Gd correspondingly to the concentration of Th producing the interfering isotope ^{233}Pa. The average precision of single determinations is 13 %. Because of the lack of significant systematic errors the accuracy is of the same magnitude.

Mineral composition

Manganese precipitate. Birnessite is the only Mn-mineral identified in the Mn precipitate by X-ray diffraction (Fig. 5; for chemical composition see Table 3, No. 1). It is a non-stoichiometric manganese oxyhydroxide which may contain various amounts of other cations, *e.g.*, Mg, Ca, K, and Na depending among other things on the cations present upon crystallization. Mn-precipitates deposited by natural waters contain considerable amounts of Fe (Table 3; Koljonen *et al.* 1976, Table 2; Carlson *et al.*, in press, Table 3). Because no iron oxyhydroxide mineral is shown in the X-ray graph (Fig. 5; Koljonen *et al.* 1976) it can be assumed that Fe is present in the form of ferrihydrite, i.e. »amorphous» FeOOH, as proposed by Giovanoli and Bürki (1975) in the context of oceanic Mn nodules.

Birnessite is a group name for synthetic and natural minerals, fine-grained and often disordered, with an O/Mn ratio from 1.74 to 1.99 (Bricker 1965). It is common both in continental Mn-precipitates (Taylor *et al.* 1964, Taylor and McKenzie 1966, Taylor 1968, Koljonen *et al.* 1976) and in oceanic Mn

Table 3. Chemical composition of the Mn, Fe precipitate and of ground and surface water in the studied area (1) Loose black cement (color 5YR 3/1); (2) Loose brown cement (7.5YR 4/6); (3) Loose brown cement (7.5YR 5/8); (4) Water on the bottom of the gravel pit; mostly 5 samples. Analyst (1—3) Antti Vuorinen, University of Helsinki and (4) Hilkka Ahola, Hannele Spetz, and Maija Ilmasti, Geological Survey of Finland.

	1	2	3	4
Mn	50.38 %	0.98 %	0.32 %	0.005—0.15 ppm
Fe	3.50	51.92	38.33	0.7 —5.0
Al	1.12	2.38	7.09	0.6 —1.0
Mg	1.36	0.48	5.67	2.9 —3.9
Ca	2.15	0.23	1.19	5.0 —9.8
K	1.70	2.61	2.09	1.3 —2.0
Na	0.07	0.11	0.23	2.5 —5.8
Ti	0.12	0.14	0.93	—
Sn	750 ppm	< 640 ppm	690 ppm	—
Pb	120	200	170	< 1 ppb
Cr	30	180	280	< 1
Ni	1140	184	120	< 2
Co	144	190	130	< 2
Zn	330	328	464	3—14
Cu	410	126	127	2
Cd	17.7	11.0	12.7	< 0.5
Rb	21.5	8.7	17.0	—
Li	108	12	120	—
K/Rb	790	3000	1230	—

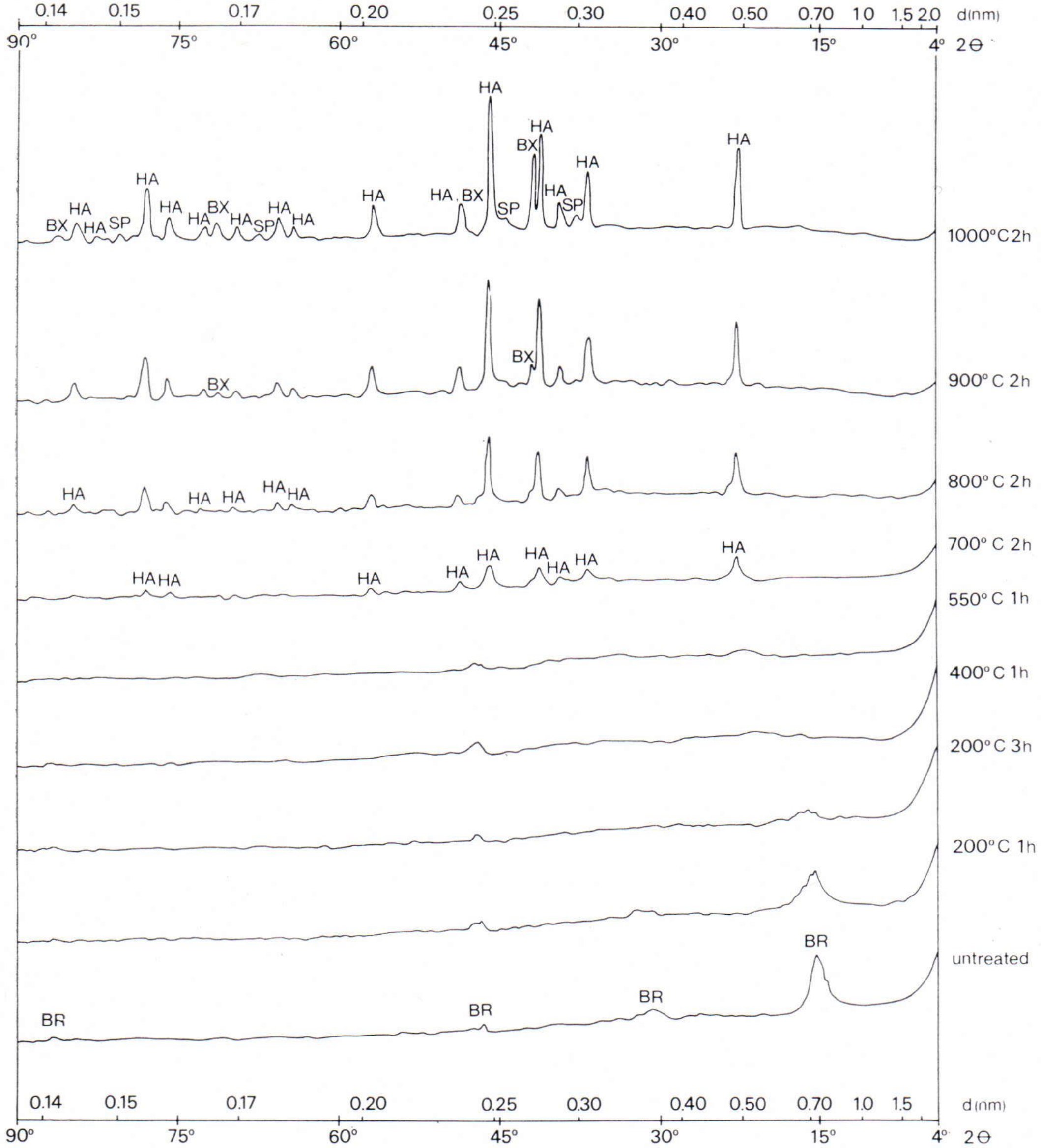

Fig. 5. X-ray data of unheated and heated Mn precipitate (Table 3, No. 1). BR, birnessite; HA, hausmannite; BX, bixbyite; SP, spinel. The graph is explained in the text.

nodules (*e.g.,* Crerar and Barnes 1974, Summerhayes and Willis 1975, Glover 1977). The crystallization of birnessite is controlled by the redox conditions of the environment. It is known to be crystallized in slightly alkaline (Taylor *et al.* 1964) to slightly acidic soils (Koljonen *et al.* 1976, Ross *et al.* 1976); in the present case the ground water that deposits Mn is almost neutral. In oceanic Mn nodules birnessite is crystallized in more oxidizing conditions than »todorokite» (Crerar and Barnes 1974, Summerhayes and Willis

1975) which according to Giovanoli and Bürki (1975) is a mixture of buserite and minor amounts of birnessite and manganite.

The typically very fine-grained birnessite is supposed to crystallize instead of the thermodynamically stable pyrolusite (β-MnO_2) because of its lower nucleation energy (Crerar and Barnes 1974). Besides kinetics, also the foreign cations present in natural waters favor its crystallization (Koljonen *et al.* 1976).

Information about the structure of birnessite (synthetic: sodium manganese(II,III) manganate(IV) and manganese(III) manganate(IV)) has been derived from electron diffraction measurements because efforts to prepare large enough crystals for single crystal X-ray methods were not successful (Giovanoli *et al.* 1970a, b; Giovanoli and Stähli 1970). The structure comprises layers of edge-shared [MnO_6] octahedra with sheets of water molecules and hydroxyl groups located between. One out of every six octahedral sites of Mn^{4+} is unoccupied, and Mn^{3+} and Mn^{2+} ions are considered to lie above and below these vacancies. The layers of [MnO_6] octahedra are separated by about 0.72 nm along the c-axis. The positon of other cations in the intermediate layer is uncertain. The crystal structure is basically hexagonal, but other cations, *e.g.* Na^+, as lattice constituents, cause a distortion to at least orthorhombic structure (Giovanoli and Stähli 1970). Natural birnessite, whose alkali ions cannot be dissolved, gives the hexagonal X-ray pattern (Giovanoli *et al.* 1970b) because of the disordered crystal structure. The hexagonal indices of the four lines typical of natural birnessite (Jones and Milne 1956, Brown *et al.* 1971) are: 0.728 nm — 001, 0.363 nm — 002, 0.245 nm — 100, and 0.1414 nm — 110 (*cf.*, Koljonen *et al.* 1976, Table 5).

Upon heat treatment the Mn precipitate is dehydrated corresponding to the broad endothermic reaction between 80°C and 250°C recorded by DTA. As the water molecules and hydroxyl groups are expelled from between the octahedral layers of birnessite the latter are gradually cleaved to form a two-dimensional lattice. On the X-ray graph the basal reflections (0.728 nm and 0.363 nm)

Table 4. REE contents in Mn and Fe precipitates. The numbers 1—3 indicate samples in Table 3; (5) Average REE contents in 13 Mn and Fe precipitates from Fennoscandia; (6) Average REE contents in 31 oceanic Mn nodules (Piper 1974); (7) REE content in Leedey L/6 chrondrite (Masuda *et al.* 1973). The values in parentheses are estimates.

No.	1	2	3	5	6	7
La	123	123	79	71	226	0.378
Ce	138	240	185	221	722	0.976
Pr	—	—	—	—	—	(0.138)
Nd	64	81	59	49	221	0.716
Sm	12	14	9.4	8.5	44	0.230
Eu	2.3	2.7	2.4	1.6	9.6	0.0866
Gd	5.7	13	—	6.6	—	0.311
Tb	1.4	1.6	1.3	1.0	7.5	(0.0568)
Dy	—	3.6	5.5	—	—	0.390
Ho	—	—	—	—	—	(0.0868)
Er	—	—	—	—	—	0.255
Tm	—	—	—	—	—	(0.0399)
Yd	3.2	3.0	3.5		20.2	0.249
Lu	0.73	0.95	0.55	0.44	3.5	0.0387
ΣREE	389	506	376	387	1445	3.95
La/Yb	38	41	23	32	11	1.5

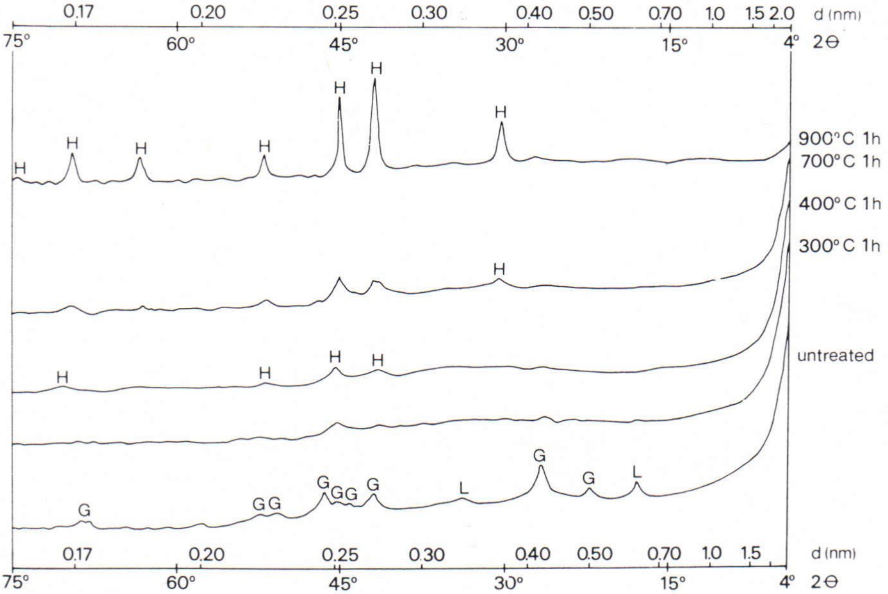

Fig. 6. X-ray data of unheated and heated Fe precipitate (Table 3, No. 2). G, goethite; L, lepidocrocite; H, hematite. The graph is explained in the text.

first become weak and diffuse and shift to smaller d-values, and then gradually disappear as the temperature is elevated (Fig. 5). The two prism reflections are left and shifted to slightly smaller d-values (the 100 reflection of birnessite from 0.2455 nm to 0.2440 nm). These lines represent octahedral Mn — Mn distances common to almost all Mn — O compounds (Giovanoli and Bürki 1975), and cannot be assigned to any particular mineral species. Probably only fragments of octahedral layers are left and the crystals of the new minerals formed are too small to give an X-ray diffraction pattern.

Hausmannite (Mn_3O_4) crystals are large enough to be recorded by X-ray diffraction after two hours at 700°C (Fig. 5). At still higher temperatures Fe and other cations are also involved in crystallization. Bixbyite ($(Mn,Fe)_2O_3$) was recorded at 900°C and a spinel at 1000°C. This order of recrystallization is typical of Mn precipitates relatively poor in Fe (Table 3, No. 1; see Koljonen *et al.* 1976). With rising temperature the minerals become better crystallized and no interconversions seem to occur. The crystallizations are simultaneous and so sluggish until ca. 1160°C that no reaction was recorded by DTA. At 1160°C the tetragonal low hausmannite was transformed to the cubic high hausmannite (van Hook and Keith 1958), a reaction known to be rapid (Muan and Somiya 1962). The TG curve shows a continuous weight loss between 100°C and 400°C caused by the dehydration of the precipitate and the reduction of Mn.

Iron precipitate. Both goethite (α-FeOOH) and lepidocrocite (γ-FeOOH) were identified in the Fe precipitate (Fig. 6; for chemical composition see Table 3, No. 2). Goethite is the stabler polymorph and is generally formed in areas of temperate humid climate. Lepidocrocite has been identified in the same climatic zone but its occurrence is restricted to hydromorphic soils (Brown 1953, Schwertmann 1959, Pawluk 1971, Koljonen *et al.* 1976, Schwertmann and Fitzpatrick, in press) where Fe is reduced under anaerobic conditions. The occurrence of lepidocrocite thus testifies to the presence of Fe^{2+}.

The simultaneous crystallization of goethite and lepidocrocite in soils is not fully understood. Synthesis experiments show that somewhat higher partial pressure of CO_2 favors goethite formation at the expense of lepidocrocite when ferrous solutions are oxidized (Schwertmann 1959, Schwertmann and Fitzpatrick, in press), goethite possibly being formed via carbonate ($FeCO_3$) and lepidocrocite via »green rust» (Fe(II,III) hydroxy compound) (Schwertmann *et al.* 1974). The complexation of Fe with organic ligands is known to favor the precipitation of goethite out of ferric solutions (Schwertmann *et al.* 1974).

Lepidocrocite and goethite have been found together in a similar environment to that studied (Koljonen *et al.* 1976): Mn and Fe were there precipitated out of ground water, rich in organic matter and reducing, at the point where the ground water came in contact with the atmosphere. A separate study to clarify what controls the simultaneous formation of goethite and lepidocrocite in soils and what are the roles of dissolution and interconversion is presently underway.

Goethite and lepidocrocite consist of Fe-centred oxygen/hydroxyl octahedra linked together to form double chains in goethite and layers in lepidocrocite. Goethite is generally the less crystalline of the two (Schwertmann and Fitzpatrick, in press) as shown by line broadening on the X-ray diffractogram (Fig. 6; Koljonen *et al.* 1976). Goethite is the stabler polymorph and lepidocrocite shows a tendency to be converted to it. The conversion proceeds via solution (Schwertmann and Taylor 1972a,b), and the foreign compounds present in soils may interfere with it. The solubility and dissolution rate of lepidocrocite is low, especially when its crystallinity is high, but is increased in the presence of ferrous iron, i.e., in a reducing environment. Laboratory experiments have proved that organic compounds and silica prevent the nucleation of goethite and thus the transformation of lepidocrocite into it (Schwertmann and Fitzpatrick, in press), but this cannot be the rate-determining factor in a system that contains goethite (Schwertmann and Taylor 1972b).

Upon heat treatment, goethite and the amorphous fraction present are converted via dehydration and rearrangement to hematite (α-Fe_2O_3). The conversion temperature varies with the crystallinity of goethite, and is lowest for the amorphous hydroxide form. Temperatures between 300°C and 400°C are usually reported (Tosson *et al.* 1974, Kodama *et al.* 1977). Lepidocrocite is converted to maghemite (γ-Fe_2O_3) at temperatures corresponding to the conversion of poorly crystallized goethite to hematite (Kelly 1956). Maghemite is readily converted to hematite upon further heating and can hardly be detected by X-ray diffraction. The first hematite reflections to appear are those shifted slightly from the position in hydrous to the position in anhydrous forms (Francombe and Rooksby 1959), indicating a similar recrystallization via partial decomposition of the parent structure (*cf.*, Feitknecht *et al.* 1973) as proposed for Mn oxyhydroxides. Upon further heating the hematite crystals grow and become more ordered (Fig. 6).

Chemical composition

The chemical composition of the Mn, Fe precipitate discussed in this paper is presented in Tables 3 and 4.

Mn is enriched in sample No. 1 and Fe in samples Nos. 2 and 3. Besides Mn and Fe the precipitate contains other cations, especially ones that form hydroxides in neutral environment. They too are zonally precipitated around the water discharge, as can be seen in the high Al, Mg, and Ti content of sample No. 3 and its lighter color compared with sample No. 2. Calcium predominates in ground water (Table 3, No. 4) but, compared with magnesium, is depleted in the precipitate. This occurs because it neither forms hydroxides nor enters the lattice of the Mn and Fe minerals. Potassium is bound more strongly than sodium on colloids and its content in the precipitate is higher (*cf.*, Koljonen and Carlson 1975). Many elements are enriched with oxidates (*e.g.*, Cronan and Thomas 1972) and the contents of Pb, Ni, Co, Zn, Cu, Cd, and REE are increased in the precipitate. Compared with K, Rb is depleted. The K/Rb ratio, which in continental rock types only rarely falls outside 160—300 (Heier and Billings 1970), is here appreciably higher (790—3000, Table 3). This indicates the precipitation of solid phases which can incorporate K. If adsorption alone had determined the K and Rb contents the latter would be enriched because of its relatively stronger adsorption on colloids, and the K/Rb ratio would be lower than found (Table 3).

The precipitate studied contains more Sn, Pb, and Cd than oceanic Mn, Fe nodules (Table 3; Bender 1972). This difference probably occurs because the bedrock and sediments in the studied area are mostly silicic and the elements mentioned are enriched in the late differentiates of the calc-alkalic suite. The contents of Ni, Co, and Cu are much lower than in oceanic nodules.

Because the Mn and Fe precipitates have been formed close to each other, from running water, their different trace element composition cannot be due to differences in the precipitating solution. The analyses show that Ti and Cr are enriched more in the Fe-rich cement (Nos. 2 and 3) and Ni and Cu more in the Mn-rich (No. 1). Na, Co, Zn, Rb, Li, and REE show no preference for one or the other.

REE are enriched in the studied precipitate, but not as much as in oceanic nodules (Table 4). The contents are higher than in common magmatic (*e.g.*, granites, REE 237 ppm, La/Yb $\sim$ 10, Koljonen and Rosenberg 1976) and metamorphic rocks or in clastic sediments (see Ronov *et al.* 1974). The La/Yb ratio (23—41, Table 4) is higher than in common rock and sediment types ($\sim$ 1—20, see Koljonen and Rosenberg 1976), indicating that during the exogenic migration the REE differentiate from each other, the heavy REE (Gd — Lu) migrating faster than the light (La — Sm). This seems to be a general rule which controls the migration of REE and brings about the enrichment of light REE in the continents during the evolution of Earth's crust.

The La/Yb ratio of oxidates reflects the ratio in the surrounding bedrock and sediments. It is much lower in oceanic nodules than in the precipitate studied (Table 4). The rocks in oceanic environment usually have lower REE contents and La/Yb ratio ($\sim$ 1) than those in continents ($\sim$ 10) (see Koljonen and Rosenberg 1975, Table 2).

Compared with La and Nd, the Ce content is increased in Fennoscandian Mn, Fe precipitates (Table 4, No. 5) and in oceanic nodules (No. 6; see Goldberg 1961) but not in the studied samples (Nos. 1—3). It seems that the Ce enrichment, common in oxidates, is brought about through dissolving and therefore is not observed in young precipitates. In solution Ce probably has the valence 3+ like the other REE and behaves upon precipitation like them. The normalized graph of a newly formed oxidate is smooth (Fig. 7). Unlike the other REE, however, Ce is oxidized to valence 4+, does not dissolve

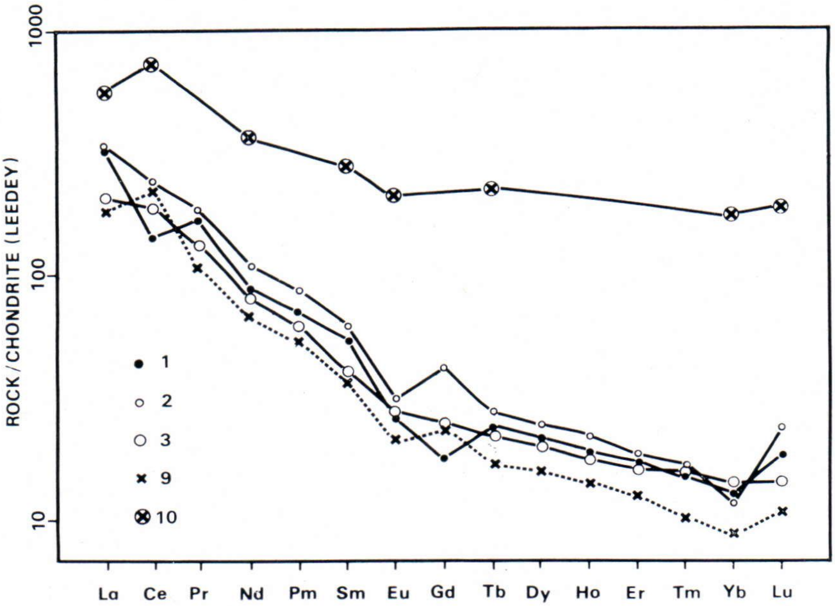

Fig. 7. REE contents normalized against chondrite (Leedey). The numbers in the graph indicate the analyses shown in Table 4.

as quickly, and is enriched upon partial dissolution of the precipitate. This suggests that the chemical composition of oxidates depends not only on the chemical composition of the surrounding solutions but is to a large extent affected by dissolution. Accordingly, it depends on the relative dissolution rate of individual elements and on the chemical composition of minerals and other solid phases present in the precipitate. The chemical composition of a precipitate thus depends considerably on its age and the chemical processes it has undergone after precipitation.

Discussion

The present precipitate was formed in an esker surrounded by vast expanses of clay and silt. In an environment like that, Mn and Fe are dissolved and migrate with ground water as organic complexes and as Mn^{2+} and Fe^{2+} (Koljonen *et al.* 1976). Their precipitation is controlled by the redox conditions of the environment. Fe is oxidized and precipitated before Mn where Eh and pH gradually increase (Krauskopf 1957). In the present case Mn has precipitated before Fe as a rim around the ground-water discharge, and Fe outside it. This order of precipitation can be explained as follows. When ground water flows fast to the surface the Eh is abruptly increased, so that the order of precipitation is controlled by the different stabilities of the Mn- and Fe-organic complexes, which control the reaction velocity; the Fe-complexes are known to be more stable than the Mn-complexes (Schnitzer and Hansen 1970). Mn and Fe are well separated from each other in the present precipitation, which in a young precipitate cannot be the result of diffusion in solid state (*cf.* Carlson *et al.*, in press).

The Mn and Fe precipitates studied are oxyhydroxides which only partly occur as identifiable crystals. The reflections of birnessite, goethite, and lepidocrocite on the X-ray graphs are weak and broadened. Besides Mn and Fe the precipitate contains other cations, which either are incorporated in the lattice of minerals (birnessite), form their own hydroxides (Al, Mg; Table 3, No. 3), or are adsorbed on colloids (Rb, Li). Upon heat treatment the precipitates are dehydrated and the minerals broken into separate layers and fragments according to their crystal structure. Upon further heating they are recrystallized as oxides and spinels in accordance with the overall chemical composition of the precipitate.

Many trace elements are enriched in the precipitate. The trace element composition clearly reflects that found in the surrounding, mostly silicic bedrock. The REE content, for example, is increased, and although the total content is lower than in oceanic Mn nodules the La/Yb ratio is much higher, indicating a greater enrichment of the light REE (La — Sm) than of the heavy (Gd — Lu). This seems to be a general rule and is brought about by a greater adsorption on colloids of the light than of the heavy REE, probably because of their greater ionic radius. Thus the La/Yb ratio increases with time in continents and the ratio, on average, is higher in continental sediments and rocks derived from them than in oceanic.

The content of Ce in relation to La, Pr, and Nd reflects the age of an oxidate and its mode of formation via precipitation and partial dissolution. Because Ce can be oxidized to higher valence than the other REE it tends to migrate more slowly and is depleted in solutions. The residence time of Ce in ocean water is much shorter than that of the other REE and it is depleted there (Herrmann 1970) but enriched in oceanic Mn nodules. The enrichment of Ce in continental sediments also helps to bring about the depletion in oceanic water. Moreover, geochemical differentiation apparently occurs during the exogenic migration of REE, causing the various REE to be unequally distributed among the different sediment groups.

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