REE patterns in latest Neoproterozoic–early Cambrian phosphate concretions and associated organic matter

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Abstract

Analyses of REE were conducted on phosphatic concretions and various types of associated organic matter in eight, key latest Neoproterozoic–earliest Cambrian, inner- to outer-shelf, marine phosphatic successions that are distributed worldwide. A pronounced REE fractionation during diagenetic degradation of the organic matter has been revealed. Selective MREE incorporation and bulk REE contents in some kerogens, organic megascopic fossils and humic acid are compatible with those recorded in associated phosphate. The similarity of REE patterns in apatite and organic matter suggests that early-diagenetic, microbial decomposition of organic matter does not only provide phosphorus and suitable sub-oxic, geochemical conditions, but it is also a likely source of REE enrichment in authigenic apatite formed at shallow depths below the marine water–sediment interface.
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1. Introduction

The growth of phosphate concretions occurs within decimetres to first meters of burial below the sediment–water intersurface during suboxic diagenesis of organic-rich mud deposits (Morad and Al-Aasm, 1994). The sources and timing of REE incorporation in marine diagenetic apatite are enigmatic mainly because REE concentrations in phosphate concretions are up to 50–100 times higher than shale-normalized values, which are several orders of magnitude greater than bulk REE content in seawater (10^{-11} g/g;

Broecker and Peng, 1982). Such high REE concentrations would thus require enormous amount of interstitial seawater. In order to form a phosphate concretion that is 5 cm in diameter containing 1 g of bulk REE and assuming a 10% level of REE extraction from surrounding water, about 1000 m^3 water per year is required. Hence, direct extraction of REE from marine pore waters may be precluded as the most important mechanism to explain the REE enrichment in authigenic phosphate.

The role of organic-matter alteration in providing suitable geochemical conditions and phosphorus for the precipitation of phosphate is well documented (e.g., Heckel, 1977; Price and Calvert, 1978). An alternative source of REE could hence be organic matter that is usually abundant in sediments hosting the phosphate

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Table 1

INAA analyses of rare earth elements content (ppm) in phosphate concretions and various types of organic matter obtained from different sedimentary units and ages

	La	Ce	Nd	Sm	Eu	Gd	Tb	Ho	Yb	Lu
(1) Layer at depth interval 29–41 m above the bottom of the Nagoryani Formation										
Phosphate concretion	25.3	152	252	111	24	103	11.2	6.6	3.4	0.22
Vendotaenides sp.	73	92	57	20.8	4.6	18	1.8	nd	1.9	nd
Vendotaenides sp.	10	34	39	15.7	3.8	16	2.4	nd	0.6	0.05
Vendotaenides sp.	8	17.4	30	14	3.5	19	2.5	nd	0.9	0.07
Kerogen	19	54	32	7.2	1.25	nd	1	nd	1.2	nd
(2) Early Cambrian, central East European Platform, Moscow syneclise, Gavrilov-Yam drill hole. Lezha Formation, depth 1918–1881 m										
Phosphate concretion	220	703	460	118	17.7	80	14	14	28.5	4.2
Sapropel films	7.2	11.4	6.2	1.45	0.34	nd	0.26	nd	0.58	nd
Sapropel films	2.2	4	2.4	0.5	0.11	nd	0.08	nd	0.15	nd
Sapropel films	4.4	6.6	1.7	0.23	0.05	nd	0.05	nd	0.43	nd
(3) Late Vendian, central East European Platform, Moscow syneclise, Gavrilov-Yam drill hole. Nepeitsyno Formation, depth 2382 m										
Phosphate concretion	41	105	62	13.1	2.9	13.2	2	2	3	0.5
Humic acid	150	470	309	75.7	15	55	9	nd	28	nd
Kerogen	180	220	80	13.5	2.4	10	3	nd	18.5	nd
(4) Sinian System, Yangtze Gorges Region, Yichang city, southern China. 32 m above the bottom of the Doushantuo Formation										
Phosphate concretion	154	523	339	90.7	18.4	83	13	8	7.4	0.7
Humic acid	8.4	26	17	4	0.87	nd	0.6	nd	0.56	nd
Humic acid	11	23	14	3.2	0.71	nd	0.5	nd	0.9	nd
(5) Upper Proterozoic Visingsö Group, southern Sweden, Vättern Basin. 10–12 m laminated mudstone of the upper unit										
Phosphate concretion	119	447	399	117	19.3	100	15	10	7	0.68
Kerogen	440	500	65	5.3	0.74	3	0.5	0.8	4.3	nd
Kerogen	1020	1350	140	16.2	3.2	16	4	9	70	nd
Kerogen	360	470	85	7.8	1.4	7	1.2	2	14	nd
Diagenetically altered organic matter from various sites and ages										
(6) Sapropel films, Riphean Mirojedikha group, Turukhansk Region, southwestern Siberia. Middle part of the formation										
	18.1	16.7	30	3.8	0.71	nd	0.7	nd	19.2	nd
(7) Bacterial mat, Vendian Khatyspyt Formation, Khorbusuonka River, eastern Siberia. 2 m below the bottom of the formation										
(A) Analysis made subsequent to acid treatment										
	9	17	10	2.5	0.46	nd	0.25	nd	0.28	nd
(B) Same sample without acid treatment										
	10	13	7	1.5	0.29	nd	0.15	nd	0.21	nd
(8) Sabellidites sp. tubes, Early Cambrian Lezha Formation, central part of the East European Platform. Average value of five analyses										
	2.6	5	1.5	0.28	0.05	nd	nd	nd	0.2	nd
(9) Modern-day marine organisms. Cyanobacterial mat, Sivash lake hypersaline lagoon, Crimea, Ukraine										
	1	2.8	1.2	0.27	0.059	nd	nd	nd	0.2	nd
(10) Pogonophoran Zenkevitchiana longissima Kuril-Kamchatka deep-water basin										
	0.6	1	0.5	0.13	0.03	nd	nd	nd	0.1	nd
(11) Vestimentipheran Ridgeia sp. Mt. Axial, active hydrothermal field, Juan de Fuca Ridge, Pacific Ocean										
	0.7	6	1	0.22	0.052	nd	nd	nd	0.2	nd

Table 1 (*continued*)

	La	Ce	Nd	Sm	Eu	Gd	Tb	Ho	Yb	Lu
Diagenetically altered organic matter from various sites and ages										
(12) Magmatic apatite, Pudozhgora sill, central Karelia										
	603	2091	1623	445	22.1	440	62	nd	90.2	10
(13) Eocene lignite humic acid after Seredin and Shpirt (1999)										
	120.5	337.1	247.7	80.3	1.5	107.6	17.4	nd	50	6.8
(14) Crude oil, Bajenovo Formation, Petelino Oil Field, Western Siberia (average of 10 analyses in ppb)										
	545	2478	450	56	10	nd	nd	nd	115	24

Analysis of igneous apatite is given for comparison.

concretions. In addition to significant amounts of metal cations, primary and microbially/thermally altered organic matter are also able to accumulate REE. Proterozoic stratiform kerogen and globular bitumen contain up to thousands parts per million of bulk REE (Mossman et al., 1993) and latest Neoproterozoic to earliest Cambrian, macroscopic organic fossils have bulk REE content up to 200 ppm (Felitsyn et al., 1998). Humic acid isolated from Miocene and Eocene coal deposits is enriched in REE with up to a thousand parts per million (Seredin and Shpirt, 1999). Organic matter has thus been pointed out as possible primary REE carrier, and a source of REE incorporated in sedimentary apatite, but there is a fractionation encountered during REE bonding by organic matter (Reynard et al., 1999). The distribution patterns of REE in phosphate concretions and biogenic apatite often display a pronounced enrichment by MREE (Grandjean-Lécuyer et al., 1993; McArthur and Walsh, 1984; Kidder and Eddy-Dilek, 1994), which are believed to substitute for Ca^{2+} in apatite lattice (Wright et al., 1987).

The objective of this work is to determine REE patterns in phosphate concretions and associated organic matter (carbonaceous macroscopic fossils, kerogen and humic acid) extracted from the host sediments (latest Neoproterozoic–early Cambrian) in order to elucidate the possibility of derivation of REE in marine apatite from the early-diagenetic, microbial decay of organic matter.

2. Material and methods

Apatite (francolite) concretions as well as humic acid, kerogen and organic fossils were isolated

from eight, latest Neoproterozoic–earliest Cambrian, inner- to outer-shelf, marine phosphatic successions worldwide (Table 1). Selection of these phosphatic successions was based on the availability of extractable organic matter and of carbonaceous macroscopic fossils. The geological settings and petrological description of phosphate concretions have been presented by Morad and Al-Aasm (1994) for the Visingsö group, Yang et al. (1997) for the Sinian system in southern China, and by Kopeliovich (1965) and Pirrus (1989) for the Vendian and Cambrian strata of the East European Platform. The studied concretions vary in diameter from 2 cm (Yangtze Gorges Region, southern China) to 15 cm (Cis-Dniester, East European Platform). Lamination in the host mudstone is bent around the concretions indicating a very early diagenetic origin of francolite (Morad and Al-Aasm, 1994). Kerogen from the host sediments was isolated using HF, HCl and HNO_3 treatment (modified from Saxby, 1970). Repeated rinsing with distilled water was undertaken in order to remove the acid-resistant minerals. The extracted kerogen was then hand picked and examined under the microscope at a magnification of X400 in order to ensure the absence of acid resistant, mineral residues. The humic-acid samples were isolated through treatment with 0.3 N NaOH and subsequent precipitation at pH of 2 (modified from Nissenbaum and Swaine, 1976). The elemental composition of separated organic residues was used to control their purity. Only samples containing <500 ppm Ti, <30 ppm Zr and <1 ppm Th, were consid-ered pure enough from contaminant minerals like sphene and/or zircon which could alter the REE pattern of the organic matter.

The investigated carbonaceous fossils consist of vendotaenids, sabelliditids and sapropel organic films. Ventotaenids are ribbon-shaped fossils, which were obtained from the Upper Vendian sequence in the south western part of the East European Platform (Cis-Dniester region), reach 5.0 mm in length and 0.5–2.0 mm in width, show a smooth surface with occasional compression wrinkles and dark brown color. The taxonomic affinity of vendotaenids is questionable (Vidal, 1989). The tubes of sabelliditids are 20 to 50 mm in length and 0.7–3.0 in width, brown to dark brown in color with the outer surface displaying a wrinkled texture without segmentation. Tubes of *Sabellidites cambriensis* Janishevsky were considered to be remnants of the oldest pogonophorans with primarily chitin-bearing composition (Sokolov, 1967).

Amorphous sapropel organic films with remains of filamentous cyanobacteria (possibly fragments of benthic matted bacterial–algal communities) reach 50 mm in diameter, are elastic and semi-transparent when wet and yellow to brown in color when dry.

For the purpose of comparison, the REE compositions in soft tissue of present-day marine organisms, crude oil, igneous apatite and humic acid isolated from lignite of Eocene age, Far East of Russia (Seredin and Shpirt, 1999) are presented in Table 1. REE contents in the phosphate concretions and associated organic matter were obtained using neutron activation analysis, instrumental technique (INAA) at the Institute for Precambrian Geology and Geochronology, St. Petersburg, Russia. Air-dried samples of 0.11 to 36 mg were placed in sealed super pure
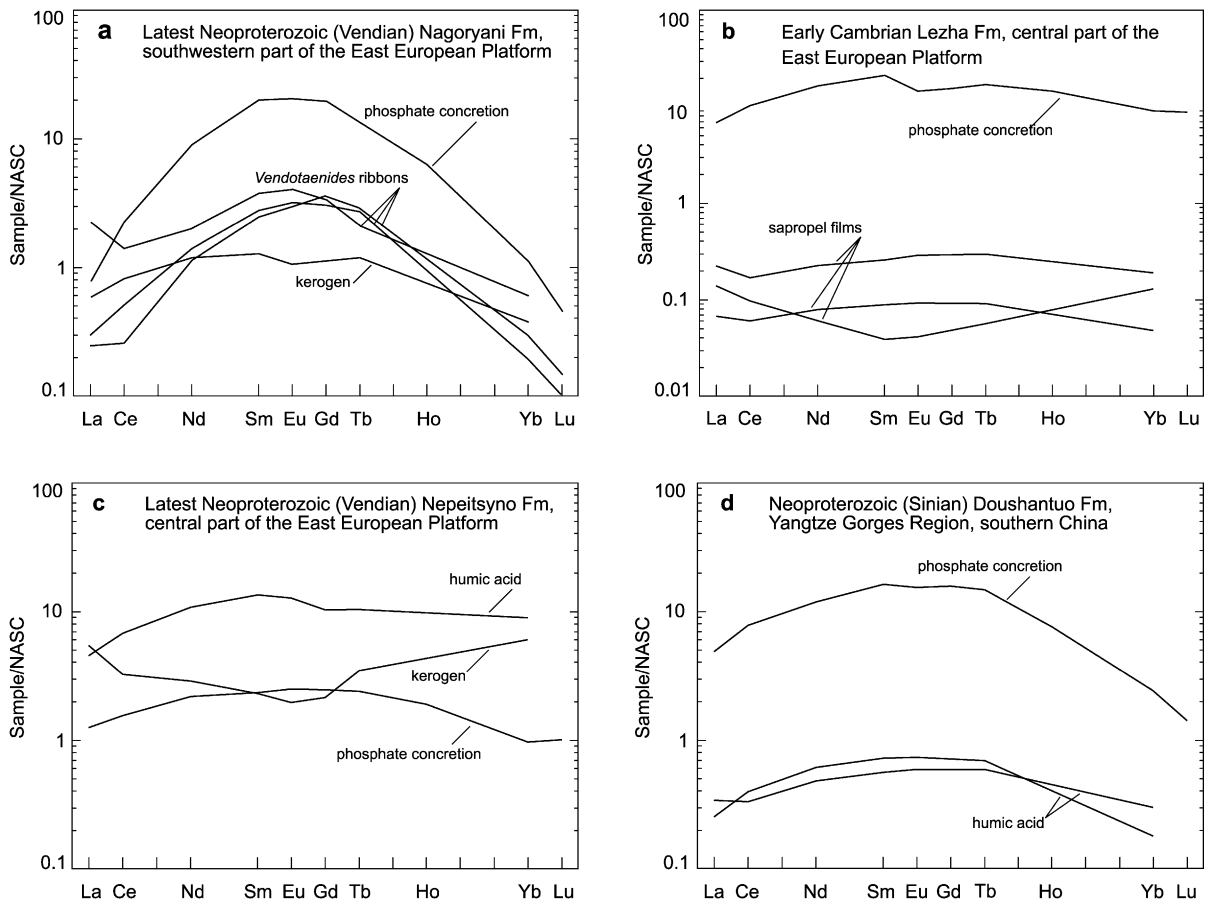

Fig. 1. The distribution patterns of REE in organic matter of various types and ages and phosphatic concretions based on data in Table 1. Note the similarity in REE patterns of most organic matter and associated phosphatic concretions and of humic acid.
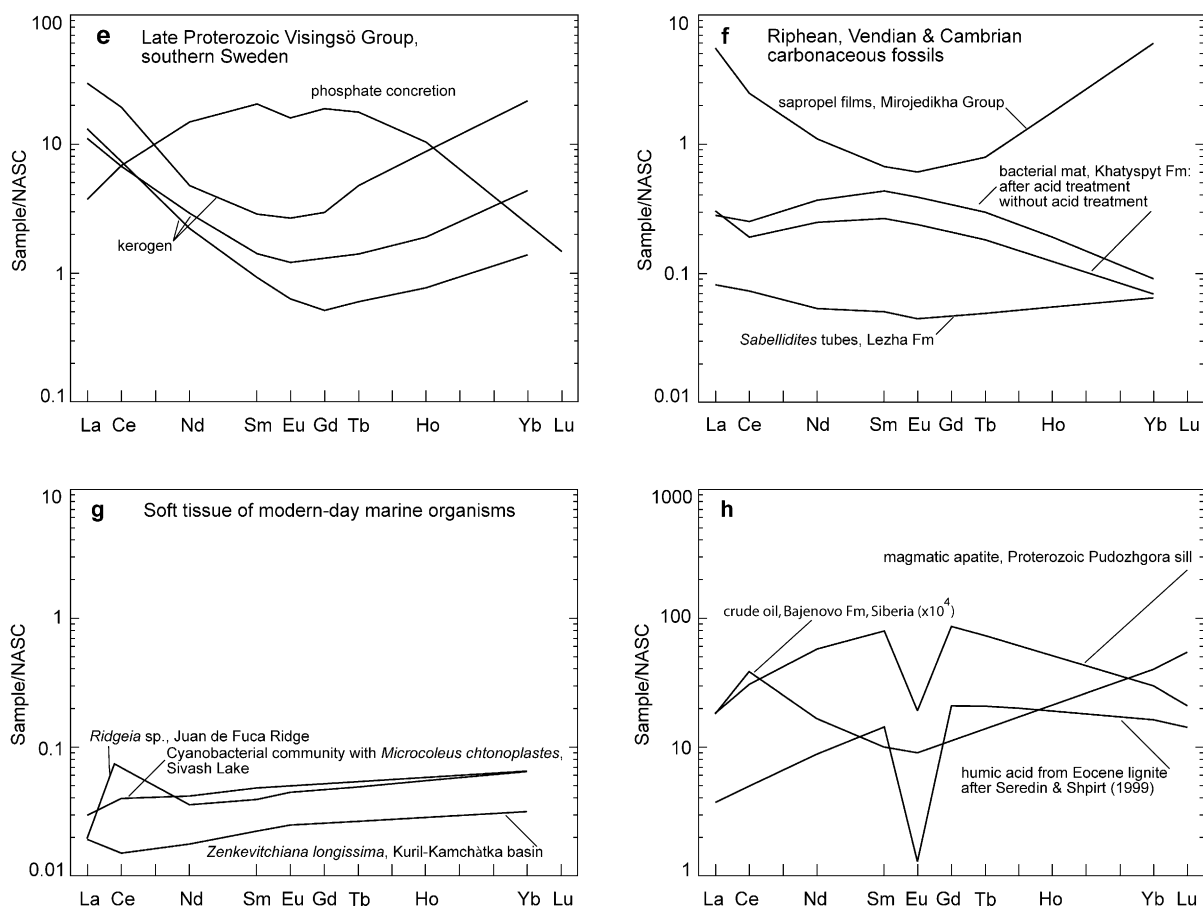
Fig. 1 (continued).

quartz ampoules and irradiated in a neutron flux of 1.1×10^{14} neutrons cm^{-2} s^{-1} for 24 h in the VVR-M nuclear reactor at the Institute of Nuclear Physics, St. Petersburg. Mean relative error is <5% for La, Ce, Sm and Eu, <10% for Nd, Yb and Lu and <12% for Gd, Ho and Tb.

In order to control the influence of acid treatment on REE pattern in organic matter, analyses were performed on selected acid-treated and untreated organic matter samples. Well-preserved organic matter from East European Platform display a mild thermal alteration index (TAI=1–3; Moczydlowska, 1991; Felitsyn et al., 1998), which is consistent with normal thermal gradient (about 2–3 °C/100 m) on ancient platforms. Mild thermal alteration was inferred from mineralogy and geochemistry of clay minerals from the Visingsö Group (AlDahan and Morad, 1986) and

based on oxygen isotopic composition of carbonate, Sinian System in the Yangtze Gorges Region, South China (Yang et al., 1999).

3. Results and discussion

The bulk REE concentration and shale-normalized distribution patterns of the studied phosphate concretions (Table 1 and Fig. 1) are similar to those reported for various types of phosphorite (McArthur and Walsh, 1984; Kidder and Eddy-Dilek, 1994) and for fossil biogenic apatite (Reynard et al., 1999). All studied phosphate concretions display a distinct enrichment in MREE with fractionation factor between Sm and Yb ranging between 9 and 18 (the Visingsö Group and the Nagoryani Formation, respectively) to between 2 and

3 (the Lezha Formation), times shale-normalized values. The Sm/La$_N$ (N refers to shale-normalised values, using standard shale composite NASC; Gromet et al., 1984) ratios vary from 1.8 to 25, which result in specific "hat-shaped" REE patterns in phosphate concretions, whereas host mudstones display REE spectra similar to those in standard post-Archean shale composite (Felitsyn and Sochava, 1996).

Organic matter isolated from rocks that host the phosphate concretions reveals two main patterns of REE distribution: (i) similar to that of the phosphate concretion with a pronounced MREE enrichment, maximal fractionation factor of 14 between Sm and Yb and of 10 between Sm and La (Fig. 1a,b,c,d) and (ii) strong MREE depletion with Sm/La$_N$ and Sm/Yb$_N$ values up to 0.07 and 0.12, respectively (Fig. 1b,c,e,f). Humic acid and kerogen extracted from the same sample display different types of REE patterns (Fig. 1c); the humic acid displays a MREE enrichment similar to that in the phosphate concretion, whereas kerogen show MREE depletion. Different types of organic matter obtained from the same location show either MREE enrichment or MREE depletion (Fig. 1b,c). Well-preserved sabelliditids tubes isolated from early Cambrian strata in central part of the East European Platform show slightly concaved REE patterns with moderate LREE and HREE enrichments (Fig. 1f); the Sm/La$_N$ and Sm/Yb$_N$ ratios are less than 1.0.

The REE patterns in ancient sedimentary organic matter are not influenced by the acid treatment. Sapropelic organic films extracted from carbonate host rock of Vendian age using the same procedure as for kerogen extraction (i.e., treatment with HF–HCl–HNO$_3$) reveal a REE pattern that is much similar to that of the same sapropel film analyzed without acid treatment (Fig. 1f). Only the "dilution effect" of host carbonate is evident inducing 30–50% higher bulk REE content in organic matter extracted by acid treatment. The carbonate phase is relatively enriched with La (Parekh, 1977), which explains the non-parallel spectra in the field of LREE. Likewise, acid treatment did not alter the REE distribution pattern in organic matter of modern-day cyanobacterial community (Felitsyn et al., 1998), suggesting strong bonding of REE by organic matter.

Soft tissues of modern-day marine organisms display REE distribution patterns similar to that in sea-

water (Fig. 1g) and with La/Yb$_N$<1.0 and Ce depletion/enrichment depending on the prevailing redox conditions (Felitsyn et al., 1998). Igneous apatite isolated from the Pudozhgora gabbroic sill (2.2 Ga; Golubev and Philippov, 1996), central Karelia, has a REE distribution with evident MREE enrichment. Such MREE enrichment is also characteristic for humic acid extracted from lignite of Eocene age (Fig. 1h). The main difference is relative enrichment of humic acid with HREE. The fractionation factor between Sm and Yb is 0.89, whereas between Sm and La is 3.8. A negative Eu anomaly is characteristic for both igneous apatite and lignite humic acid. These data suggest that the REE patterns are similar in phosphate concretions and different types of associated organic matter (kerogens, humic acid and organic fossils), which are, in turn, similar to that in the igneous apatite. Hence, there is a similar pattern of REE incorporation into these different materials.

The role of REE in vital functions and metabolism of present-day organism seems to be negligible, because the bulk REE content in soft tissues usually does not exceed a few parts per million (Bowen, 1979; Eisler, 1981). Soft tissues of present-day marine organisms incorporate elements without fractionation, which result in a REE distribution pattern similar to that of open- and coastal seawater (Fig. 1g). The bulk REE content is usually about 1–5 ppm in dry soft tissue, with a variable cerium anomaly that depends on the redox conditions (Felitsyn et al., 1998). Thus, REE concentrations up to thousands of parts per million in organic matter result from post-mortem enrichment. A limited number of published data renders a reliable evaluation of REE abundance in ancient organic matter difficult. Moreover, values reported in the literature may, in some cases, include kerogen that is probably contaminated by acid-resistant minerals (Hirner et al., 1990). Extracted humic acid that is devoid of detrital minerals accounts for a number of elements, such as higher REE than uranium, which may in turn reach concentration of 100 to 1000 ppm (Szalay, 1964). The incorporation of various elements into humic acid could be due to cation exchange, sorption on the surface, chelate formation and coagulation (Kabata-Pendias and Pendias, 1984). Determination of speciation for each bonded element is a hard task that renders quantitative modeling of element partition between organic matter and sea-

water/pore water difficult. Nonetheless, the REE spectra in humic acid are similar to those of igneous apatite (Fig. 1h) that are in equilibrium with marine porewater and magma, respectively.

A pronounced MREE enrichment recorded both in phosphate concretions and organic matter suggests that: (i) similar to francolite, the REE in humic acids, kerogen and carbonaceous fossils substitute for Ca, and (ii) REE patterns in organic matter are, at least partially, controlled by the ionic radii of the REE. Calcium concentration in marine humic substances extracted from present-day sediments reaches thousands of parts per million to more than 2.0 wt.%. Ca-oxalate, salts of long chain fatty acids and polyols are regarded as the main organic compounds containing Ca (Nissenbaum and Swaine, 1976). The equilibrium constant of calcium-humic complexes (log K=6.5) is comparable with those of Mn, Cd, Fe and Mg at pH=7 (Kabata-Pendias and Pendias, 1984). Carboxyl and phenolic hydroxyl groups play a significant role in binding Ca^{2+} and other elements during thermal maturation of organic matter (Halbach et al., 1980). A certain portion of REE (mainly MREE) could be chelated by porphyrin complexes (Wong et al., 1974; Radzki et al., 1987), which could survive the mild thermal alteration of the studied organic matter. Phospholipids may also bind REE due the large affinity of REE to phosphate groups (e.g., Bowen, 1979). Some plants, like *Carya* sp., are known to accumulate significant amounts of REE (Shacklette, 1980). Experimental sorption of REE onto xylene and other humic substances display a strong MREE enrichment with a fractionation factor of 10 between Sm and La, the lack of negative Eu anomaly and a typical hat-shaped REE distribution pattern (Seredin and Shpirt, 1999).

The microbial decay of organic matter results in the formation of polar fractions (Galimov, 1985) with hat- or bell-shaped REE patterns which are typical for ancient organic matter. Many other trace elements (e.g., Co, Zn, Ag, Au and U) are incorporated in partially biodegraded organic compounds (Felitsyn et al., 1998; Turchenko and Felitsyn, 1997). The biodegradation and concomitant enrichment of organic matter with various elements (including REE), due to the formation of unsaturated bonds, presumably starts in the water column (Galimov, 1985). Biodegradation of organic matter is believed to have been

unusually complete prior to the appearance of organisms forming fecal pellets in earliest Cambrian (Logan et al., 1995). Therefore, the role of organic particulates as carriers of elements extracted from the water column during their slow settlement to the seafloor is expected to be more considerable during the Precambrian. This postulation is supported by the MREE enrichment in Vendotaenids ribbons (Fig. 1a), which are considered to represent planktonic organisms (cf. Vidal, 1989), compared to the moderate MREE enrichment of benthic sabelliditids and bacterial–algae matt communities (Fig. 1b and f).

Polymerization of humic acids and the formation of kerogen in sediments, which is accompanied by the loss of active functional groups like COOH, OH, SH, CO_2H (Galimov, 1985), has a significant impact on REE fractionation between organic matter and pore water. The REE analyses of heavy, asphaltene-rich crude oil from a Petelino oil field of Mesozoic age, western Siberia show low Sm/Yb_N and Sm/La_N ratios (0.27 and 0.59, respectively). The shale-normalized, REE distribution pattern displays a concave shape with substantial MREE depletion (Fig. 1h). As asphaltene represents an oxygen-poor component of crude oil, the postulation that the oxygenated groups of the humic polymer preferentially bind MREE is confirmed by REE patterns in the Siberian crude oil. The oxic to suboxic decay of organic matter leads to oxidative cleavage of the side chain at the double bond, loss of functional groups and release of bonded elements, such as REE.

The released oxygen-rich, slightly condensed and polymerized compounds during the maturation of organic matter are enriched with MREE, whereas the highly aromatic residual organic matter acquires a concave REE distribution similar to some of the studied kerogen (Fig. 1c and e). The proportion between released and remaining parts of organically bonded REE is difficult to determine, because the original REE distributions in precursor organic matter, as well as the original organic-matter content in the sediment, are unknown.

Sapropel films of latest Neoproterozoic (late Vendian) age from the northwestern part of the East European Platform (southern coast of Baltic Sea, Izhora River) are compositionally similar to those of Cambrian age studied here. The Vendian sapropel films with vendotaenids contain 0–4 wt.% humic

acids (Uspensky et al., 1951). Such proportion of humic components isolated from organic matter obtained at the same location is attributed to the mobility of humic acids and/or different degrees of organic-matter decay. The REE patterns in kerogen (MREE poor) and associated humic acid (MREE rich) isolated from the same sample complement each other (Fig. 1c). The hat-shaped, REE patterns in humic acid are similar to that in phosphate nodules. This together with the high bulk REE content in the humic acid are important lines of evidence for the genetic links between these organic matter and phosphate.

4. Conclusions

The REE patterns obtained for phosphate concretions and for carefully separated and purified associated kerogen, humic acid and macroscopic organic fossils of latest Neoproterozoic–earliest Cambrian age underlines the important role of organic matter in the bulk enrichment and distribution pattern of REE in authigenic phosphate. Two types of REE patterns occur in the organic matter.

(i) Convex or hat-/bell-shaped with distinct MREE enrichment and fractionation factor of $10-15$ between Sm and La, as well as between Sm and Yb (shale-normalized values). This partitioning probably increases simultaneously with an increase in the degree of organic-matter biodegradation during early, suboxic diagenesis.

(ii) Concave REE distribution pattern in kerogen with Sm/La_N and Sm/Yb_N ratios of up to 0.07 and 0.11, respectively. The most probable process leading to a concave REE pattern in organic matter is the loss of mobile compounds (e.g., humic acids) enriched with MREE.

Partial microbial degradation of sinking organic particulates and concomitant incorporation of REE, is suggested to start in the seawater column. Thus, the diagenetic decomposition of organic matter and formation of mobile components (e.g., MREE-rich humic acid) may not only provide phosphorus and suitable early sub-oxic conditions for apatite precipitation, but it is also a likely source of REE enrichment. The similar REE patterns encountered in phosphate concretions, ancient biogenic apatite, organic matter and igneous apatite could point towards a common mechanism of REE incorporation in these materials, that is the substitution of Ca in apatite lattice or in organic compounds.

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