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The Affinity of Lanthanides to Carrier Phases in Soils

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Abstract—A new index of lanthanide affinity to carrier phases in soil, A_{Ln}, differing from the traditional index of lanthanide affinity, pC_{Ln}, has been proposed. The new affinity index has critical value $A_{Ln\text{-critical}} = 1$ and makes it possible to compare phases extracted with different-strength reagents. The phase is enriched in lanthanides at $A_{Ln} > 1$ and depleted in them at $A_{Ln} < 1$. The index of lanthanide affinity, A_{Ln}, has shown its advantage over the accepted pC_{Ln} index during analysis of Russian and Swedish soils.

Keywords: sequential chemical extraction of heavy metals, lanthanide carrier phases, European soil lanthanide clarkes

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INTRODUCTION

Large-scale determination of the content of lanthanides in soils started after the introduction of inductively coupled plasma mass spectroscopy and neutron activation methods [8, 11].

The growing interest of soil scientists in lanthanides is determined by two reasons: first, by the expansion of the use of lanthanides in crop production [3, 19], which requires the identification of negative geochemical anomalies, when the addition of lanthanides gives the maximum effect, and, second, by the growing environmental pollution with lanthanides. Among the sources of pollution are industrial and medical pollution [7, 12]. All of this requires assessment of the hazard posed by lanthanides in soils.

Most often, the content of heavy metals (including lanthanides as their component) associated with carrier phases is determined by the method of sequential chemical treatment of soils [8, 11, 17]. The sequence of treatment and types of reagents vary in different schemes; however, reagents for dissolving three or four different lanthanide carrier phases are generally used in practice. They include, among other things, exchangeable lanthanides + lanthanides fixed by carbonates, as well as lanthanides fixed by organic matter and lanthanides fixed by Fe and Mn oxides with different degrees of crystallization.

The findings (the content of heavy metals including lanthanides) associated with carrier phases) are then processed. During the processing of the resulting data, the distribution of each metal between the phases is expressed as the pC_{HM} index (% of its total content in the soil) [6, 8, 9, 17]:

$$pC_{HM} = 100 \times HM_{fraction}/HM_{total}, \qquad (1)$$

where $HM_{fraction}$ is the concentration of the heavy metal in each fraction and HM_{total} is the total content of this metal in the soil.

The pC index is then used in diagrams or for statistical calculations, e.g., the determination of the relationship of a given lanthanide with the yield of agricultural crops [20].

The proportion of the content of metal, pC_{HM}, reflects the degree of its affinity to the given phase. The pC_{Ln} values are used to construct series of affinity of metals (lanthanides) to the given phase: the higher the proportion of a given metal, the higher its affinity to the given phase, and vice versa. A high pC_{Ln} value indicates the affinity of the given metal to the phase, while its low value shows the absence of the affinity.

However, the problem is that formula (1) does not provide the critical C_{Ln} value differentiating the presence and absence of the affinity of the metal. The main thing is that the value of 1% of the index differs for each of the extracts, which excludes comparison of the degree of metal affinity to different phases. At the same time, lanthanides are analyzed using extracts of different "strengths," which makes it impossible to use the pC_{Ln} index for determining the degree of affinity of heavy metals, including lanthanides, to different carrier phases in soils.

It is necessary to introduce a new indicator of affinity of metals to their carrier phases in soils. It should have a clear critical value, on the one hand, and allow one to compare the affinity of lanthanides to phases extracted from different-strength reagents, on the other.

The objectives of this research are (1) to propose a new index of the affinity (A) of lanthanides to carrier phases in soils, which has critical value A_{cr} and makes it possible to compare the affinity of lanthanides to phases extracted from different-strength reagents and (2) to compare the new A index with the old pC_{Ln} index on soils of the forest zone in Europe.

MATERIALS AND METHODS

Objects of Research

We analyzed the published data on the content of lanthanides in several soils of Europe.

Two soil samples were taken from the city of Perm in the Cis-Ural region and from areas in the vicinity of the city. Sample 1 (alluvial soil sample, Histic Fluvisol Petrogleyic Eutric) was taken from the floodplain of the Kama River opposite the city of Perm. It was collected from the humus horizon at a depth of 0–10 cm. The soil is enriched in organic matter: C_{org} = 13%, pH_{H_2O} 5.7 [8].

Sample 2 (aerially contaminated urban soil) was taken from a small park in the city of Perm, 0.5 km from an engine plant. The soil is soddy-podzolic (Albeluvisol Umbric). The sample was collected from the humus horizon at a depth of 0–10 cm. The soil contains C_{org} = 4.7%, pH_{H_2O} 7.4 [8].

A podzol with the spodic B horizon, formed on granite eluvium, was studied in northern Sweden. Two samples from horizons B (10–15 cm) and C (80–85 cm) were analyzed. In the illuvial horizon, the concentration of C_{org} is 2.4%; in rock, C_{org} = 0.2%. In horizon B, the pH_{H_2O} value is 5.5; it increases to 6.4 in the parent rock [11].

Methods

The content of lanthanides in the initial soils and chemically extracted fractions was determined by inductively coupled plasma mass spectrometry [8, 11].

Soil Samples from the Cis-Ural Region

The total content of lanthanides is designated as "initial" content and the initial phase by number 1 in the tables below.

CH_3COOH at a concentration of 0.43 M was used as the first extractant [8]. This phase includes cations associated with carbonates. This phase is designated as "cations associated with carbonates" by number 2 in the tables.

Hydrochloric hydroxylamine, used at concentrations of 0.15 M with pH 2, dissolves lanthanides weakly fixed by Fe and Mn compounds. This phase is designated as "amorphous Fe" content by number 3.

Sodium pyrophosphate solution was used as reagents dissolving organic matter [8]. The content of this phase is designated as "organic matter" by number 4 in the tables.

The stronger solution, hydrochloric hydroxylamine, at a concentration of 1 M, dissolves crystalline iron hydroxides [8]. This phase is designated as "crystalline Fe" content by number 5 in the tables.

The residue after the treatment with reagents is designated as "residue" by number 6 in the tables.

Soil Samples from Sweden

The order of fraction distribution used for the Swedish podzol [11] somewhat differed from that used in Russia.

The total content of lanthanides is designated as "initial" content by number 1 in the tables.

The next phase includes cations associated with carbonates. This phase is designated as "cations associated with carbonates" by number 2 in the tables.

Organic substances were extracted with 1 M $Na_4P_2O_7$ solution. The content of this phase is designated as "organic matter" by number 3 in the tables.

Hydrochloric hydroxylamine solution at a concentration of 0.1 M was used to dissolve amorphous Fe oxides. This phase is designated as "amorphous Fe" content by number 4 in the tables.

Hydrochloric hydroxylamine at a concentration of 1 M was used to dissolve crystalline iron hydroxides. This phase is designated as "Fe-crystalline" content by number 5 in the tables.

The residue is designated as "residue" by number 6 in the tables.

When interpreting the results, it is more convenient to discriminate the main lanthanide carrier phases and omit the secondary phases. The secondary phases in the studied soils include Mn compounds due to the negligible content of Mn in soils. For instance, the content of total and fractional Fe is dozens and hundreds of times higher than the content of total and fractional Mn in podzol samples from Sweden. The higher content of total Fe than that of Mn varies from

Table 1. Normalized content of lanthanides in soils of the Cis-Ural region. Primary source [8]

Lanthanides	European Clarke [6]	Soil fractions on the Kama-1 River						Soil fractions in the city of Perm-2					
		1	2	3	4	5	6	1	2	3	4	5	6
La	26	0.9615	0.0100	0.0154	0.2577	0.0769	0.5385	0.3615	0.0146	0.0146	0.0538	0.0269	0.2231
Ce	52.2	1.0536	0.0096	0.0134	0.448	0.1073	0.5747	0.3831	0.0111	0.0111	0.0536	0.0306	0.0306
Pr	6.0	1.0333	0.0088	0.0092	0.3000	0.1000	0.5833	0.4000	0.01	0.0033	0.0550	0.0333	0.2167
Nd	22	1.0454	0.0086	0.0082	0.3591	0.1091	0.5454	0.4045	0.0109	0.0036	0.0636	0.0364	0.2182
Sm	4.3	1.1163	0.0116	0.0079	0.4419	0.1186	0.4651	0.3953	0.0132	0.0033	0.0651	0.0372	0.2326
Eu	0.85	1.2941	0.0106	0.0106	0.5059	0.1294	0.5176	0.4588	0.0129	0.0035	0.0788	0.0435	0.2941
Gd	4.2	1.0000	0.0109	0.0105	0.4429	0.1071	0.4286	0.3810	0.0143	0.0043	0.0714	0.0333	0.1786
Tb	0.64	0.9375	0.0094	0.0047	0.3906	0.0969	0.4375	0.3594	0.0094	0.0030	0.0594	0.0344	0.1562
Dy	3.6	0.9722	0.0103	0.0125	0.4167	0.0805	0.4167	0.3611	0.0128	0.0039	0.0611	0.0278	0.2055
Ho	0.72	0.9722	0.0083	0.0125	0.3889	0.0625	0.4861	0.3611	0.0097	0.0040	0.0583	0.0250	0.2083
Er	2.1	0.9524	0.0076	0.0119	0.3809	0.0476	0.5238	0.3809	0.0114	0.0038	0.0476	0.0209	0.2143
Tm	0.31	0.9032	0.0064	0.0097	0.2903	0.0290	0.5484	0.3548	0.0071	0.0032	0.0452	0.0139	0.2097
Yb	2.1	0.9048	0.0062	0.0086	0.3000	0.0286	0.5238	0.3333	0.0062	0.0026	0.0405	0.0157	0.2524
Lu	0.31	0.9355	–	–	0.2903	0.0258	0.5484	0.3226	0.0068	–	0.0323	0.0152	0.2258
ΣLn_n		14.092	0.104	0.1351	5.11	1.1193	7.1379	5.2574	0.1504	0.0642	0.7857	0.3941	2.8661
pC_{Ln-n}, %			0.74	1.0	36.2	7.9	50.6		2.9	1.2	14.9	7.5	54.5

In Tables 1 and 2: ΣLn_n is the sum of all normalized fractions; pC_{Ln-n}, %, is the traditional index of content of all lanthanides in each phase.

90 to 450 times in hor. B and from 40 to 120 times in hor. C. Therefore, since the fraction of Mn is insignificant, the involvement of manganese compounds in the fixation of lanthanides can be ignored, assuming that all lanthanides are fixed by Fe compounds in the first approximation.

RESULTS

Traditional Index of Lanthanide Affinity, pC_{Ln}

A drawback of the index is a high variation in the content of lanthanides in soils/sediments. This problem can be easily solved by normalizing lanthanides based on clarke values. Thus, the clarke value for European soils varies from 52.2 ppm for Ce to 0.31 ppm for Lu [10]. The values of lanthanides are balanced based on the normalization method; i.e., the content of each lanthanide was divided by its reference value. In the geochemistry of lanthanides, chondrite [1, 12] or earth's crust [14] are commonly used as a reference.

For the decision of soil problems, it would be more relevant to use global or, even better, continental soil clarkes [10]. The normalized content of the Ln lanthanide is designated as Ln_n. Lanthanide clarkes in European soils are given in Tables 1 and 2 according to [10].

For lanthanides, expression (2) is used instead of expression (1):

$$pC_{Ln} = 100 \times Ln_{fraction}/Ln_{total}, \qquad (2)$$

where $Ln_{fraction}$ is the content of lanthanide in each fraction and Ln_{total} is the total content of this lanthanide in the soil.

After lanthanides were normalized, their total content in European soils was as follows: Σ_{La} = (26:26) + Ce (52.2:52.2) + ... + Lu (0.31:0.31) = 14 (i.e., the same as that in the periodic system).

The main disadvantage of the old pC_{Ln} index is that it has no critical value, i.e., no boundary between the low value and high value. This is due to the simplified structure of formula (1). Therefore, this index does not make it possible to distinguish between phases, as opposed to the method using different-strength reagents.

Sometimes, the method of sequential chemical treatment involves a large number of samples, which makes it possible to reveal the static fractionation of phases on the same object [5]. Due to the complexity of the procedure of sequential chemical soil treatment, it is often carried out on a single sample without replications [8, 9, 11].

New Index of Affinity (A) in Chemical Soil Fractionation

To eliminate the disadvantage of the pC_{Ln} index (the absence of the critical value), it is necessary to create a new structure for the new affinity formula.

Table 2. Normalized content of lanthanides in the Swedish podzol. Primary source [11]

Lanthanides	European Clarke [6]	Sample fractions from hor. B (10–15 cm)						Sample fractions from hor. C (80–85 cm)					
		1	2	4	3	5	6	1	2	4	3	5	6
La	26	0.7346	0.0154	0.0209	0.0596	0.0337	0.536	1.1846	0.0450	0.0152	0.2088	0.1448	0.618
Ce	52.2	0.9521	0.0189	0.0221	0.0594	0.0444	0.716	1.5211	0.0650	0.0261	0.2600	0.1468	0.813
Pr	6.0	0.9167	0.0167	0.0273	0.0717	0.0480	0.726	1.4467	0.0620	0.0193	0.2080	0.1207	0.840
Nd	22	1.0773	0.0210	0.0327	0.0800	0.0559	0.832	1.5682	0.0718	0.0216	0.2249	0.1216	0.840
Sm	4.3	1.0302	0.0233	0.0367	0.0814	0.0670	0.804	1.3488	0.0651	0.0213	0.1893	0.0856	0.868
Eu	0.85	1.0753	0.0321	0.0488	0.1129	0.0932	1.043	1.6941	0.0721	0.0235	0.2023	0.0740	1.388
Gd	4.2	0.8214	0.0255	0.0359	0.0817	0.0590	0.704	1.2190	0.0707	0.0186	0.1874	0.0648	0.758
Tb	0.64	1.3906	0.0323	0.0498	0.1141	0.0891	1.050	1.6250	0.0730	0.0237	0.2156	0.0734	1.123
Dy	3.6	1.2278	0.0278	0.0419	0.1061	0.0878	0.892	1.4000	0.0578	0.0207	0.1792	0.0555	1.011
Ho	0.72	1.1333	0.0269	0.0451	0.0992	0.0833	0.939	1.4722	0.0555	0.0200	0.1736	0.0525	1.047
Er	2.1	1.1286	0.0237	0.0421	0.0895	0.0786	0.882	1.4952	0.0476	0.0205	0.1590	0.0476	0.978
Tm	0.31	1.2710	0.0217	0.0474	0.0890	0.0848	1.081	1.6097	0.0429	0.0253	0.1564	0.0481	1.061
Yb	2.1	1.4762	0.0206	0.0500	0.0819	0.0886	1.244	1.6048	0.0402	0.0273	0.1505	0.0476	1.291
Lu	0.31	1.1548	0.0203	0.0474	0.0684	0.0752	1.074	1.3806	0.0397	0.0305	0.1390	0.0452	0.990
ΣLn_n		15.3899	0.3262	0.5481	1.1949	0.9886	12.23	20.5700	0.8084	0.3136	2.6540	1.1282	13.636
$pC_{Ln\text{-}n}$, %			2.1	3.6	7.8	6.4	81.4		3.9	1.5	12.9	5.5	66.3

Let us use the coefficients previously proposed by geochemists. Thus, we used an approach to calculating the coefficient of "enrichment of an element in a sample with respect to the Earth's crust" [14]:

$$K_{\text{enrichment}} = (C/C_{\text{norm}})_{\text{sample}} / (C/C_{\text{norm}})_{\text{earth's crust}}. \quad (3)$$

The enrichment factor has its own critical value, $K_{\text{enrichment}} = 1$. The degree of enrichment of the element is higher at $K_{\text{factor}} > 1$ and lower at $K_{\text{enrichment}} < 1$ than that in the Earth's crust.

The same approach was used by geochemists to compare the leaching capacity of extracts with respect to heavy metals [18]. This indicator was called the "index of anthropogenicity," $K_{\text{anthropogenicity}}$:

$$K_{\text{anthropogenicity}} = (C_{\text{fraction}}/C_{\text{total}}) / (C_{\text{fraction}}/C_{\text{total}})_{\text{Al}}, \quad (4)$$

where the numerator is the ratio of the concentration of the leached form of the element (C_{fraction}) to its total content in the sample and the denominator is the same ratio for the aluminum concentration.

This coefficient also has the critical value $K_{\text{anthropogenicity}} = 1$. The extract is insensitive to a significant destruction of aluminosilicate particles at $K_{\text{anthropogenicity}} < 1$ and vice versa at $K_{\text{anthropogenicity}} > 1$.

In the new formula, we replaced the C values in the numerator and denominator of formulas (3) and (4) by two sums: $\Sigma C_{\text{Ln-phase}}$ and $\Sigma C_{\text{Ln-soil}}$, respectively. As a result, we found a new index of lanthanide affinity, A_{Ln}, for this phase:

$$A_{\text{Ln}} = (C_{\text{Ln-phase}}/\Sigma C_{\text{Ln-phase}}) / (C_{\text{Ln-soil}}/\Sigma C_{\text{Ln-soil}}). \quad (5)$$

The critical value of $A_{\text{Ln-critical}}$ is 1 both in formulas (3) and (4) and in formula (5). At $A_{\text{Ln}} > 1$, the degree of enrichment of the phase with lanthanide is high compared to the initial soil; at $A_{\text{Ln}} < 1$, the enrichment of the phase is lower than the initial soil.

An Example of Calculation of the Affinity Index

The normalized content of lanthanides in the fraction for the soils of the Kama region and Sweden is given in Tables 1 and 2. The calculation of the values of the new index of affinity (A) to carrier phase lanthanides is given in Table 3.

As an example, let us determine the index of lanthanum affinity to the organic phase (Table 3). The $A_{\text{Ln-phase}}$ value in the floodplain of the Kama River is determined from the formula

$$A_{\text{La-phase}} = (C_{\text{La-phase}}/\Sigma C_{\text{Ln-phase}}) / (C_{\text{La-soil}}/\Sigma C_{\text{Ln-soil}}) = (0.2577 : 5.11) / (0.9615 : 14.092) = 0.74.$$

As can be seen, lanthanum has a weak affinity to the organic phase.

Table 3. Indices of selectivity of lanthanides (A) to carrier phases in soils: city of Perm, northern Sweden

Fractions	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Σ
Kama-1 River															
2	1.24	1.08	1.01	0.98	1.24	0.98	1.30	1.19	1.16	1.02	0.95	0.84	0.82		13.81
3	1.63	1.31	0.92	0.81	0.74	0.85	1.08	0.51	1.31	1.31	1.29	1.11	0.99		13.86
4	0.74	0.90	0.80	0.95	1.09	1.08	1.22	1.15	1.18	1.10	1.10	0.89	0.91	0.86	13.97
5	1.01	1.28	1.22	1.31	1.34	1.26	1.35	1.30	1.04	0.81	0.63	0.40	0.40	0.35	13.70
6	1.10	1.08	1.11	1.03	0.82	0.79	0.84	0.92	0.85	0.99	1.09	1.20	1.14	1.16	14.12
City of Perm-2															
2	1.73	1.28	0.89	0.96	0.95	0.82	1.22	0.90	1.16	1.19	1.07	0.97	0.84		13.98
3	3.31	2.37	0.68	0.73	0.68	0.62	0.92	0.68	0.88	0.91	0.82	0.74	0.64		13.98
4	1.00	0.94	0.92	1.05	1.10	1.15	1.25	1.11	1.13	1.08	0.84	0.85	0.81	0.66	13.89
5	0.99	1.06	1.11	1.20	1.25	1.26	1.17	1.28	1.03	0.92	0.73	0.52	063	0.63	13.78
6	1.13	1.46	0.99	0.99	1.08	1.18	0.86	0.80	1.04	1.06	1.03	1.08	1.39	1.28	13.37
Podzol in Sweden, hor. B															
2	0.99	0.94	0.86	1.07	1.07	1.41	1.46	1.10	1.07	1.12	0.99	0.81	0.66	0.83	14.38
4	0.80	0.65	0.84	0.85	1.00	1.27	1.23	1.01	0.96	1.12	1.05	1.05	0.95	1.15	13.93
3	1.04	0.80	1.01	0.96	1.02	1.35	1.28	1.06	1.11	1.13	1.02	0.90	0.71	0.76	14.15
5	0.71	0.77	0.81	0.85	1.01	1.35	1.12	1.00	1.11	1.14	1.08	1.04	0.93	1.01	13.93
6	0.90	0.92	0.97	0.95	0.96	1.19	1.05	0.93	0.89	1.02	0.96	1.04	1.04	1.14	13.96
Podzol in Sweden, hor. C															
2	0.97	1.09	1.09	1.16	1.23	1.08	1.47	1.14	1.05	0.96	0.81	0.68	0.62	0.73	14.08
4	0.84	1.12	0.87	0.90	1.03	0.91	0.99	0.96	0.97	0.90	0.90	1.03	1.12	1.45	13.99
3	1.37	1.32	1.11	1.11	1.09	0.92	1.19	1.03	0.99	0.91	0.82	0.75	0.73	0.78	14.09
5	2.84	2.24	1.94	1.80	1.47	1.01	1.23	1.05	0.92	0.83	0.74	0.69	0.69	0.76	17.21
6	0.79	1.03	1.07	1.07	1.10	1.24	0.94	1.06	1.09	1.09	0.99	0.99	1.21	1.08	14.75

Σ is the sum of the selectivity of lanthanides in each fraction.

Table 4. Values of the pC_{hm} indices and A affinity in soil fractions and selected lanthanides

Fractions	$pC_{Ln\text{-}n,\ \%}$	A_{Ln}	A_{La}	A_{Yb}	$pC_{Ln\text{-}n,\ \%}$	A_{Ln}	A_{La}	A_{Yb}	$pC_{Ln\text{-}n,\ \%}$	A_{Ln}	A_{Eu}	A_{Ce}	$pC_{Ln\text{-}n,\ \%}$	A_{Ln}	A_{La}	A_{Lu}
	Kama-1 River				City of Perm-2				Podzol, hor. B				Podzol, hor. C			
2	0.74	0.99	1.24	0.82	1.9	1.00	1.73	0.84	2.1	1.03	1.41	0.94	3.9	1.00	0.97	0.73
3	1.00	0.99	1.63	0.99	1.2	1.00	3.31	0.64	3.6	0.99	1.27	0.65	1.5	1.00	0.84	1.45
4	36.2	1.00	0.74	0.91	14.9	0.99	1.00	0.81	7.8	1.01	1.35	0.80	12.9	1.00	1.37	0.78
5	7.9	0.98	1.01	0.40	7.5	0.98	0.90	0.63	6.4	0.99	1.35	0.77	5.5	1.23	2.84	0.76
6	50.6	1.01	1.08	1.14	54.5	0.95	1.13	1.39	81.4	1.00	1.19	0.92	66.3	1.05	0.79	1.08

At $A_{Ln\text{-}phase} > 1$, the phase is enriched in this lanthanide; on the contrary, the phase is depleted in this lanthanide at $A_{Ln\text{-}phase} < 1$ compared to the initial soil.

The new index makes it possible to compare the increase/decrease in the affinity of light (La–Gd) or heavy (Tb–Lu) lanthanides to the given phase compared to the initial soil.

DISCUSSION

Let us compare the effectiveness of the new formula of affinity (A) with the traditional pC_{Ln} index based on soils significantly differing in genesis. Let us, first, determine the content of normalized lanthanides (A) in soil fractions and, then, (Table 4) compare the advantage of the structure of the formula for the A affinity over the traditional pC_{Ln} index.

Affinity to the Phase: Exchangeable Cations Associated with Carbonates

Soil samples from the Kama River region. In the floodplain of the Kama River, the phase of cations associated with carbonates is enriched in light lanthanides, in particular, gadolinium ($A_{Gd} = 1.30$) (Table 3). This phase is most significantly depleted in ytterbium: $A_{Yb} = 0.82$.

The urban soil in the city of Perm is dominated by light lanthanides. Among them, a significant excess is recorded for the content of lanthanum ($A_{La} = 1.73$). The “cations associated with carbonates” phase is significantly depleted in europium: $A_{Eu} = 0.82$.

Podzol samples from Sweden. In the “cations associated with carbonates” phase (horizon B), the maximum accumulation is recorded for gadolinium: $A_{Gd} = 1.46$. The minimum content in the phase is recorded for ytterbium: $Y_b = 0.66$.

The rock in this phase is dominated by gadolinium: $K_{Gd} = 1.47$. The minimum value is recorded for ytterbium: $A_{Yb} = 0.62$.

Affinity to Siderophiles

Soil samples from the Cis-Ural region. The proportion of lanthanides fixed by Fe phases is different in the background soil (Kama-1). The highest excess is recorded for lanthanum and gadolinium. Amorphous Fe minerals are enriched in La; the A_{La} affinity for them is 1.63. Crystalline Fe minerals are enriched in gadolinium: $A_{Gd} = 1.35$.

In urban soddy-podzolic soil (the city of Perm-2), amorphous Fe minerals are highly enriched in lanthanum ($A_{La} = 3.31$) and depleted in ytterbium ($A_{Yb} = 0.64$). The maximum value in the crystalline Fe minerals phase, the value is maximal for europium ($A_{La} = 3.26$) and minimal for thulium ($A_{Tm} = 0.52$).

Podzol samples from Sweden. The fixation of lanthanides by Fe minerals in the illuvial horizon can be seen from the strong enrichment of amorphous Fe minerals with europium ($A_{Eu} = 1.35$). The minimum value is recorded for ytterbium ($A_{Yb} = 0.71$). Europium also prevails in crystalline Fe minerals ($A_{Eu} = 1.35$). The minimum value is recorded for lanthanum ($A_{La} = 0.71$).

In rock, the siderophile phase is clearly enriched in light lanthanides. Amorphous Fe minerals are dominated by light lanthanum ($A_{La} = 1.37$). The rock is depleted in heavy ytterbium: $A_{Yb} = 0.73$. The crystalline phase of Fe minerals is also dominated by light lanthanum ($A_{La} = 2.84$); this phase is depleted in the heaviest lanthanide, namely, lutetium ($A_{Lu} = 0.76$).

Affinity to Organophiles

Soil samples from the Cis-Ural region. In [7], the authors draw attention to the confinement of lanthanides to the organic phase of these soils. This is evident when using the pC_{Ln} index. Indeed, analysis of the organic fractions in the soil in the floodplain of the Kama River results in high values: the $pC_{La\text{-}n}$ value is 36.2% for the background soil of the Kama-1 River and $pC_{La\text{-}n} = 14.89\%$ for urban soils in Perm-2 (Table 4). As mentioned above, the $pC_{La\text{-}n}$ index does not have a critical value.

Unlike the $pC_{Ln\text{-}n}$ index, the determination of the affinity (A) of lanthanides suggests that A = 1.00–0.99. With respect to the criterion of affinity to organic matter, there is no enrichment in lanthanides compared to the initial soil.

Podzol samples from Sweden. In Swedish podzol samples, the content of C_{org} varies from 2.4 in hor. B to 0.2% in rock. Despite the strong difference in the content of organic matter (by more than ten times), the accumulation of lanthanides in the fraction of “labile humus extracted with sodium pyrophosphate” decreased by only 2.5 times (Table 3). It is evident that the effectiveness of this reagent is doubtful for weakly humus soils in rock. The disadvantages of the method of successive chemical extraction of carrier phases of heavy metals were discussed in [4]. The 0.1 M pyrophosphate solution designed for dissolving organic matter can also dissolve ferrihydrite and goethite crystals [13, 16]. The use of sodium pyrophosphate at the initial stages of sequential dissolution is possible for hor. B and unsuitable for rock.

In horizon B, the fraction of organic matter is enriched in europium ($A_{Eu} = 1.27$) and depleted in cerium ($A_{Ce} = 0.65$). The reasons for this will be discussed below.

Affinity to the Insoluble Residue

Soil samples from the Cis-Ural region. The soil sediment from the Kama-1 has a high value of the traditional index $pC_{Ln\text{-}n}$ = 50.6%. However, the new indices of lanthanide affinity in the sediment are close to 1: A_{Ln} = 1.01, which indicates a similarity of the composition of the residue to the initial content of lanthanides.

The contaminated urban soil of the city of Perm has a high value of the traditional $pC_{Ln\text{-}n}$ index (54.5%). However, the new A_{Ln} affinity index for this soil is 0.95; i.e. the content of lanthanides proved to be even slightly lower than the content of lanthanides in the initial soil.

Sample soils from Sweden. Horizon B is characterized by a very high value of the traditional $pC_{Ln\text{-}n}$ index (81.4%). The new indices of lanthanide affinity to the residue are equal to 1: A = 1.00. This indicates a similarity of the accumulation of lanthanides in the residue to the initial soil.

Therefore, the new affinity index does not increase the residue, as opposed to the traditional $pC_{Ln\text{-}n}$ index.

Comparison of Two Affinity Indices

Table 4 presents the generalized values of the traditional $pC_{Ln\text{-}n}$ index and new A_{Ln} affinity index. In addition, Table 4 provides data on two lanthanides differing in the atomic number (from light to heavy ones). For the soils of the Kama region, these are two lanthanides: the lightest lanthanide (lanthanum) and heaviest lanthanide (ytterbium). The most contrasting lanthanides are given for the rock in the Swedish podzol: light lanthanum and heavy lutetium. A particular case is the illuvial horizon in the Swedish podzol. Two lanthanides are clearly distinguished here: one with the maximum enrichment of phases (A_{Eu}) and the other with the minimum depletion of phases (A_{Ce}).

Samples from the Kama region. There are differences between the old pC_{Ln} index and new index of lanthanide affinity (A). With respect to the pC_{Ln} index, the proportion of crystalline Fe clearly exceeds the proportion of amorphous Fe in the Fe-amorphous and Fe-crystalline fractions (7.9 vs. 1.0). However, the index of lanthanide affinity (A) to iron phases remains the same: 0.98 for Fe-crystalline fractions vs. 0.99 for Fe-amorphous fractions.

In the Kama-1 soil, the enrichment of almost all phases in light lanthanum is higher than that in heavy ytterbium. Affinity index A is particularly noticeable for the phase of amorphous Fe compounds: A_{La} = 1.63 versus A_{Yb} = 0.99. Therefore, amorphous Fe phases are highly enriched in light lanthanides.

The "cations associated with carbonates" phase is also enriched in light lanthanides: A_{La} = 1.24 versus A_{Yb} = 0.82. Therefore, light lanthanides are strongly sorbed by phases extracted with the mildest reagents.

The same is true for the Perm-1 urban soil: affinity index A is higher for siderophilic phases: for the amorphous Fe phase, A_{La} = 3.31 versus A_{Yb} = 0.64. The same is true for the "cations associated with carbonates" phase: A_{La} = 1.73 versus A_{Yb} = 0.84. Here, light lanthanides are also strongly sorbed by the phases extracted with mild reagents.

With respect to the traditional pC_{Ln} index, the proportion of crystalline Fe compounds (in soils of the Kama region) clearly exceeds the proportion of amorphous compounds: 7.5 versus 1.2. However, with respect to affinity A, the ratios between the phases are almost the same: 0.98 for Fe-crystalline compounds versus 1.00 for Fe-amorphous compounds. On the whole, the affinity of lanthanides to Fe phases by index A is close to 1.0 in soils of the Kama region.

The ratio of lanthanides to organic matter also varies. The values are high for the traditional pC_{Ln} index (from 7.8 to 36.2); however, they are close to the initial value (i.e., to 1) for the affinity of the new A index.

Podzol samples from Sweden. In horizon B, there is a strong difference in the accumulation of europium or cerium. This is determined by the fact that almost all lanthanides in soils generally have the valence Ln^{3+}. However, there are two exceptions: the valence of cerium can also be Ce^{4+}, in particular, under oxidizing conditions, when mineral cerianite (CeO_2) is formed [1]. The second exception is europium, the valence of which decreases to Eu^{2+} in a reducing medium [2]. As follows from Table 4, Eu clearly prevails over Ce in the soluble fractions in the podzol of hor. C: in all fractions (except the residue), the A_{Eu} value is 1.27–1.47 vs. A_{Ce} = 0.65–0.94. The higher content of europium than that of cerium may be due to two reasons. The first reason is the enrichment of the soil with monazite (lanthanide-rich phosphate), some of the forms of which are enriched in europium [15]. The other reason is the reducing medium in the illuvial horizon of the podzol, as follows from studies by microbiologists. These studies also show that the process of reduction (gleying) is of microbiological nature. The vital activity of reductant bacteria requires an energy source. Bacteria require energy for performing the exothermal process (the reduction of elements with a high variable valence to the lower level) (Fe, Mn, etc.). Therefore, the biological reduction of microbes develops most actively in soils with a high content of sugars contained in the humate part of organic matter. In the illuvial horizon of the podzol, the content of C_{org} reaches 2.4%, which may determine the creation of the reducing medium. This issue cannot be solved without the knowledge of the chemical composition of humus and mineralogical composition (absence of monazite).

An increase in the amount of residue is observed for the rock in the Swedish podzol: for the traditional pC index, $pC_{Ln\text{-}n} = 66.3$. However, it decreases for the new affinity index (A = 1.05) close to the initial soil. With respect to the A index, there is no clear difference between light lanthanum and heavy lutetium in the rock.

CONCLUSIONS

The prediction of the behavior of lanthanides (along with other heavy metals) in soils requires the study of their associations with different carrier phases, which are determined using the method of sequential chemical treatment. During the processing of chemical extraction data, the amount of lanthanides is normalized to the clarke number to determine the normal $pC_{Ln\text{-}n}$ index. This approach has a drawback: the $pC_{Ln\text{-}n}$ index does not have a critical value and is not suitable for ranking lanthanides when reagents of different strengths are used.

To solve this problem, it is proposed to use the new method of data processing based on the coefficients developed by geochemists; these coefficients have critical value $K_{\text{crit}} = 1$. We proposed a similar approach in the new affinity formula, where $A_{\text{crit}} = 1$. At $A_{\text{Ln}} > 1$, the degree of enrichment of the phase in lanthanide is high compared to the initial soil; at $A_{\text{Ln}} < 1$, the degree of enrichment of the phase is lower than that of the initial soil. The new formula was used to determine the affinity of lanthanide, A_{Ln}, to the given fraction.

The effect of the two indices, the old pC index and new A index, was compared based on the example of carrier phases in soils of Russia and Sweden. It was revealed that the gradation values of the pC index were abnormally high for the phases of organic matter and residue and were not confirmed by the formulas, the structure of which was determined from the new formulas. The failure of the pC formula is the absence of the critical value of pC_{crit}.

The use of the modern formula of geochemists, including the A affinity formula, showed that the soils of the Kama region were clearly enriched in light lanthanum and depleted in heavy ytterbium.

In the Swedish podzol, there is no significant difference between lanthanum and lutetium. However, there is a dependence associated with the valence of lanthanides. Almost all lanthanides in soils have the valence Ln^{3+}. However, there are two exceptions: the first exception is that the valence of cerium can be Ce^{4+}, in particular, under oxidizing conditions; the second exception is europium, the valence of which decreases to Eu^{2+} in a reducing medium. In the podzol of hor. B, Eu clearly prevails over Ce in the phases. The greater content of europium than that of cerium may be determined by two reasons. The first reason is the enrichment of the soil in monazite (lanthanide-rich phosphate); some of its forms are enriched in europium. The second reason is the reducing medium in the illuvial horizon of the podzol. The content of C_{org} in this horizon reaches 2.4%, which may determine the reducing medium.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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