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我国土壤中稀土元素背景值特征

魏复盛 刘廷良 滕恩江 芮葵生

(中国环境监测总站)

摘要 本文报道了中国土壤15个稀土元素的背景含量、共生组合关系及稀土元素的分异系数和分布模式。讨论了41种土类,35个省市行政区域土壤稀土元素背景含量的差异及其原因。

关键词 土壤;稀土元素;背景值。

我国是稀土资源丰富的国家。近年来,随着稀土资源的开发及稀土微肥在农业上的应用,有必要搞清我国土壤中稀土元素的背景值。美国在大陆连片地区土壤背景值研究中测定了五个稀土元素^[1],在阿拉斯加州土壤背景值研究中测定了6个稀土元素^[2]。我国在过去土壤背景值研究中测定了8个稀土元素^[3]。英国、罗马尼亚及日本等国的土壤背景值研究均未涉及稀土元素^[4]。

本项研究从全国41个土类采集863个样点的土壤样品。样品经碱融, P₂O₅ 萃淋树脂(或阳离子交换树脂)分离富集后,用 ICP-AES 测定,检出率在90%以上,接着讨论了稀土元素背景值的分布特征。

一、我国土壤中稀土元素背景值特征

(一) 稀土元素的分布类型

全国863个土壤样品中,15个稀土元素含量的频数分布均接近对数正态,符合微量元素分布的一般特征。

图1为全国稀土总量 (TR = ΣLa - Lu, + Y) 的频数分布图,其余各稀土元素频数分布与总稀土类似。

(二) 稀土元素共生组合关系

我国土壤化学元素的相关和聚类分析的结果表明,稀土元素是一组共生关系最为密切的元素,八百

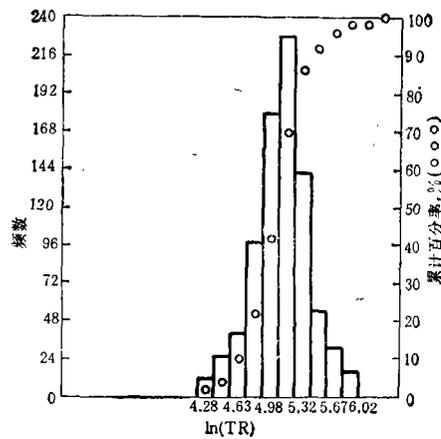


图1 中国土壤中稀土总量对数频数分布 (n = 863)

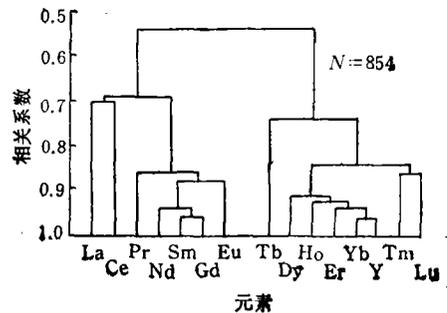


图2 土壤中稀土元素聚类分析

表 1 全国土壤 (A 层) 稀土元素背景值基本统计量

元素	样点数	顺 序 统 计 量								算 术		几 何		95%范围值	
		最小值	5% 值	10% 值	25% 值	中位值	75% 值	90% 值	95% 值	最大值	平均	标准差	平均		标准差
钪	863(26)	0.50	10.2	13.6	18.2	22.1	25.9	31.8	39.3	130.7	22.9	7.63	21.8	1.38	11.4—41.6
钪	863(19)	0.26	18.7	23.3	29.5	36.8	46.6	57.7	70.6	242.0	39.7	14.40	37.4	1.42	18.5—75.3
铈	863(24)	0.02	32.4	39.6	52.9	65.2	78.0	100.2	116.9	265.4	68.4	23.48	64.7	1.40	33.0—126.6
镧	853(29)	0.10	2.96	3.80	5.18	6.57	8.38	10.80	12.40	40.50	7.17	2.828	6.67	1.464	3.11—14.30
铈	863(34)	0.05	11.4	14.8	20.6	25.2	30.9	37.4	44.2	100.8	26.4	8.65	25.1	1.39	13.0—48.4
钆	863(30)	0.004	2.21	3.01	4.04	4.99	6.02	7.23	8.49	20.10	5.22	1.764	4.94	1.397	2.53—9.65
铈	863(39)	0.01	0.42	0.56	0.80	1.00	1.20	1.40	1.61	5.15	1.03	0.328	0.98	1.378	0.52—1.86
钪	853(26)	0.19	2.12	2.74	3.64	4.44	5.26	6.48	7.76	16.80	4.60	1.466	4.38	1.377	2.31—8.30
铈	863(45)	0.005	0.18	0.28	0.42	0.59	0.74	0.95	1.12	3.10	0.63	0.260	0.58	1.523	0.25—1.33
铈	853(22)	0.07	2.03	2.53	3.32	4.03	4.71	5.80	7.03	14.40	4.13	1.309	3.93	1.374	2.08—7.43
铈	853(25)	0.04	0.42	0.51	0.68	0.84	1.00	1.22	1.48	3.04	0.87	0.279	0.83	1.374	0.44—1.56
铈	853(23)	0.13	1.26	1.52	2.02	2.47	2.90	3.52	4.34	9.37	2.54	0.813	2.42	1.371	1.29—4.55
铈	853(23)	0.04	0.18	0.22	0.29	0.36	0.42	0.51	0.62	1.40	0.37	0.115	0.35	1.367	0.19—0.65
铈	863(27)	0.02	1.18	1.48	1.93	2.35	2.75	3.36	4.20	7.68	2.44	0.786	2.32	1.363	1.25—4.32
铈	863(43)	0.002	0.18	0.23	0.29	0.35	0.42	0.51	0.62	1.90	0.36	0.108	0.35	1.337	0.19—0.62
TR	853(13)	18.0	99.7	118.1	148.6	181.1	213.1	259.1	310.2	582.7	187.6	58.6	179.1	1.36	97.1—330.2
Σ Ce	853(30)	15.4	78.5	93.0	116.3	142.8	170.2	210.9	249.2	492.6	143.2	41.46	136.9	1.36	74.0—253.3
Σ Y	853(37)	2.6	19.5	23.5	31.3	37.9	43.8	54.0	66.6	185.0	37.2	10.41	35.6	1.36	19.8—65.8

1. Σ Ce——铈组稀土 (=La + Ce + ... + Eu) Σ Y——钪组稀土 (=Gd + ... + Lu, Y)

2. 样点数栏圆括弧内数据为剔除样点数。

3. 顺序统计量——原始数据按大小排列的顺序值

余样点的稀土元素相关系数为 0.4—0.9。聚类分析结果见图 2。

由图 2 可见,土壤稀土元素间共生组合关系,十分明显地可分为轻重稀土两组(仅 Gd 落在轻稀土内),说明了轻重稀土元素在表生作用过程中地球化学行为仍有一定的差异。

(三) 土壤中稀土元素背景值特点

全国 863 个土壤样品(A 层土壤)中稀土元素背景值基本统计量见表 1。

本研究结果表明,土壤中稀土元素含量严格符合这样的规律,即原子序数为偶数的元素含量明显高于与其相邻的两个奇数元素。这种现象称为奥多-哈尔金斯规则(图 3)。

我国土壤中稀土总量与北美页岩和地壳值接近(表 2),但轻重稀土比值($\Sigma Ce/\Sigma Y$)高于北美页岩和地壳值,显示出土壤相对富集轻稀土,而重稀土相对较易淋失的特点。

土壤中稀土分布模式与北美页岩及地壳类似(图 4)。

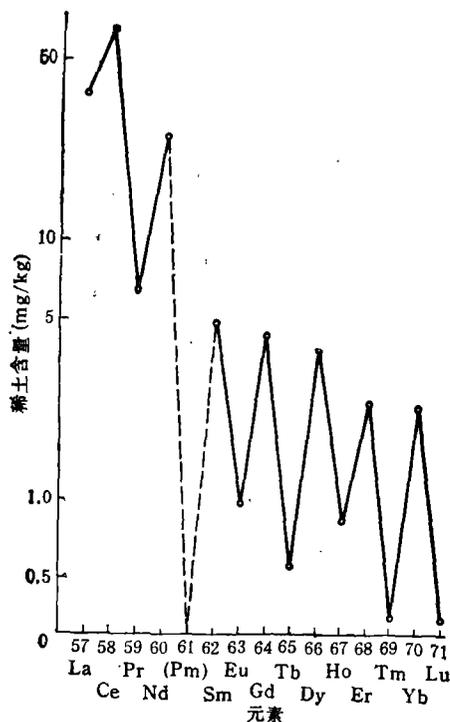


图 3 我国土壤中稀土元素含量(几何均值)

二、各土类中稀土元素背景值特点

表 3 为全国 41 个土类中稀土元素总量及分异系数。稀土元素含量最高的土类为石灰(岩)土,最

表 2 我国土壤中稀土元素总量及分异系数

内容	中国土壤*	北美页岩 ^[2]	地壳 ^[6]
TR(mg/kg)	187.6	187.0	188.8
$\Sigma Ce/\Sigma Y$	3.72	2.98	2.81
δCe^*	0.92	0.92	0.78
δEu^*	0.66	0.66	0.49

* 算术均值

* δCe 和 δEu 表示 Ce 和 Eu 的异常程度,其计算是以科里尔图解为根据的,其计算式分别为

$$\delta Ce = \frac{(Ce)_N}{\sqrt{(La)_N(Pr)_N}}$$

$$\delta Eu = \frac{(Eu)_N}{\sqrt{(Sm)_N(Gd)_N}}$$

(Ce)_N, (La)_N, (Pr)_N, (Eu)_N, (Sm)_N, (Gd)_N 分别为该元素实测值的球粒陨石标准化值。一般认为 δCe 和 $\delta Eu > 1.05$ 为正常, δCe 和 $\delta Eu < 0.95$ 为负异常。

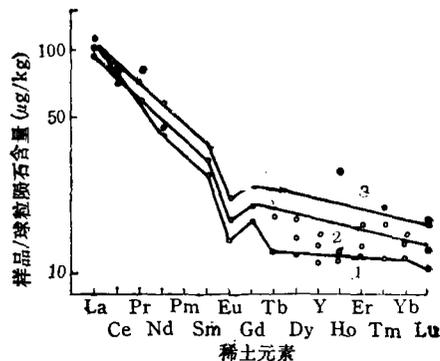


图 4 我国土壤北美页岩^[2]及地壳^[6]稀土分布模式
1.我国土壤 2.北美页岩 3.地壳值

低的为风沙土(除磷质石灰土)。10 个磷质石灰土样均采自西沙群岛,采用中子活化分析法测定了 8 个稀土元素。磷质石灰土中稀土总量极低,仅为 1—3mg/kg。其分布特征为铈强烈的负异常,与海水、珊瑚等有共同特征。反映了西沙磷质石灰土中稀土元素来源于海水。

各土类中稀土总量与全国均值比较的,检验结果表明,石灰(岩)土,水稻土,塍土及黑土极显著偏高;风沙土,栗钙土,棕漠土,棕色针叶林土,绿洲土及灰棕漠土极显著偏低。

我国森林土壤中稀土分异系数 δCe 和 δEu 值从南至北呈有规律的变化(见图 5)。

从南至北, δCe 值逐渐降低,而 δEu 值有逐渐升高的趋势,反映了南方土壤较北方淋溶作用更强。

表 3 全国 41 种土类稀土元素总量 (TR = $\Sigma La - Lu + Y$) 背景值及分异系数

土类名称 (样点数)	TR(mg/kg)				土类名称 (样点数)	TR(mg/kg)				分异系数			分异系数		
	中位值	算术 均值	变异 系数	全 距		中位值	算术 均值	变异 系数	全 距	$\frac{\Sigma Ce}{\Sigma Y}$	δCe	δEu	$\frac{\Sigma Ce}{\Sigma Y}$	δCe	δEu
绵土(12)	174.1	169.2	14	125.9—209.7	3.53	0.87	0.69	74.3—205.1	3.47	0.88	0.73	3.47	0.88	0.73	
壤土(4)	210.8	205.9	7.8	183.1—219.1	3.82	0.78	0.71	101.2—194.7	3.64	0.79	0.66	3.64	0.79	0.66	
黑垆土(7)	158.8	186.4	52	104.1—395.8	3.63	0.81	0.71	142.9—174.8	3.22	0.96	0.66	3.22	0.96	0.66	
黑土(11)	192.3	209.9	29	154.8—372.5	3.69	0.82	0.70	138.0—253.5	2.82	0.76	0.63	2.82	0.76	0.63	
白浆土(10)	183.6	185.6	20	130.7—246.7	3.83	0.90	0.66	94.6—308.3	3.20	0.85	0.68	3.20	0.85	0.68	
黑钙土(18)	177.7	170.0	24	99.1—227.1	3.64	0.75	0.63	68.2—272.6	3.45	0.85	0.62	3.45	0.85	0.62	
潮土(51)	189.1	190.2	21	102.1—305.6	3.65	0.91	0.65	70.2—332.6	3.74	0.85	0.66	3.74	0.85	0.66	
绿洲土(16)	147.7	158.9	14	78.0—213.6	3.53	0.91	0.65	106.9—270.2	3.88	0.82	0.66	3.88	0.82	0.66	
水稻土(58)	210.6	226.2	31	69.1—409.1	3.84	0.87	0.62	79.2—363.7	3.79	0.84	0.64	3.79	0.84	0.64	
砖红壤(7)	133.4	170.3	37	18.0—258.6	3.00	0.99	0.36	117.9—202.1	4.17	0.62	0.64	4.17	0.62	0.64	
赤红壤(30)	203.6	206.3	42	61.7—414.1	3.42	1.09	0.51	91.3—520.1	3.39	0.96	0.64	3.39	0.96	0.64	
红壤(77)	191.1	209.9	42	82.2—582.5	3.98	1.04	0.55	125.6—362.3	4.18	0.81	0.63	4.18	0.81	0.63	
黄壤(37)	177.4	189.0	34	94.9—357.1	4.11	1.11	0.55	67.5—321.8	3.72	0.87	0.96	3.72	0.87	0.96	
燥红土(5)	165.4	172.2	46	64.5—286.2	2.80	0.83	0.45	111.4—257.0	3.83	0.89	0.60	3.83	0.89	0.60	
黄棕壤(35)	166.8	196.3	23	94.7—307.0	3.94	0.89	0.64	94.4—335.5	3.82	0.94	0.67	3.82	0.94	0.67	
棕壤(53)	176.5	178.9	27	88.5—503.4	4.04	0.91	0.62	121.6—187.6	3.78	0.94	0.60	3.78	0.94	0.60	
褐土(45)	192.5	196.7	24	102.6—370.8	3.73	0.94	0.65	92.1—336.2	4.01	0.97	0.60	4.01	0.97	0.60	
灰褐土(5)	172.8	191.9	22	156.9—263.7	3.52	0.79	0.66	130.9—248.8	3.89	0.96	0.66	3.89	0.96	0.66	
暗棕壤(29)	183.2	93.1	24	101.2—324.8	3.93	0.86	0.64	154.2—271.0	3.83	0.84	0.64	3.83	0.84	0.64	
棕色针叶林土(10)	168.5	59.8	30	82.5—223.0	4.16	0.80	0.57	—	—	—	—	—	—	—	
灰色森林土(5)	167.3	93.3	33	135.9—294.0	3.67	0.73	0.62	1—3	—	—	—	—	—	—	

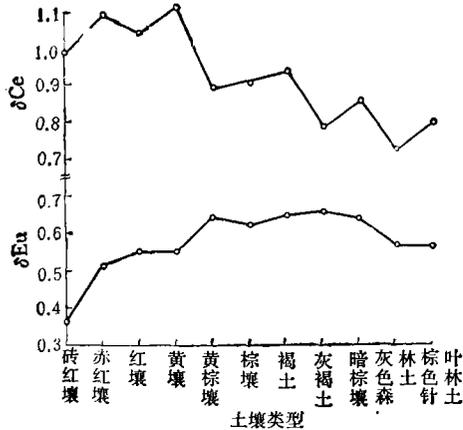


图 5 我国森林土壤中 δCe 和 δEu 值变化趋势

Ce⁺⁺ 易在风化壳上层沉积下来而与其它稀土元素分离; Eu⁺⁺ 较易从风化壳上层淋失, 所以 δCe 和 δEu 值除受母岩的影响外, 在一定程度上反映了土壤风化作用的程度。

森林土壤系列中 δEu 值均低于全国值, 反映了森林土壤发生过程以淋溶为主。

草原土壤系列中稀土元素分布特点为稀土总量低于全国值, δEu 值与全国值接近。稀土总量偏低与草原土壤质地较粗, 粘土矿物较少有密切关系。

荒漠土壤(灰漠土, 灰棕漠土及棕漠土)稀土总量低于全国背景值。三种土壤的稀土分异系数极为相近, 表明发育在干旱地区土壤背景值的区域性。

各种高山土壤虽然有机质含量和质地有较大差异, 但稀土含量和分布没有明显差异。

我国水成土(包括半水成土)和农作土壤多发育在各种沉积母质上, 其稀土总量和分布与全国背景值相比, 大多差异不明显。但水稻土, 垆土和黑土中稀土总量偏高, 可能与它们的粘粒含量和有机质含量有关。

三、不同地区稀土元素背景值特点

29 省市和 5 个沿海开放城市郊区土壤中稀土

元素总量与全国均值的 t 检验结果如下:

极显著偏高的有云南 (236.3mg/kg), 厦门 (235.6mg/kg), 湖北 (223.5mg/kg), 贵州(221.9 mg/kg), 江西 (211.0mg/kg), 天津 (207.6mg/kg) 及广西 (202.1mg/kg); 极显著偏低的有青海 (156.1mg/kg), 甘肃 (156.0mg/kg), 大连 (145.9 mg/kg) 及内蒙 (142.6mg/kg)。以上所列值均为几何均值。

云南、贵州、广西稀土总量较高与石灰(岩)土较多有关, 石灰岩中稀土总量并不高, 但由于石灰岩特殊的化学风化成土过程, 使稀土元素富集。江西、厦门土壤多发育在酸性火成岩母质上, 所以其稀土总量偏高。内蒙, 甘肃, 青海等省区土壤质地较粗, 有机质含量也较少, 所以稀土总量不高。其余省市(包括辽宁, 河北, 山东, 江苏, 浙江, 福建, 广东, 黑龙江, 吉林, 山西, 河南, 安徽, 湖南, 陕西, 四川, 宁夏, 新疆, 西藏, 北京, 上海, 温州, 深圳及宁波等省市)与全国均值比较没有大的差异, 其几何平均值介于 160—200mg/kg 之间。

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This paper introduces several common high sulfate-containing organic wastewater and analyses the detrimental effect of sulfate on anaerobic biological treatment. This includes the first inhibiting effect of sulfate-reducing bacteria on the anaerobic fermentation and the second inhibiting effect of hydrogen sulfide, the reduction product of sulfate, on the methane-producing bacteria. The main factors which determine the extent of the effect of sulfate on the anaerobic treatment, such as COD/SO₄(II) and heavy metal ion concentration of the wastewater to be treated, and pH of digestive juice, anaerobic sludge concentration etc., were discussed. It is found that COD/SO₄(II) of the wastewater is the key factor. Several methods for treatment of this kind of wastewater were also reviewed.

Key Words: Sulfate, Anaerobic treatment, Inhibition.

Environmental Organism Investigation and Environmental Quality Assessment of Intakes of Yangtze River, The Second Water Source of Shanghai. Zhao Lihua, Yao Gendi, Guo Luji, Zheng Liexun, Jiang Xinpo, Zhang Min (Shanghai Fisheries Research Institute), Yang Hequen (Shanghai Fisheries University): *Chin. J. Environ. Sci.*, 12(5), 1991, pp. 74—78

The environmental quality of two water intakes in the Yangtze River, the second water source of Shanghai was assessed by using the phase-dividing method of aquatic organisms and saprobe system. Two sampling stations. Liuhe and Langgang, both located on the southern shore of the Estuary of Yangtze River were selected. Investigations of phyto- and zooplankton were conducted at inshore (5 meters deep) and offshore (10 meters deep and upper, lower layers) sections of the stations in low water (Feb. to March) and high water (July) period of 1989, respectively. Results of synthetic assessment showed that these two intakes belonged to B-mesosaprobic Zone, within the area of clean zone. However, the environmental quality of Langgang station is comparatively better than that of Liuhe station; off-shore better than inshore; flood tide of high water period better than the ebb. It was also found that the water quality in low water period at Liuhe station is better than that in high water period, but at Langgang station, the situation is quite the contrary. The water quality was mainly influenced by the flow from the adjacent rivers, by the sewage discharges from Shanghai and by the flowing direction changes of sewage during flood and ebb tide. These reflected the complexity of the estuary environment.

Key Words: Yangtze water intake, environmental organism, assessment of water quality.

A Survey on the Background Contents of

15 Rare Earth Elements in Chinese Soil. Wei Fusheng, Liu Tingliang, Teng Enjiang and Rui Kusheng (China National Environmental Monitoring Center, Beijing): *Chin. j. Environ. Sci.*, 12(5), 1991, pp. 78—82

863 soil samples were collected from 41 kinds of Chinese soils and the contents of 15 rare earth elements in the soil samples were determined. The REE patterns and their fractions in Chinese soils were discussed and their midvalues, arithmetic means, geometric means, standard deviations and the range values with the confidence level of 95% were given. The differences of REE contents in 41 kinds of soil and in 34 districts were also discussed.

Key Words: Chinese soils, rare earth elements, background contents.

Prediction of Pollution Effect of Jiujiang Power Station on Lushan Natural Reserve Area—A Study on the Application of Complex Terrain Diffusion Model (CTDM). Xu Dashi, Pan Zaitao (Academy of Meteorological Science, State Meteorological Administration), Liu Zulan, Wu Wanyou (Institute of Meteorology, Jiangxi Meteorological Bureau): *Chin. J. Environ. Sci.*, 12(5), 1991, pp. 83—88

By using the complex terrain diffusion model enacted by EPA of the United States in November 1987, the possible pollution effect of sulfur dioxide from the first, second phases and the third phase, which is under construction, of Jiujiang Power Station on Lushan Natural Reserve Area is estimated. The computation shows that CTDM is versatile and convenient to apply. The distribution of SO₂ concentration resulting from airflow both passing over and turning around the mountain body is well defined and reasonable.

Key Words: diffusion model, SO₂ pollution.

The Fuzzy Decision Method of Water Quality Nutrition Evaluation of Lakes. Cao Bin, Song Jianshe (The Second Artillery Engineering Institute, Xi'an): *Chin. J. Environ. Sci.*, 12(5), 1991, pp. 88—91

In the light of the fuzzy characteristic among grades of water quality nutrition evaluation in lakes and on the basis of fully considering the weights of water quality pollution factors, the water quality nutrition evaluation model of lakes was established by applying the fuzzy, composite assessment. The nutrition levels of five major lakes in our country were studied with a more satisfactory result compared with other methods. Thus, an accurate and effective decision method has been provided for water quality nutrition evaluation of lakes.

Key Words: water quality nutrition, environmental quality evaluation, fuzzy composite.