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BIOGEOCHEMICAL DISTRIBUTION OF RARE EARTHS AND
OTHER TRACE ELEMENTS IN PLANTS AND SOILS

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ABSTRACT

The rare earth concentrations in vegetables (corn, potatoes, peas and butternut squash) have been found to be extremely low: 10^{-8} g/g - 10^{-10} g/g. The chondritic normalized vegetable REE patterns are fractionated, including a negative Eu anomaly, and behave as a smooth function of the REE ionic radii. These patterns may be governed by the geochemistry of accessory minerals in the host soils. The depletion factors for various elements by vegetables relative to bulk soils are $\sim 10^{-4}$ for REE, Hf, Ta, Th, and U; $\sim 10^{-3}$ for Al, As, Ba, Cr, Fe, Mn, Sc, Se, and Sr; $\sim 10^{-2}$ for Co, Cs, Na, Ni and Sb; $\sim 10^{-1}$ for Rb; and ~ 1 for K, Zn, and Br.

INTRODUCTION

We have investigated the uptake of 35 trace elements, including the rare earth elements (REE), by vegetables from their host soils. The uptake study of the REE is particularly important as it may provide an indicator of the long-term behavior of their transuranic analogs in the natural environment. In the past there has been little known about the concentration levels of REE, their behavior, and their uptake by plants from soils. Robinson (1943) and Robinson et al. (1958) reported extremely high concentrations of the total REE (2300 ppm) in hickory leaves. The hickory leaves are exceptional in the plant kingdom in the sense that they are excellent accumulators of the REE. However, in general the REE levels in plants are very low, with the result that their precise measurements by classical methods have been rather limited (Cossa, 1870; Scribner, 1939).

In this study, we used the highly sensitive technique of neutron activation analysis (NAA) for elemental determinations. While our work focuses mainly on the REE, the biogeochemical distribution of other trace elements in ^{vegetables} ~~vegetables~~ and soils is also addressed. Plausible mechanisms in soils which control the availability in the REE and other trace elements are discussed in this paper.

EXPERIMENTAL

Samples

The samples we analyzed were received from the following locations:

1) North Eastham, Massachusetts. We received from E. P. Hardy (Health and Safety Laboratory, HASL, New York) six soil layers from different depths and the interior portions of four vegetables grown on the same soil. These were: Soils: S-1958 (0-5 cm), S-1959 (5-10 cm), S-1960 (10-15 cm), S-1961 (15-20 cm), S-1962 (20-25 cm), S-1963 (25-30 cm). Vegetables: F-4383 (corn), F-4385 (potatoes), F-4387 (peas), F-4410 (butternut squash). A detailed description of these vegetable samples and the cultivation and harvesting techniques used has been given by Hardy and Bennett (1977).

2) Richland, Washington. We received from the PNL Arid Lands Ecology Reserve one surface soil (S-0004) and a sample of cheatgrass (F-0004).

Sample preparation was performed in a clean room. About 0.2-0.5 g of a sample aliquot was weighed into a clean 2/5 dram polyethylene vial and the 2/5 dram vial was heat sealed. The 2/5 dram vial was then placed in a 2 dram polyethylene vial which was also heat sealed.

Procedure

Our instrumental and radiochemical neutron activation analysis (INAA and RNAA) scheme used here has been previously reported by Laul and Rancitelli (1976). In brief, our sequential INAA consisted of two irradiation periods and four counting intervals to optimize the detection sensitivities of individual elements. Samples and standards were irradiated in a TRIGA reactor at Washington State University. The irradiated samples were counted on a 130 cc Ge(Li) detector (FWHM 1.8 keV for 1332 keV γ of ^{60}Co). The γ -ray spectra from samples and standards were stored on a magnetic tape and the data reduced by a PDP-15 computer. A USGS BCR-1 sample was used as an internal control in our INAA and RNAA experiments.

Our radiochemical scheme consisted of Ba(U), Sr, and REE group separations. The irradiated samples were fused with $\text{Na}_2\text{O}_2 + \text{NaOH}$ mixture, with the Ba, Sr, and REE mixed carriers already dried in Ni crucibles. The fusion cake was decomposed with H_2O and neutralized with HCl. The Ba and Sr were precipitated as sulfates with H_2SO_4 , and the supernate containing the REE was precipitated as a group hydroxide. The $\text{REE}(\text{OH})_3$ was dissolved in HCl and precipitated with

NH_4HF_2 and HF . The REE fluoride was dissolved in H_3BO_3 and HNO_3 and precipitated as $\text{REE}(\text{OH})_3$ with NH_4OH . The fluoride and hydroxide cycle was repeated twice prior to their counting. The Ba and Sr precipitate was converted to carbonate by boiling with K_2CO_3 . The carbonate was then converted to nitrate with fuming HNO_3 . Using $\text{Fe}(\text{OH})_3$ scavenging, Ba was precipitated as BaCrO_4 at pH 5 and Sr as oxalate from the supernate.

The REE group aliquots were counted twice on the $\text{Ge}(\text{Li})$ system to optimize the detection sensitivities for relatively long-lived isotopes of Ce, Nd, Eu, Gd, Tb, and Tm. Chemical yields of the REE were determined by reactivation. The Ba and Sr were also counted on the $\text{Ge}(\text{Li})$ system. In Ba counting, U was determined via fission products of $12.8\text{d }^{140}\text{Ba}$ - ^{140}La (816,1597 keV) radionuclide. Chemical yield of Sr was measured by reactivation.

RESULTS AND DISCUSSION

Our INAA and RNAA data for 35 elements are shown in Table I. In INAA, the estimated errors due to counting statistics based on BCR-1 are: ± 1 -3% for Al, Fe, Mn, Na, Sc, Co, Rb, Ba, Sr, La, Sm, Eu, Yb, and Lu, and Hf; ± 5 for Br, Ca, K, Cs, Ta, Th, and Zn; and ± 5 -10% for As, Cr, Ni, Sb, Se, Ce, Nd, and Tb. In RNAA, the estimated errors due to counting statistics based on BCR-1 are relatively small: ± 1 -5%. In cases where the concentrations are very low, especially in plants, the error due to counting statistics is somewhat larger: ± 5 -20%. The detection limits in Table I are 3σ of the peak areas. The concentrations for many elements, in particular Cs, Ba, Sr, Th, and REE are extremely low in plants. These concentrations represent the lowest values ever reported for vegetables.

The REE data for vegetables and their host soils are normalized to chondrites, and these REE patterns are shown in Figures 1 and 2. The North Eastham, Massachusetts HASL soils are fairly uniform in their bulk chemical compositions within the depth profile. This is expected as these are cultivated soils. The HASL soils fall in the range of granitic type rocks. This classification is supported by the fact that the chondritic normalized REE patterns show steep negative Eu anomalies which are typical only of some terrestrial granites. The HASL soils are considerably enriched in As, Br, and Se. The Richland soils S-0004 also shows a slight negative Eu anomaly. However, based on major, minor and trace elements, the soil seems to consist of about equal proportions of granitic and basaltic components.

Rare Earth Patterns

The most striking feature observed in our plant study is that the chondritic normalized REE patterns behave as a smooth function of the REE ionic radii. The chondritic normalized REE patterns (Fig. 1) in HASL vegetables relative to the host soil are somewhat fractionated. All the vegetables show similar REE patterns (Fig. 1) in HASL vegetables relative to the host soil are somewhat fractionated. All the vegetables show similar REE patterns, including the negative Eu anomaly, and a steeper slope from the light REE to the heavy REE with the chondritic normalized La/Lu ratio of ~ 25 as compared to a La/Lu ratio of ~ 10 in the host soil.

The possibility of soil contamination in the HASL plants is remote. The REE concentrations in these vegetables relative to the host soils are extremely low ($\sim 10^4$ times); 2-18 ppb for La to 0.02-0.04 ppb for Lu, and these concentrations most likely represent indigenous contents in plants. Furthermore, these samples represent the interior portions of the vegetables produced, which were never exposed to any soil contamination. On the other hand, cheatgrass (F-0004) was probably contaminated with soil due to the nature of its growth characteristics. It also contained higher concentrations of the REE, and displayed a REE pattern identical to its host soil S-0004 (Fig. 2). Based on the REE and other trace elements (Se, Cr, Sb, Cs, Hf, Th, and U), the soil contamination was estimated to be 0.5% in the cheatgrass. Thus, the REE concentrations and their patterns, together with other trace elements, provide us a strong indication of whether a plant has been contaminated by its host soil.

Mechanisms Controlling Availability

The REE patterns are fractionated in plants and are similar to the REE pattern observed in the mineral apatite (Haskin and Schmitt, 1967). This suggests that the REE uptake by plants from host soils may be dominated by the geochemistry of accessory materials. The accessory minerals such as apatite, biotite, hornblende, etc. have very high distribution coefficients for the REE relative to the major minerals such as olivine, plagioclase, orthopyroxene, clinopyroxene, etc. (Haskin and Schmitt, 1967; Laul and Schmitt, 1975). On weathering of the rock minerals in soil, the accessory minerals are the first to become loose or decompose releasing the REE to become freely available in the soil. Thus, a soil can be considered to consist of two types of components. Component 1 includes mostly accessory minerals and demineralized material that contain a significant fraction of the REE and other trace elements which are soluble or amenable to dissolution to form a pool that serves as a reservoir

for the uptake of the REE and other trace elements by plants. Component 2 includes the minerals (mostly major) that are insoluble or resistant to dissolution and also contains the remaining REE and other trace elements. The REE patterns in soils (Figs. 1 and 2) are comprised of Components 1 and 2, whereas the REE patterns observed in plants (Fig. 2) are perhaps reminiscent of Component 1 which may be governed by the accessory minerals, provided there is no significant fractionation of the REE uptake by plants. We are pursuing aqueous and chemical extracts of the soils to characterize Component 1.

At this stage we cannot rule out the possibility of selective uptake of the REE by plants from Component 1 in a manner which behaves as a smooth function of the REE ionic radii. Plants are known to cause fractionation in elements which behaves geochemically alike in terrestrial systems, depending on the selective charge and size of a metal ion (Epstein, 1972; Mortvedt, et al., 1973; Schneiderman, et al., 1975). This is supported by our data on other trace elements (Table 1), where the elemental ratios of geochemically alike pairs such as Rb/Cs, Fe/Mn, Sb/As, Ba/Sr, etc. are different in soils than in plants. However, the fractionation of REE by plants is less likely due to the fact that the physical and chemical properties of the REE, unlike other geochemical pairs, are very much alike. This is supported by our data on a 9% hydrogen peroxide extract from the soil. The chondritic normalized REE pattern in the peroxide fraction is similar to those observed in plants. This suggests strongly that the plants are probably not fractionating the REE during their uptake. We estimated the % REE extracted by H_2O and 9% H_2O_2 fractions from the soil. Based on La, for example, the H_2O fraction contains $3.0 \times 10^{-3}\%$ La and the H_2O_2 fraction contains 0.56% La relative to the total La concentration in the bulk soil. These estimates yield 0.90 ppb La in the H_2O fraction/gram of soil, and 170 ppb La in the H_2O_2 fraction/gram of soil, which are potentially available for the uptake by plants from the Component 1 pool. The mean La concentration in HASL plants is 7 ppb, which corresponds to 800% (essentially complete) uptake from the H_2O extract fraction and 4% uptake from the H_2O_2 extract fraction, respectively. Our future experiments should enable us to investigate more on this aspect.

Hogdahl (1966) has reported REE data for sea water, which suggests that Ce in aqueous systems can exist as the +4 state. Further, Robinson et al. (1958)

in their work on REE in hickory leaves reported large fluctuations in the proportion of Ce relative to La and Nd, and Ce seemed to correlate with oxidation-reduction conditions in the host soil profile. They attributed this anomalous behavior of Ce to the presence of Ce^{+4} which is strongly retained in oxygenated subsoil, and thus is less available to plants relative to the other REE that do not undergo valence change under soil conditions. However, based on the smooth REE patterns observed in soils and plants, and H_2O and 9% H_2O_2 soil extracts, we note that Ce most likely exists in the +3 state in the Component 1 pool of the soil and during its uptake by plants.

The solubility of the REE in the pool is another factor which may govern the observed REE patterns during their uptake by plants. The REE in aqueous systems at pH 5-8 form $REE(OH)_3$, and their solubility products vary decreasingly from La = 1×10^{-19} to Lu = 2.5×10^{-24} (Stevenson and Nervik, 1961). If we plot the REE solubilities in a fashion similar to that shown in Figures 1 and 2, the pattern is not at all a smooth function of the REE ionic radii. This suggests that either the REE uptake is via different chelating systems, in which case the hydroxide solubility products are not applicable, or the REE concentrations in the pool are well below the hydroxide solubility products.

Depletion Factors

We have plotted in Figure 3 the concentration ratios of the REE and other trace elements (Table 1) in HASL plants relative to the bulk host soil. These ratios may change somewhat, depending on the elemental concentrations in Component 1 of the soil. Nevertheless, the gross pattern shows the relative degree of biogeochemical distribution of various elements by plants, assuming the proportion of Components 1 and 2 remains constant during the uptake. The elements in Figure 3 are arranged in decreasing order. The depletion factors in major groups are $\sim 10^{-4}$ for REE, Hf, Ta, Th, and U; $\sim 10^{-3}$ for Al, As, Ba, Cr, Fe, Mn, Sc, Se, and Sr; $\sim 10^{-2}$ for Co, Cs, Na, Ni, and Sb; 10^{-1} for Rb; and ~ 1 for K, Zn, and Br. The elements K and Zn are essential nutrients in plants. Bromine is monovalent and very mobile, and thus is easily taken up by plants. The high uptake factor for Rb is due to substitution for K (Epstein, 1972). The Cs, being a larger ion (1.78 Å) than Rb (1.56 Å), has less tendency for substitution and thus less uptake. The higher oxidation states +3 and +4 metal ions have in general extremely low (10^{-3} to 10^{-4}) uptake factors. The uptake mechanism by plants is quite complex and selective for different elements. Our

gross pattern (Figure 3) supports the notion that the selective charge and size of an ion play a dominant role in plant uptake from Component 1 in soils. However, the REE are probably taken up without significant fractionation by plants from Component 1. Under steady state conditions, the depletion factors essentially yield the maximum uptake limits by HASL plants from their host soil. We should point out, however, that our results for 35 trace elements in peeled vegetables are a limited data base at this stage and thus need not represent a mean of all plants. We plan to pursue our work on other plants grown on other soils and test our general proposed plausible mechanism of the uptake of REE and other trace elements by plants.

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FIGURE CAPTIONS

- Fig. 1 The REE abundances in HASL vegetables and soils are normalized to chondrite meteorites. The chondritic abundances used for normalization are: La 0.34, Ce 0.91, Pr 0.12, Nd 0.64, Sm 0.195, Eu 0.073, Gd 0.26, Tb 0.047, Ho 0.078, Er 0.20, Tm 0.032, Yb 0.22, and Lu 0.034 (Laul and Schmitt, 1975).
- Fig. 2 The REE abundances normalized to chondrite meteorites. See Fig. 1 for chondritic values.
- Fig. 3 Average elemental concentration ratios in HASL vegetables to HASL bulk soil.

TABLE 1 ELEMENTAL ABUNDANCES (ppm) BY INAA AND RNAA IN SOILS AND PLANTS*

ELEMENTS	EASTHAM MASS. SOILS, VEGETABLES; HASL NO.											RICHLAND, WA.		
	S-1958 0-5 cm	S-1959 5-10 cm	S-1960 10-15 cm	S-1961 15-20 cm	S-1962 20-25 cm	S-1963 25-30 cm	MEAN SOIL	F-4383 CORN	F-4385 POTATOES	F-4387 PEAS	F-4410 SQUASH	S-0004 SURFACE SOIL	F-0004 CHEAT GRASS	BCR-1 USGS STD.
Al	3.4 E + 4	3.0 E + 4	3.2 E + 4	3.6 E + 4	-	-	3.3 E + 4	70	50	60	110	9.3 E + 4	720	7.2 E + 4
Fe	1.3 E + 4	1.4 E + 4	1.1 E + 4	1.1 E + 4	1.3 E + 4	1.3 E + 4	1.3 E + 4	40	40	90	50	5.1 E + 4	260	9.5 E + 4
Mn	350	350	340	340	-	-	345	6.0	5.0	10	10	1130	50	1400
Na	4200	4500	3900	3900	4500	4800	4300	40	50	50	70	1.5 E + 4	100	2.4 E + 4
K	1.1 E + 4	1.1 E + 4	-	-	-	-	1.1 E + 4	1.2 E + 4	2.4 E + 4	2.3 E + 4	2.5 E + 4	-	4170	1.4 E + 4
Sc	2.9	3.0	2.7	2.4	2.8	2.8	2.8	5.0 E - 3	5.0 E - 3	5.0 E - 3	7.0 E - 3	17.0	0.074	32.0
Cr	130	140	130	90	120	140	120	0.60	0.32	0.31	0.73	60	0.43	18
Co	2.4	2.5	2.2	1.7	2.2	2.4	2.2	0.015	0.13	0.10	0.17	18.5	0.18	36.0
Ni	40	40	40	30	40	50	40	<0.5	0.80	1.5	1.1	<15	<1	<10
Zn	40	35	30	30	35	30	33	34	21	38	37	160	12	130
Br	5.1	6.7	5.4	6.1	6.0	7.7	6.1	0.90	4.2	3.3	9.5	1.3	2.8	-
As	3.8	4.7	4.3	4.1	3.5	2.2	3.8	<0.03	<0.03	<0.03	<0.06	3.3	0.07	-
Sb	0.25	0.28	0.22	0.23	0.25	0.44	0.28	<2 E - 3	<2 E - 3	0.014	0.010	0.60	0.029	0.70
Se	4.7	3.2	3.3	2.4	2.6	5.1	3.5	<0.03	<0.03	<0.03	<0.05	1.7	<0.03	-
Rb	32	34	24	24	33	34	30	3.0	5.4	3.4	12.7	55	0.9	46
Cs	0.76	0.82	0.65	0.64	0.80	0.74	0.73	<2 E - 3	8.0 E - 3	3.5 E - 3	0.013	2.7	0.016	0.92
Ba	140	170	180	150	200	250	180	0.050	0.12	0.12	0.28	640	20	670
Sr	40	45	40	45	60	60	50	<0.2	<0.2	0.62	0.76	290	5.4	330
La	23.0	28.9	28.2	33.2	32.0	35.0	30	5.0 E - 3	2.0 E - 3	5.1 E - 3	0.018	36.1	0.17	26.0
Ce	47.5	65.7	50.4	72.4	70	74	63	0.010	2.5 E - 3	6.4 E - 3	0.016	74.7	0.33	54.0
Pr	4.9	8.2	6.8	7.9	-	-	7.0	<1 E - 3	<2 E - 3	<2 E - 3	< E - 3	8.4	0.040	6.7
Nd	21.3	34.8	26.9	35.0	27	30	29	<0.010	<0.010	<0.010	<0.010	34.6	0.15	30.0
Sm	3.68	7.00	4.26	5.34	5.30	5.70	5.2	7.4 E - 4	2.1 E - 4	5.5 E - 4	1.0 E - 3	6.60	0.035	6.60
Eu	0.39	0.57	0.43	0.49	0.47	0.44	0.46	1.0 E - 4	3.0 E - 5	4.0 E - 5	2.0 E - 4	1.55	8.4 E - 3	1.90
Gd	3.2	5.2	3.4	4.3	-	-	4.0	<2 E - 3	<2 E - 3	<2 E - 3	<3 E - 3	6.2	0.037	6.7
Tb	0.46	0.87	0.49	0.64	0.51	0.55	0.58	<1 E - 4	1.0 E - 4	<1 E - 4	2 E - 4	0.95	8.6 E - 3	1.0
Ho	0.68	1.2	0.84	0.99	-	-	0.93	1.2 E - 4	8.7 E - 5	6.2 E - 5	1.4 E - 4	1.5	<0.02	1.2
Er	1.8	2.6	2.0	2.4	-	-	2.2	<5 E - 4	<2 E - 3	<5 E - 4	<5 E - 4	3.9	<0.5	3.5
Tm	0.28	0.40	0.29	0.37	-	-	0.33	<3 E - 4	<1 E - 4	<2 E - 4	<2 E - 4	0.59	0.05	0.52
Yb	1.8	2.5	2.0	2.4	2.6	2.3	2.3	2.0 E - 4	0.80 E - 4	9 E - 5	4.2 E - 4	3.5	0.020	3.5
Lu	0.27	0.38	0.30	0.37	0.39	0.32	0.34	2.7 E - 5	<2 E - 5	1.3 E - 5	4 E - 5	0.51	3.0 E - 3	0.52
Hf	8.9	9.5	8.0	8.0	11.1	9.7	9.2	<3 E - 3	<2 E - 3	<3 E - 3	<4 E - 3	8.1	0.026	4.7
Ta	2.7	2.2	2.1	2.0	1.9	3.0	2.3	<1 E - 3	<1 E - 3	<1 E - 3	<6 E - 3	1.1	5 E - 3	0.80
Th	14	14	10	14	14	15	14	<5 E - 3	8 E - 3	0.015	0.020	8.2	0.040	6.0
U	3.2	3.3	2.4	3.5	-	-	3.1	8 E - 4	8 E - 4	<1 E - 3	<1 E - 3	2.5	0.012	1.7

*E IS BASE TO 10 - Ba, Sr, REE (La-Lu) AND U ELEMENTS EXCEPT IN S-1962 AND S-1963 WERE OBTAINED BY RNAA.