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ABSTRACT

The plant uptake from several bulk soils has been determined for neodymium, a chemical analog to the transuranium elements americium and curium, and several other native rare earth elements as well. These investigations have demonstrated that neodymium, which has very similar chemical properties to americium and curium and should have a similar environmental behavior, does behave indistinguishably under both laboratory and field conditions. The uptake of the weathered or mobile forms of these elements from soils is expected to be governed primarily by their identical oxidation states and nearly identical ionic radii. This hypothesis is strongly supported by the chondritic (primordial) normalized rare earth element patterns in several plants. In these samples, the entire series of rare earth elements behaves as a smooth function of the REE ionic radii, as is also seen in the contiguous soils. This behavior suggests that the plant uptake of other ions with similar chemical properties (i.e., americium and curium) would also be governed by ionic size and charge.

INTRODUCTION

Current theoretical and empirical data are not adequate to predict the effects of long-term biogeochemical weathering processes on the geochemical mobilization (or immobilization) and biological availabilities of the transuranium elements. The inability to predict these effects creates a serious problem in estimating the ultimate consequences of the release of the transuranics into the environment. The long-term

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behavior of transuranic elements may be modeled effectively by the behaviors of naturally occurring analog elements that have been subjected to very long-term biogeochemical weathering processes and which have reached a steady-state equilibrium within the environment. Natural weathering processes should effect similar changes in analog elements and the corresponding transuranic elements based on similar chemical properties of the analog:transuranic pairs.

The chemical properties which are the most significant in the choice of analog:transuranic elemental pairs include: a) the oxidation states likely under normal Eh and pH conditions; b) the ionic radii; c) the hydrolysis constants; and d) the solubility products of the principal species. Although the actinide elements have a much wider range of potentially stable oxidation states, they are quite similar to the lanthanide series elements. Only the +3 state is possible in typical soil systems for Am, Cm, and the lanthanides. The known chemical behavior of the trivalent actinides is nearly identical to the behavior of the trivalent lanthanides except for a slightly greater effect of covalency in the bonding strength of the actinides. Using these criteria (principally ionic charge and ionic radius), the analog:transuranic elemental pairs listed in Table I were selected. The emphasis of this research has been on the Am:Nd and the Cm:Nd transuranic:analog pairs.

● Pu^{+4}	**0.98**
Th^{+4}	**1.07**
● Pu^{+6}	**0.89**
U^{+6}	**0.92**
● Am^{+3}	**1.07**
Nd^{+3}	**1.07**
● Cm^{+3}	**1.06**
Nd^{+3}	**1.07**

TABLE I. IONIC RADII OF ANALOG: TRANSURANIC ELEMENTAL PAIRS

The proposed analog elements are all naturally occurring and are present in major, minor, and accessory minerals, and the reaction products due to weathering processes which form terrestrial soils. The distributions of the analog elements between these geological compartments and soil solutions or other aqueous phases are expected to be governed by the steady-state processes that are the result of long environmental equilibration times and by their chemical properties. Once the analog elements are released from mineral phases, they equilibrate in the soil system. The same chemical, biological, and physical processes which affect them will also affect transuranic elements which enter the environment. In an environmental steady-state condition, the transuranic elements would be expected to be distributed throughout the various weathered phases of the soil system in the same manner as their analog elements. Thus, measurements of the concentration ratios for the biological incorporation of analog elements from soils to plants should permit an estimation of the concentration ratios for environmentally equilibrated transuranium elements.

While it is not possible to examine long-term behaviors, both laboratory and field investigations have been performed comparing the relatively short-term behaviors of two analog element:transuranic element pairs. These include physical-chemical soil investigations and determinations of plant uptake using the transuranic elements Am and Cm and both native and amended Nd.

EXPERIMENTAL

Determination of $K_{D\text{-Experimental}}$

Operationally defined experimental distribution coefficients ($K_{D\text{-exp}}$) were determined for trace concentrations of ^{241}Am, ^{244}Cm, and ^{147}Nd between a solution of 0.05 M $Ca(NO_3)_2$ and a sample of Ritzville silty loam as a function of pH, contact time, and soil pretreatment conditions. The $K_{D\text{-exp}}$ values were determined for duplicate soil suspensions adjusted to initial pH values of 1.5 to 7.0 and equilibrated with continuous shaking for time periods of 1, 4, 8, and 24 hours. A $Ca(NO_3)_2$ solution:soil (particle size, <100 mesh) ratio of 10:1 was used. Each of the radiotracer elements was added to the soil suspension in the nitrate form and at a concentration level which was chosen to be at least a factor of 100 below the solubility limit established by the metal hydroxide solubility product constants. These pH conditions and equilibration times were duplicated for both unwashed Ritzville silty loam soil and for soil which had been pre-washed by three sequential treatments with 0.05 M $Ca(NO_3)_2$ to remove fine soil colloids. After shaking of the soil suspensions for the appropriate time interval, the samples were settled for one hour, and the supernate was filtered through a 0.45μ Nucleopore filter. An aliquot of the filter supernate was evaporated to dryness on an aluminum planchet and counted on an intrinsic Ge diode for measurement of the 91 keV ^{147}Nd γ-ray, the 59.6 keV ^{241}Am γ-ray, and the ^{244}Cm 17.8 keV X-ray peaks. Standards for geometric and matrix calibration were prepared in the same manner. $K_{D\text{-exp}}$ was calculated from the following equation:

$$K_{D\text{-exp}} = \left(\frac{C_o - C_e}{C_e}\right)\left(\frac{V}{W}\right)$$

V = total sample solution volume
W = total sample weight
C_o = initial activity in solution
C_e = final activity in solution

Rare Earth Element Analysis by Neutron Activation

The concentrations of Nd and other members of the lanthanide series in plant materials and some soil samples were determined by neutron activation followed by a radiochemical group separation step and subsequent

γ- or X-ray counting using a Ge(Li) diode or an intrinsic Ge diode. Samples and standards were irradiated at a neutron flux of approximately 6 x 10^{12} n/cm^2/sec for 6 hours. After a 2-day decay time, the samples were transferred into nickel crucibles with a rare earth element mixed carrier already dried therein. The samples were then fused using a Na_2O_2-NaOH mixture. The resulting fusion cake was dissolved in H_2O and neutralized with HCl. The rare earth elements were precipitated as the hydroxides with NH_4OH, redissolved in HCl, and precipitated as the fluorides with NH_4HF_2. This fluoride and hydroxide precipitation carrier cycle was repeated three times to insure a radiochemically pure product. The resulting group of rare earth elements was then counted on a Ge(Li) or intrinsic Ge system. After a decay period of 20 to 30 days, the samples were again counted, this time for 100-1000 minutes to optimize detection sensitivities for the longer-lived isotopes. Chemical yields for the rare earth elements were determined by reactivation. A more detailed description of this RNAA technique is given elsewhere in these proceedings by Laul, et al (1). The concentrations of the rare earth elements in some soil samples were determined by instrumental neutron activation analysis. Details of the INAA procedure are given elsewhere (2).

Plant and Soil Samples from the Health and Safety Laboratory

Freeze-dried samples of the fruiting portions of four vegetable species and of six different depth layers of contiguous soils were obtained from the Health and Safety Laboratory (HASL) garden plot in North Eastham, Massachusetts. The vegetables included squash, corn, potatoes, and peas. These plants were grown during the summer season of 1975 and were harvested that fall. Extreme care was exercised during the collection, processing, and analysis of these vegetable samples to ensure that no surface dust contamination was transferred into the fleshy portions of the vegetables which were actually analyzed. A complete description of the cultivation and harvesting procedures has been given by Hardy and Bennett (3). The contents of the rare earth elements in these vegetables and soils were determined by RNAA.

Plant Samples from the Arid Lands Ecology Reserve

Samples of cheatgrass (*Bromus tectorum*) were cultivated in amended lysimeters at the Battelle-Northwest Arid Lands Ecology (ALE) Reserve in Richland, Washington. The lysimeters, containing Ritzville silty loam soil, were spiked with the nitrate forms of ^{244}Cm, ^{241}Am, and stable Nd. These amendments were added to a small quantity of soil which was placed as a 0.5 cm thick layer near the tops of the lysimeters and was covered with a 10 cm layer of unspiked soil. A complete description of the spiking, planting, and harvesting procedures used for the lysimeters has been reported by Schreckhise, et al (4).

The cheatgrass samples were grown under naturally prevailing arid conditions and were harvested after a seven-month growing season. The samples were washed three times with triply distilled water to remove any surface dust contamination. The concentration of Nd was determined by RNAA. The concentrations of ^{244}Cm and ^{241}Am were determined by wet ashing of the sample, ion exchange chromatography cleanup of the digestate, and standard alpha energy analysis of electroplated samples (5).

Plant Samples from Oak Ridge National Laboratory

Snap beans (Phaseolus vulgaris) were cultivated in growth chamber pots of homogeneously mixed soil at Oak Ridge National Laboratory (ORNL). The growing medium was a floodplain soil that had been contaminated approximately 30 years ago (6). To this soil which already contained ^{241}Am were added the citrate forms of ^{244}Cm and a stable enriched Nd isotope (>95% ^{146}Nd). Stems and leaves portions of mature plants were analyzed. The ^{244}Cm and ^{241}Am contents were determined by alpha energy analysis after dry ashing, acid leaching, solvent extraction cleanup of the leachate, and electroplating. The Nd concentration was determined by INAA.

RESULTS AND DISCUSSION

$K_{D\text{-}exp}$

The purpose of the laboratory determination of experimental distribution coefficients ($K_{D\text{-}exp}$) was to compare the rates at which the three isotopes ^{147}Nd, ^{241}Am, and ^{244}Cm distributed themselves between the solid soil phase and the $Ca(NO_3)_2$ phase as a function of system pH and soil pretreatment conditions and to determine the ultimate distributions. At the trace concentration levels used, the processes removing the isotopes from solution include principally ion exchange, adsorption and occlusion. Precipitation of insoluble species was avoided by the choice of metal concentrations. Representative data (averages of duplicate samples) for $K_{D\text{-}exp}$ as a function of final system pH are shown in Figure I for two different contact times. These data indicate that the values of $K_{D\text{-}exp}$ for these three isotopes co-vary systemically and that the same proportions of each of these elements is held in soil solution in these experimental systems.

The combinations of time, pH, and soil pre-treatment experimental conditions yielded approximately 40 sets of $K_{D\text{-}exp}$ data for the three elements. Correlation coefficients for the covariance of the $K_{D\text{-}exp}$ values for the analog:transuranic elemental pairs were determined by simple regression. Results are given in Table II. In all size cases, the

SIMPLE CORRELATION COEFFICIENTS (r) FOR

ANALOG-TRANSURANIC PAIR	WASHED SOIL	UNWASHED SOIL	WASHED + UNWASHED SOILS
Nd-Am	0.95	>0.99	0.99
Nd-Cm	0.95	0.98	0.98

TABLE II. CORRELATION OF ANALOG: TRANSURANIC $K_{D\text{-}EXP}$ VALUES correlation of the analog element distribution coefficient with the transuranic element distribution coefficient is quite good, with r values of 0.95 or greater, and indicate that there are no discernible differences in the behaviors of the analog:transuranic pairs under the conditions evaluated by these techniques. These data suggest quite strongly that similar mechanisms for each of these elements may function under a variety of experimental conditions to control the proportion of the total elemental concentration that is held in soil solution. This is particularly significant since the uptake of these elements by plants is related to the concentrations which may be maintained in solution in soil systems.

Rare Earth Patterns in HASL Soils and Plants

The incorporation of non-essential trace elements by plant species is a complex function of many factors. Two of these factors which may be particularly significant are the ionic charge and the ionic radius of the element in question. All of the lanthanide elements commonly exhibit the same environmental oxidation state, +3, and, therefore, offer a unique opportunity to evaluate uptake as a function of uniformly decreasing ionic radius, due to the lanthanide contraction. The concentrations of the rare earth elements (REE), normalized to chondritic (primordial) REE concentrations (7), for four layers of cultivated soil and for the four HASL vegetable samples are depicted in Figure II as a function of REE ionic radii. It is very significant that the uptake of the naturally occurring REE by these vegetable samples under normal growing conditions behaves exactly as a smooth function of the REE ionic radii, as do the REE patterns in the contiguous soils. These data strongly suggest that the REE are taken up from soils as they are made available to the plant roots, a feature that may be controlled by the REE ionic radius.

The curves in Figure II show that there is an apparent increase in the La/Lu ratio in the plants over that in the soil samples. This increase would suggest a discrimination by the plants against the heavier REE during uptake. This apparent fractionation is related to the fact that rare earth patterns for the soils are for the bulk soils, where plant uptake is from a small portion of this total pool, the portion that may freely enter the soil solution. The pool of plant-available elements will have a slightly different rare earth pattern from that observed for the bulk soil (8). The smooth REE pattern should be identical in the plants and the plant-available pool, the relative uptake of each REE being identical. Studies are presently underway to define the precise REE patterns of the pools of weathered, potentially biologically available REE in natural soil systems.

These data further suggest that since the chemical properties of the lanthanide elements and their corresponding actinide elements are in several instances quite similar, an estimate of the potential uptake of selected transuranic elements may be obtained from the uptake of the REE with the same ionic charge and similar ionic radius. More specifically, the uptake of the lanthanide Nd and the actinides Am and Cm should be nearly identical because of the very similar chemical properties of these three elements.

Uptake of Am, Cm, and Nd

The results of the laboratory $K_{D\text{-}exp}$ investigations demonstrated that physical-chemical principles will effect indistinguishable behaviors of Am, Cm, and Nd in soil suspension. The uptake of the series of REE by the HASL vegetable samples further demonstrated that the native REE with similar charge/radius ratios are not fractionated during plant uptake. A summary of the additional studies of the plant uptake of Am, Cm, and Nd from two different plantings is given in Table III. These data are reported as concentration ratios (CR's). (The CR is defined as the ratio of the concentration of the element in the plant to the concentration of the element in the soil, both concentrations given on a dry weight basis.) The same forms of all three elements (as a nitrate) were added to the ALE soil. The citrate forms of Nd and Am were added to the ORNL soil, while the Am was already present. [However, data suggest that this Am was monomerically dispersed throughout the soil, as would also be expected for the ultimate distribution of the Nd and Cm (6). Therefore, the ultimate effect is one of essentially identical chemical forms available for uptake by the snap beans.]

PLANT	**CONCENTRATION RATIO**		
	Am	**Cm**	**Nd**
ALE CHEATGRASS-LEAVES AND STEMS (LYSIMETERS)	4.8×10^{-4}	2.5×10^{-4}	6.5×10^{-4}
ORNL SNAP BEANS-LEAVES AND STEMS (GROWTH CHAMBER)	0.8×10^{-3}	0.7×10^{-3}	1.2×10^{-3}

TABLE III. PLANT UPTAKE OF Am, Cm AND Nd UNDER CONTROLLED CONDITIONS

These data in Table III show that both the dry land cheatgrass species grown on a sandy, low organic matter soil and the snap beans grown in a humid greenhouse environment on a soil with a greater humus content did not differentiate significantly between these three isotopes during their uptake. The CR's for the Am, Cm, and Nd were not distinguishable for the individual plant species. This evidence, together with the laboratory sorption experiment data, indicates that Nd acts as a good short-term analog element for Am and Cm, and further, suggests that it should serve as a useful long-term predictor of transuranic behavior, since no measureable geochemical or biochemical fractionation has been observed during these short-term studies.

SUMMARY

1. Based on several fundamental geochemical properties, Nd appears to be an ideal chemical analog for the transuranic elements Am and Cm.
2. The chondritic normalized REE patterns in several plants behaves as a smooth function of the REE ionic radius, as do the REE patterns in the contiguous soils.

3. Laboratory sorption investigations indicate that both the rate of Am, Cm, and Nd removal from soil solutions by the particulate phase and the fraction ultimately removed are indistinguishable for these three elements.

4. Both greenhouse and field experiments have demonstrated that plant CR values for Am, Cm, and Nd are not measureably different.

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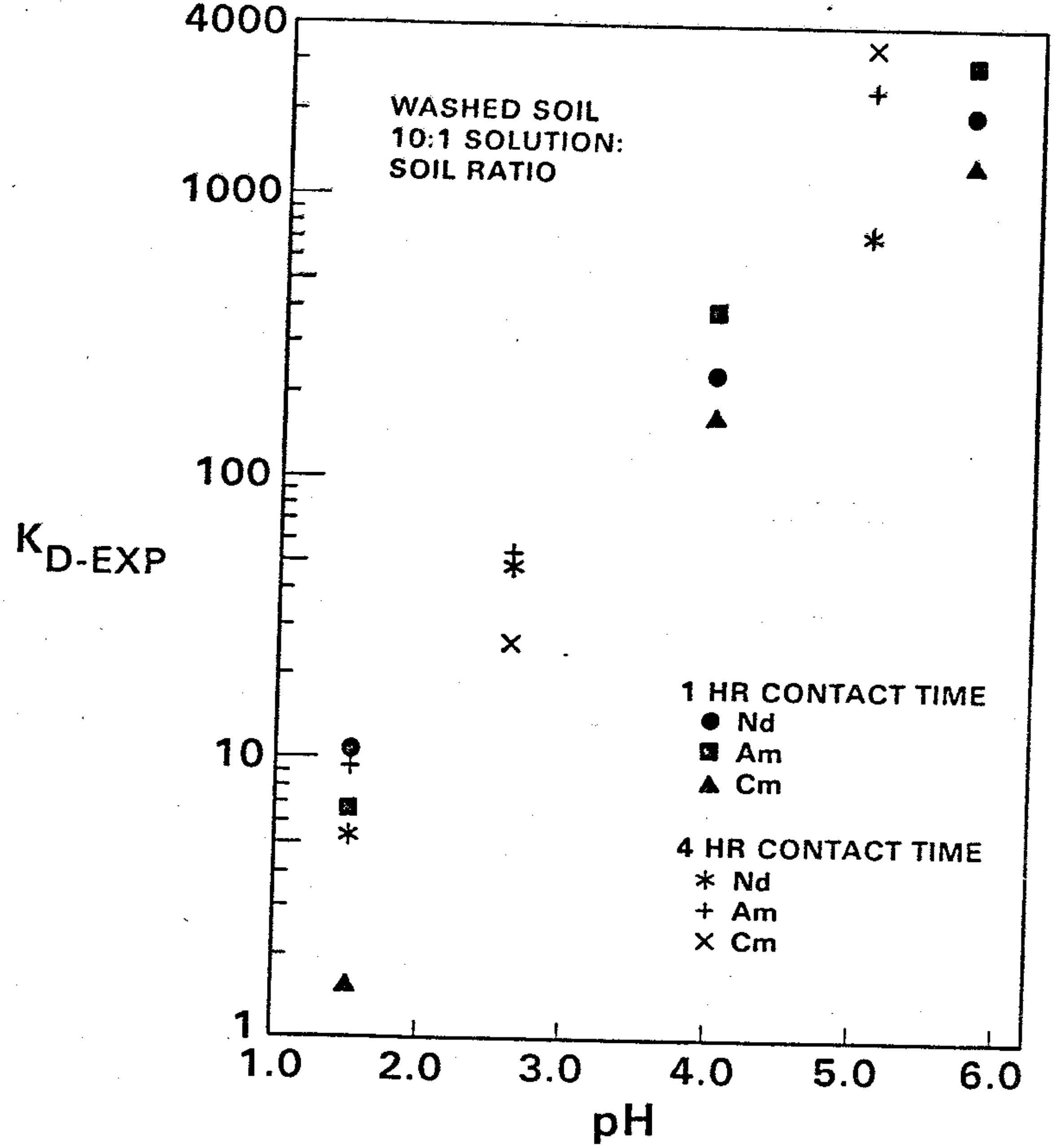

FIGURE 1. ELEMENTAL DISTRIBUTION COEFFICIENTS IN SOIL: $Ca(NO_3)_2$ SYSTEMS

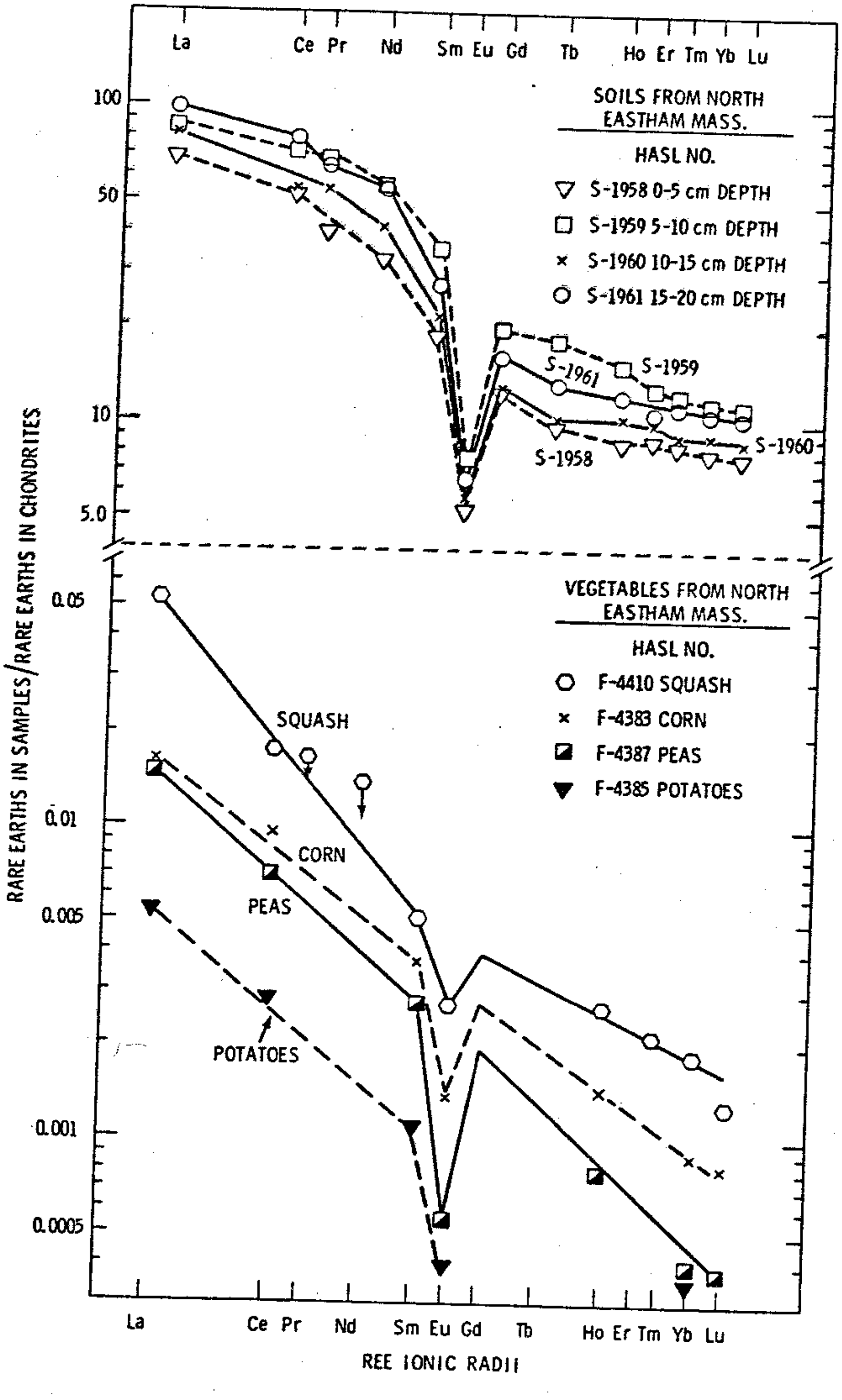

FIGURE II. RARE EARTH PATTERNS IN HASL SAMPLES