

The effect of weathering regime on uranium decay series and osmium in two soil profiles

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Two soil profiles from the United States with radically different emplacement and climatic histories were analyzed for U, Th and members of the ^{238}U decay series (^{234}U , ^{230}Th , ^{226}Ra , ^{210}Pb), ^{137}Cs and osmium isotopes. The arid New Mexico profile is developed on an approximately 250,000 years old colluvium while the temperate New Hampshire profile is formed on till after the last glaciation at about 10,000 years ago. Both the profiles show significant $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ and $^{226}\text{Ra}/^{230}\text{Th}$ disequilibria, however, in the New Hampshire profile, the disequilibria are far more pronounced in mid-depths (20–50 cm). High Os concentration with highly radiogenic $^{187}\text{Os}/^{188}\text{Os}$ is another characteristic of the mid-depths of the New Hampshire profile. This layer, particularly at about 30–40 cm depth has the characteristics of a soil developed on black shale, as evidenced from both the high U and Os concentrations and the large excess of ^{230}Th over ^{238}U . This profile clearly shows that the regolith on which the contemporary soil is developing was not homogeneous. The presence of measurable excess ^{226}Ra activity over ^{230}Th activity in both profiles suggests the need for a source of ^{226}Ra external to the regolith in both cases. Atmospheric deposition of ^{226}Ra is a possible source for this ^{226}Ra excess and brings to light the important role of atmospheric deposition of nuclides and their transport in the soil profile in pedogenic processes. It also shows that regolith developed by glacial processes need not be homogeneous, thereby confounding the understanding of vertically modified soil profiles.

Keywords: uranium decay series, osmium isotope, soil, New Mexico, New Hampshire

INTRODUCTION

Soils may be thought of as open systems that are the result of the chemical weathering of primary minerals, the formation of secondary minerals and the acquisition of solutes from percolating water. The process of soil formation is complex and may involve congruent and incongruent dissolution of minerals, differing rates of alteration of various phases, physical transport of solid phases, solution and re-precipitation, and addition or removal of both solid and liquid phases from the soils. The distribution of elemental and isotope abundances in soils and their parent material can provide insight into these chemical weathering processes and the mobility of various elements in the earth surface environment.

Radioactive disequilibria among members of ^{238}U and ^{232}Th decay series have been used as tracers of elemental fractionation during weathering and as tools to derive erosion rates (Rosholt *et al.*, 1966; Hansen and Stout,

1968; Moreira-Nordemann, 1980; Greeman *et al.*, 1990; Osmond and Ivanovich, 1992; Scott *et al.*, 1992; Mathieu *et al.*, 1995; Vigier *et al.*, 2001; Dequincey *et al.*, 2002; Chabaux *et al.*, 2003). These applications rely on two important characteristics of these nuclides: (i) their supply rates to the system can be assessed fairly accurately and (ii) they have different chemical (and nuclear) properties that contribute to fractionation among the members of the decay chain during weathering and transportation. Earlier studies have shown that in general U and Ra are more mobile than Th during rock (soil)-water interactions and that ^{234}U is released to solution preferentially over ^{238}U during weathering due to α -recoil effects (Chabaux *et al.*, 2003).

Analogous to the U-Th series isotopes, Os and its isotopic composition $^{187}\text{Os}/^{188}\text{Os}$ are potential tools to study soil formation and weathering processes (Peucker-Ehrenbrink and Blum, 1998; Peucker-Ehrenbrink and Hannigan, 2000; Pierson-Wickmann *et al.*, 2002) as well as aqueous element transport (Sharma *et al.*, 1997; Peucker-Ehrenbrink and Ravizza, 2000; Williams, 2002). The basis of these applications can be strengthened if the geochemical behavior of Os in the hydrological cycle, particularly during rock (soil)-water interactions, is better understood as these processes regulate the supply of Os to solution and eventually to the oceans (Peucker-

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Ehrenbrink and Blum, 1998; Peucker-Ehrenbrink and Hannigan, 2000).

In this study, measurements of U-Th series nuclides and Os isotopes were made in two soil profiles with different histories to understand the behavior and transport of these nuclides.

METHODOLOGY

As part of a separate study to determine Rn emanation rates from soils, several soil cores were collected from across the United States and analyzed for the distribution with depth of ^{210}Pb , ^{226}Ra and ^{137}Cs (Graustein and Turekian, 1990). Of these, two cores were selected for this study because they represented opposite ends of the range of the rate and intensity of chemical alteration. Like most soils of the United States, they are both developed on transported surficial deposits, rather than the result of *in situ* alteration of the underlying bedrock.

The NM01 soil core was obtained from grassland on the Double Arrow Ranch near Winston, New Mexico ($33^{\circ}28' \text{N}$, $107^{\circ}40' \text{W}$; 2105 m elevation). Like many soils in the region, this profile is developed on a uniform mid-Pleistocene colluvium and is classified in the standard soil taxonomy as an aridisol (e.g., Buckman and Brady, 1969). The "Desert Project", one of the detailed studies of the relations between soil development, geology and geomorphology in this environment, was carried out about 100 km south of this site (e.g., Gile and Hawley, 1981) and it is expected that the findings there are applicable to the NM01 site. The two most notable aspects of transport in soils in this area are the accumulation of CaCO_3 by precipitation from solution at depths on the order of a meter and the accumulation of clay by illuvation (transport of the solid phase through the soil pores) above the zone of carbonate accumulation. For both clay and carbonate, the amount of accumulation increases with the geomorphic age of the parent material. In the older soils, the clay forms "skins", layers of individual grains with their *c* axes aligned, around the peds (or clods). Compared visually to the soils described in the Desert Project, the NM01 profile is at an early stage of development, with modest carbonate accumulation and a small degree of chemical alteration. The core shows no evident clay "skins" and other signatures of major alteration of the parent colluvium. Based on comparison with the profiles described and dated in the Desert Project, the age of the NM01 profile is estimated to be roughly 250,000 years.

In comparison, the NH47 soil core, collected from under a lowland boreal forest on level terrain near the Dead Diamond River in northern New Hampshire ($44^{\circ}55' \text{N}$, $71^{\circ}5' \text{W}$; 440 m), exhibits intense alteration in a relatively short period of time. The profile is developed on poorly sorted glacial till and is classified as a spodosol.

The defining characteristic of these soils is a near-surface zone of intense leaching in which weathering resistant minerals such as quartz remain. Below this zone generally there is a layer that is enriched in humic matter and sesquioxides of iron and aluminum (cf., Buckman and Brady, 1969). In contrast to NM01, the amount of mass transport since the parent material was exposed by deglaciation roughly 10,000 years ago was sufficient to change the texture and appearance of the upper 60 cm of the parent material significantly.

These two cores were analyzed for ^{238}U series nuclides and ^{232}Th , Os concentration and $^{187}\text{Os}/^{188}\text{Os}$. In addition, the New Hampshire soil was analyzed for organic carbon and potassium. The procedures used for these measurements are described briefly in the following sections.

U and Th isotopes by alpha-spectrometry

U and Th isotope measurements were made on ashed samples. For each sample, several grams of air dried material were ashed at 550°C overnight in a muffle furnace. The weight loss during ashing ranged from ~3% to 12% in the New Hampshire samples and from ~6% to 11% in the New Mexico samples. For U and Th isotopes, 1–2 g of ashed samples were accurately weighed into "Savillex" containers, wetted with water and a few milliliters of concentrated HNO_3 . To this, a precise amount of ^{232}U - ^{228}Th spike (corresponding to about 7.7 dpm) was added and let stand overnight. The samples were digested in HF-HNO_3 to bring them into solution. Many samples, even after repeated digestion, had visible amounts of residue. These were centrifuged and the residue was further digested with HF-HNO_3 . This process was repeated until the samples were brought into complete solution. In a few samples, a thin film of floating dark flakes was noticed during dissolution, these samples were digested with HClO_4 . The solutions from repeated digestions were combined and processed for U and Th isotopes following the procedure of Krishnaswami *et al.* (1984). The purified U or Th separates were electro-deposited onto Pt discs and assayed for their α -activities using a surface barrier detector. ^{238}U , ^{230}Th and ^{232}Th concentrations and $^{230}\text{Th}/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$ activity ratios were calculated from the α spectra (Krishnaswami *et al.*, 1984). To check on the reproducibility of measurements, several samples were analyzed in duplicate.

The ^{232}U - ^{238}Th spike used was calibrated using NIST ^{238}U standard. In addition, an independent check on the calibration of the spike was made by analyzing a coral sample, PR-16, (provided by Dr. Larry Edwards of the University of Minnesota) whose ^{238}U , ^{230}Th concentrations and $^{234}\text{U}/^{238}\text{U}$ were determined by mass spectrometry. The ^{238}U and ^{230}Th concentrations (as activity) based on mass spectrometry are 1.732 ± 0.01 and 1.604 ± 0.008 dpm g^{-1} respectively. This compares with

Table 1. New Mexico core NM01 (Collected July 3, 1983)

Depth (cm)	²³⁸ U*	²³⁰ Th*	²²⁶ Ra*	²¹⁰ Pb*	²³² Th*	²³⁴ U/ ²³⁸ U	²³⁸ U/ ²³² Th	²³⁰ Th/ ²³⁴ U	²²⁶ Ra/ ²³⁰ Th	O _s ** (ppt)	¹⁸⁷ Os/ ¹⁸⁸ Os	Os ^e (ppt)	¹⁸⁷ Os/ ¹⁸⁸ Os	¹³⁷ Cs*
5-10	1.73 ± 0.04	2.13 ± 0.07	2.66 ± 0.10	2.12 ± 0.30	3.13 ± 0.09	0.86 ± 0.02	0.55 ± 0.02	1.43 ± 0.05	1.25 ± 0.06	13	1.116 ± 0.01	0.8	1.307 ± 0.02	-0.02 ± 0.04
10-15	1.90 ± 0.04	2.18 ± 0.07	2.67 ± 0.07	2.37 ± 0.25	3.08 ± 0.10	0.86 ± 0.02	0.62 ± 0.02	1.33 ± 0.04	1.22 ± 0.05				0.05 ± 0.03	
15-20	1.80 ± 0.04	2.16 ± 0.06	2.28 ± 0.07	1.85 ± 0.23	2.94 ± 0.08	0.87 ± 0.02	0.61 ± 0.02	1.38 ± 0.04	1.06 ± 0.05				0.01 ± 0.03	
20-30	1.64 ± 0.02	1.93 ± 0.06	2.29 ± 0.07	2.23 ± 0.22	2.69 ± 0.08	0.91 ± 0.02	0.61 ± 0.02	1.30 ± 0.04	1.19 ± 0.05	16	1.280 ± 0.036	0.7	1.663 ± 0.017	0.04 ± 0.03
30-40	1.64 ± 0.04	2.04 ± 0.06	2.65 ± 0.07	2.28 ± 0.26	2.94 ± 0.08	0.93 ± 0.02	0.56 ± 0.02	1.33 ± 0.05	1.30 ± 0.06				0.10 ± 0.04	
40-50	1.66 ± 0.04	2.08 ± 0.07	2.62 ± 0.08	2.48 ± 0.26	2.99 ± 0.09	0.90 ± 0.02	0.55 ± 0.02	1.38 ± 0.05	1.26 ± 0.05				0.08 ± 0.04	
70-80	1.29 ± 0.03	1.30 ± 0.04	1.57 ± 0.02	1.66 ± 0.08	1.71 ± 0.05	0.94 ± 0.02	0.75 ± 0.03	1.07 ± 0.04	1.21 ± 0.07				0.06 ± 0.03	

*In units of dpm g⁻¹.
 **In bulk samples.
 @ 6% H₂O₂ leach.

Table 2. New Hampshire core NH47 (Collected September 13, 1985)

Depth (cm)	²³⁸ U*	²³⁰ Th*	²²⁶ Ra*	²¹⁰ Pb*	²³² Th*	²³⁴ U/ ²³⁸ U	²³⁸ U/ ²³² Th	²³⁰ Th/ ²³⁴ U	²²⁶ Ra/ ²³⁰ Th	O _s ** (ppt)	¹⁸⁷ Os/ ¹⁸⁸ Os	K ₂ O (%)	Org. C (%)	¹³⁷ Cs*
0-5	n.d.	n.d.	0.82 ± 0.12	19.6 ± 0.49	n.d.	n.d.	n.d.	n.d.	n.d.	47	0.766 ± 0.006	-0.2 ± 0.8	44.1	5.14 ± 0.18
5-10	1.70 ± 0.04	1.86 ± 0.06	2.10 ± 0.08	2.89 ± 0.23	2.42 ± 0.08	0.98 ± 0.02	0.70 ± 0.03	1.09 ± 0.04	1.13 ± 0.06	15	0.733 ± 0.002	2.9 ± 0.3	1.49	1.69 ± 0.06
10-15	1.86 ± 0.04	1.87 ± 0.06	2.16 ± 0.09	2.23 ± 0.28	2.74 ± 0.08	0.95 ± 0.02	0.68 ± 0.02	1.01 ± 0.04	1.16 ± 0.06	13	0.572 ± 0.002	4.5 ± 0.2	1.30	0.12 ± 0.04
15-20	1.82 ± 0.05	1.94 ± 0.07	2.52 ± 0.09	2.17 ± 0.26	2.81 ± 0.09	0.99 ± 0.02	0.65 ± 0.03	1.07 ± 0.05	1.30 ± 0.07	28	0.686 ± 0.004	4.6 ± 0.3	2.73	-0.02 ± 0.04
20-30	2.67 ± 0.07	4.90 ± 0.15	5.64 ± 0.12	4.01 ± 0.31	3.14 ± 0.10	1.04 ± 0.02	0.85 ± 0.03	1.84 ± 0.07	1.15 ± 0.04	249	2.007 ± 0.006	4.9 ± 0.2	2.54	0.08 ± 0.04
30-40	3.70 ± 0.08	11.26 ± 0.28	12.03 ± 0.13	9.56 ± 0.33	3.79 ± 0.10	1.01 ± 0.02	0.98 ± 0.03	3.05 ± 0.10	1.07 ± 0.03	390	2.272 ± 0.004	7.0 ± 0.4	0.76, 0.61	0.04 ± 0.04
40-50	1.89 ± 0.04	2.77 ± 0.08	3.64 ± 0.10	2.84 ± 0.28	2.10 ± 0.06	0.98 ± 0.02	0.90 ± 0.03	1.47 ± 0.05	1.31 ± 0.06	61	2.015 ± 0.011	3.4 ± 0.3	3.20	0.00 ± 0.04
50-60	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.7 ± 0.2	0.91	0.00 ± 0.03
60-64	1.88 ± 0.04	1.99 ± 0.05	2.16 ± 0.05	1.84 ± 0.16	2.57 ± 0.06	0.96 ± 0.01	0.73 ± 0.02	1.06 ± 0.03	1.09 ± 0.04	21	1.855 ± 0.016	3.6 ± 0.2	0.54	0.03 ± 0.02

*In units of dpm g⁻¹.
 **In bulk samples.
 n.d. = not determined.

Table 3. Results of repeat measurements by acid digestion. Core: NM-01, Double Arrow, New Mexico.

Depth (cm)	Year of analysis	²³⁸ U	²³⁰ Th	²³² Th	²³⁴ U/ ²³⁸ U	²³⁰ Th/ ²³⁸ U
10–15	1994	1.90	2.18	3.08	0.86 ± 0.02	1.15 ± 0.04
	1996	1.76	1.96	2.91	0.89 ± 0.02	1.12 ± 0.05
30–40	1994	1.64	2.04	2.94	0.93 ± 0.02	1.24 ± 0.04
	1996	1.65	2.02	2.78	0.87 ± 0.02	1.22 ± 0.05
40–50	1994	1.66	2.08	3.0	0.91 ± 0.02	1.25 ± 0.04
	1996	1.70	—	—	0.90 ± 0.02	—
70–80	1994	1.29	1.30	1.71	0.94 ± 0.02	1.00 ± 0.03
	1996	1.30	1.30	1.61	0.96 ± 0.02	1.00 ± 0.04

*Concentration in dpm g⁻¹. Typical ±1σ uncertainties in concentration ±3%.

the α-spectrometric values of 1.83 ± 0.04 and 1.79 ± 0.04 dpm g⁻¹ for ²³⁸U and ²³⁰Th. The concentrations determined by mass spectrometry and α-spectrometry are marginally outside 2 sigma uncertainties and reflect the errors associated with calibration and measurements. The ²³⁴U/²³⁸U and ²³⁰Th/²³⁸U activity ratios determined by the two methods agree reasonably well within ±2σ analytical uncertainties.

²²⁶Ra, ²¹⁰Pb and ¹³⁷Cs by gamma-counting

²²⁶Ra, ²¹⁰Pb and ¹³⁷Cs concentrations in the soil samples were determined by non-destructive γ-spectrometry (Graustein and Turekian, 1990). Briefly, the soil samples were sealed in Al-cans, stored for several months and then counted for their γ-activities using a high resolution, low background γ-ray detector. The detector was calibrated using a NIST ²²⁶Ra standard. ²²⁶Ra and ²¹⁰Pb activities were calculated from the gamma-counting data after appropriately correcting for self-absorption.

Since in this study, results obtained by both γ-spectrometry and α-spectrometry are used to deduce parent-daughter equilibrium systematics, an inter-comparison of these systems are needed. The PR-16 coral data provide a means to inter-compare the α and γ systems. The ²³⁰Th concentrations in the PR-16 coral measured by α-spectrometry (1.79 ± 0.04 dpm g⁻¹) compares with the ²²⁶Ra values (1.64 ± 0.02 dpm g⁻¹) determined by γ-spectrometry. These results, if anything show that the γ values are lower than the α values by ~10% for a coupled system such as the ²²⁶Ra/²³⁰Th activity ratio.

Osmium isotopes

Osmium concentration and ¹⁸⁷Os/¹⁸⁸Os were measured in both bulk and leach samples for the New Mexico core and in bulk samples only for the New Hampshire core following the procedures of Pegram *et al.* (1992, 1994) and Pegram and Turekian (1999). Bulk samples were analyzed by isotope dilution following addition of a ¹⁹⁰Os spike. The procedure involved Os extraction by nickel-

sulfide bead fusion, digestion of the metallic bead by HCl, double distillation of Os and final purification by single grain ion-exchange chemistry. The Os isotope measurements were made by NTIMS at the Woods Hole Oceanographic Institution. To determine the concentration of the leachable fraction of Os and its isotope composition, a few samples were leached with 6% hydrogen peroxide in an acidic medium. Os from leachates were purified by distillation and ion-exchange chemistry.

Organic carbon and potassium concentrations in the New Hampshire soil profile

Organic carbon was determined using the method of Krom and Berner (1983). In brief, samples are dried at 80°C and then combusted at 1250°C in a LecoTM carbon analyzer. The percent total carbon is calculated from the volume of the evolved CO₂. The inorganic carbon is measured after preheating of the samples at 550°C overnight to drive off the organic carbon. The organic carbon is found by the difference between the total and inorganic carbon.

Potassium concentrations were measured by γ-counting of ⁴⁰K using a coaxial Li-Ge detector with suitable standards.

RESULTS

The U and Th isotopes (α-spectrometry) and ²²⁸Ra, ²¹⁰Pb and ¹³⁷Cs (γ-spectrometry) concentrations (as activities) and activity ratios for the New Mexico and the New Hampshire soil profiles are given in Tables 1 and 2. The errors given in the tables are ±1σ and are cumulative for counting statistics and tracer calibration. The results of repeat measurements of U and Th isotopes in four samples, performed about two years apart are given in Table 3. The repeat measurements show good agreement, suggesting that on average the reproducibility of analytical and counting procedures for concentration and activity ratio measurements are generally better than ~5%. For

Table 4. Comparison of acid digestion and fusion results. Core NH-47, Forks of Diamond, New Hampshire.

Depth (cm)	Method ^(a)	²³⁸ U*	²³⁰ Th	²³² Th	²³⁰ Th/ ²³⁸ U
30–40	D	3.70 ± 0.08	11.3 ± 0.28	3.79 ± 0.10	3.05 ± 0.10
	F	4.20 ± 0.08	12.1 ± 0.33	3.97 ± 0.12	2.89 ± 0.10
20–30	D	2.67 ± 0.07	4.90 ± 0.15	3.15 ± 0.10	1.84 ± 0.07
	F	3.08 ± 0.06	5.12 ± 0.13	3.18 ± 0.08	1.66 ± 0.05
10–15	D	1.86 ± 0.04	1.87 ± 0.06	2.74 ± 0.08	1.01 ± 0.05
	F	2.05 ± 0.04	—**	—	—

^(a)D: acid digestion, F: metaborate fusion.

*In dpm g⁻¹, errors are ±1σ.

**Poor chemical yield.

further verification, three samples from the New Hampshire profile were analyzed for their U and Th isotope concentrations by lithium metaborate fusion. The results of these analyses (Table 4) show that in all the samples, U and Th isotope abundances determined by the fusion method were slightly higher than those measured by acid digestion, the difference being 3% to 7% for ²³⁰Th and about 10% for ²³⁸U. The ²³⁰Th/²³⁸U activity ratios measured by the two methods, however, were within or slightly outside 2 sigma errors. These data, if typical of all samples analyzed in this study, would lead to the inference that generally the acid digestion procedure used does not fractionate between U and Th isotopes.

Table 2 also contains potassium, organic carbon and bulk Os concentrations and Os isotope compositions for the New Hampshire samples. Tables 1 shows ¹⁸⁷Os/¹⁸⁸Os values for both bulk and leachable Os concentrations and Os isotope compositions in the New Mexico samples.

DISCUSSION

The soil profiles from New Hampshire and New Mexico have different histories and contemporary climatic regimes. For that reason, each will be discussed separately prior to determining weathering trends across the two regimes.

The New Mexico soil profile

Atmospherically derived nuclides: ¹³⁷Cs and ²¹⁰Pb The profile of ¹³⁷Cs in the New Mexico profile shows the highest activity at the surface, with detectable activities distributed between 30 and 70 cm. The only source of ¹³⁷Cs in soils is fallout from atmospheric testing of nuclear weapons, which reached a peak in 1960–62. In most US soils collected around 1980, 90% or more of the ¹³⁷Cs is retained in the upper 10–15 cm of the profile (Graustein and Turekian, 1990). ¹³⁷Cs is strongly adsorbed by organic material and by illitic clays, making its penetration to greater depths, as observed in the New Mexico soil

core, quite uncommon. Possible explanations for the presence of ¹³⁷Cs deeper in this core include (1) the aridity of the region. This leads to soil solutions with high ionic strength that reduces sorption of Cs, (2) low content of organic matter near the soil surface which reduces retentivity of Cs in soil, and (3) illuvation of clay from the upper horizons to lower ones, which physically transports ¹³⁷Cs activity from surface to deeper sections.

The distribution of ²¹⁰Pb in the New Mexico soil profile shows an excess of ²¹⁰Pb over ²²⁶Ra in the top five cm with deficiencies to a depth of about 60 cm. This distribution is due to the atmospheric supply of ²¹⁰Pb in the top five cm with loss of ²²²Rn from the soil down to a depth of about 60 cm. The amount of ²¹⁰Pb transferred from the surface to depth by the same processes as for ¹³⁷Cs cannot be directly determined because of the depletion of ²¹⁰Pb at depth resulting from radon loss.

²³⁸U and ²³²Th Both ²³⁸U and ²³²Th, the primordial parents of their respective decay chains, are nearly uniformly distributed between 5 and 50 cm. The activity of both these nuclides in the 70–80 cm interval, however, is 20%–40% lower than in the upper part of the profile. This decrease is presumably due to dilution by the accumulation of CaCO₃ during the process of soil formation.

The ²³⁸U/²³²Th values show a more distinct pattern than either of its components. From 5–50 cm depth the average ²³⁸U/²³²Th is 0.59; from 70–80, where the activities of both nuclides are lower than the upper parts of the core, it rises to 0.75. This change is consistent with the leaching of U from the upper horizon and partial coprecipitation with CaCO₃.

²³⁸U-²³⁴U-²³⁰Th systematics ²³⁸U concentrations in core NM-01 (Table 1) are nearly uniform in the surface to 50 cm depth interval with values centering around 1.7 dpm g⁻¹. ²³⁰Th in these samples is slightly higher than ²³⁸U with values of about 2.1 dpm g⁻¹, yielding ²³⁰Th/²³⁸U activity ratio of ~1.2. In the 70–80 cm sample, both ²³⁸U and ²³⁰Th are lower, ~1.3 dpm g⁻¹ with activity ratio of 1.0. The ²³⁴U/²³⁸U activity ratio is <1.0 in all the samples

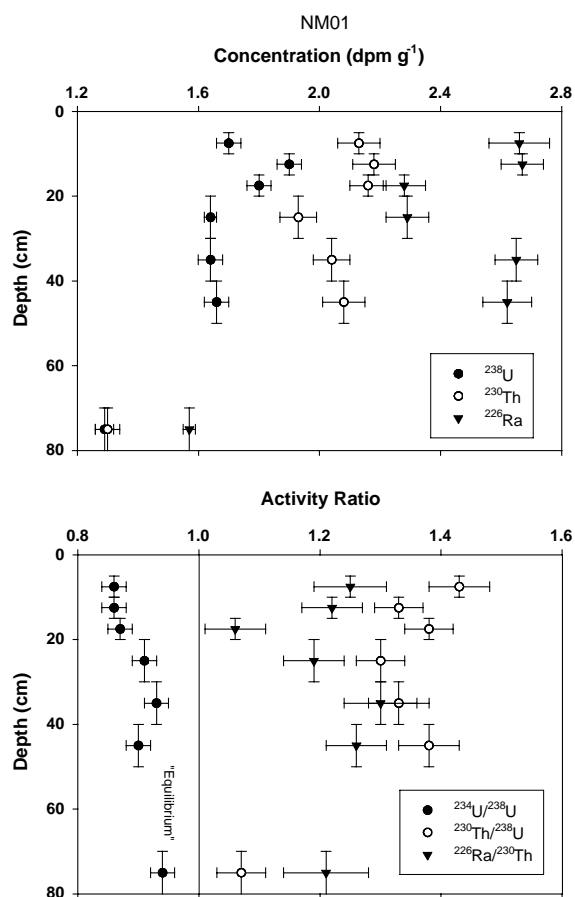


Fig. 1. Distribution of ^{238}U , ^{230}Th , ^{226}Ra , $^{230}\text{Th}/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$ and $^{226}\text{Ra}/^{230}\text{Th}$ with depth in a New Mexico profile. The deficiency of ^{234}U and excess of ^{230}Th over ^{238}U in the upper ~50 cms of the profile is evident.

analyzed, with distinctly lower values, ~0.86 in the upper 20 cm of the profile; the highest value, 0.94, is in the 70–80 cm interval.

The distributions of ^{234}U , ^{238}U and ^{230}Th activities with depth are shown in Fig. 1. Similar patterns of activities where $^{234}\text{U} < ^{238}\text{U} < ^{230}\text{Th}$ in the upper 50 cm of soils have been reported by Rosholt *et al.* (1966) and Muhs *et al.* (1990).

This pattern of disequilibrium in the upper 50 cm is consistent with leaching of U in preference to Th. The deficiency in ^{234}U with respect to ^{238}U in the solid phase suggests its preferential solution due to the effects of α -recoil and subsequent removal. The deficiency of ^{234}U with respect to ^{230}Th indicates that U is more mobile than Th and that its removal is part of the ongoing soil forming process since the initial emplacement of the colluvium about 250,000 years ago. On the other hand the 250,000 year half-life of ^{234}U allows for the possibility that some portion of the preferential removal of ^{234}U compared to

^{238}U could have taken place prior to the emplacement of the minerals in the present location.

In the zone of carbonate accumulation at 70–80 cm depth, the ^{238}U , ^{234}U and ^{230}Th activities are nearly equal and are all less than the upper parts of the profile. We presume that the decreased activities are due to dilution by pedogenic carbonate. The physical accumulation of carbonate can retard or stop the leaching of U and allow the decay chain to grow into equilibrium. Since only bulk samples were analyzed and activities of the three nuclides are the same, inferences about ages cannot be made.

^{226}Ra There is excess ^{226}Ra at all depths in the soil profile compared to its parent ^{230}Th with activity ratios of $^{226}\text{Ra}/^{230}\text{Th}$ from 1.06 and 1.30. Thus ^{226}Ra is in excess of ^{230}Th and ^{230}Th is in excess of ^{238}U . As the New Hampshire soil core also shows similar excess of ^{226}Ra over ^{230}Th , the discussion of the ^{226}Ra result is deferred until after the data for the New Hampshire profile are presented.

Os isotopes Bulk osmium concentrations were measured only in two samples of the New Mexico core; the values were 13 and 16 ppt in these two samples with $^{187}\text{Os}/^{188}\text{Os}$ of 1.116 ± 0.010 and 1.280 ± 0.034 respectively (Table 1). H_2O_2 leach of the samples from this core show that the fraction of leachable Os in these soil samples is quite small, ~5% (Table 1).

This bulk/leach concentration ratio of about 20 is significantly higher than that measured in other sediments (Williams, 2002), suggesting that either the osmium is contained in a leach resistant phase or that natural soil processes have already removed the soluble osmium from the system. The leached osmium, despite being a small proportion of the bulk osmium, is only slightly more radiogenic. This further suggests that most osmium is contained in either a single phase resistant to degradation or leaching, or in multiple phases with similar isotopic compositions. The latter possibility would require either young phases or phases with similar Re/Os ratios.

The $^{187}\text{Os}/^{188}\text{Os}$ in the 20–30 cm section is more radiogenic than that at 5–10 cm by approximately 0.20 isotopic units. This could be caused by heterogeneity of source composition (Piersen-Wickmann *et al.*, 2002), leaching of more radiogenic osmium from the near surface samples and its re-deposition at depth or by atmospheric deposition of anthropogenic osmium at the surface which is generally less radiogenic than unweathered cratonal material. Atmospheric osmium of anthropogenic origin may be relatively more labile since this Os absorbs onto particle surfaces and is not contained within a mineral structure. Thus, the leach is expected to have a less radiogenic isotopic composition if atmospheric Os is a major component of its total Os. The lower osmium concentration at the surface of the core and high $^{187}\text{Os}/^{188}\text{Os}$ in leach relative to bulk seem to suggest that anthropo-

genic supply is not a significant source of Os to this site (Williams and Turekian, 2002). The leaching of Os from surface and its subsequent re-deposition also seems a less likely cause for the higher $^{187}\text{Os}/^{188}\text{Os}$ at depth considering similar Os abundances in both the sections and the low fraction of leachable Os in the deeper sample.

New Hampshire profile

Atmospherically derived nuclides: ^{137}Cs and ^{210}Pb The distribution of ^{210}Pb and ^{137}Cs in the New Hampshire soil profile is typical of profiles in non-arid regions of the United States (Graustein and Turekian, 1986): the main accumulation of atmospherically deposited ^{137}Cs and ^{210}Pb is in the top 15–20 cm. Unlike the New Mexico profile, there is no evidence for transport of atmospherically derived nuclides below 20 cm. We therefore presume that any variation in the abundance of the other nuclides must be derived from soil forming processes or inhomogeneity of the parent material.

U and Th isotopes In the New Hampshire profile (Table 2), the concentrations of ^{238}U , ^{230}Th and ^{232}Th show significant change with depth, with peaks in concentration for all three at 30–40 cm. These peaks in ^{238}U , ^{230}Th and ^{232}Th coincide with that of Os concentration (Table 2). In samples from the surface to 20 cm and in the deepest sample 60–64 cm, ^{238}U and ^{230}Th concentrations are ~ 1.8 and ~ 1.9 dpm g^{-1} respectively. The $^{230}\text{Th}/^{238}\text{U}$ activity ratios, however, can be considered at equilibrium within analytical uncertainties. The concentrations of ^{238}U and ^{230}Th in sections 20–50 cm are significantly higher than those above and below (Table 2). These samples also exhibit considerable excess of ^{230}Th over ^{238}U , with an activity ratio as high as 3.05 ± 0.07 in the 30–40 cm depth. The $^{234}\text{U}/^{238}\text{U}$ activity ratios in all the samples analyzed are at equilibrium within analytical errors.

The extent of disequilibrium in the New Hampshire profile, except in the intermediate depth, 20–50 cm, is less pronounced relative to those in the New Mexico core (Fig. 2). The $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ activity ratios are at or near equilibrium within analytical errors (Fig. 2). The lack of $^{234}\text{U}/^{238}\text{U}$ disequilibrium in this profile contrasts with that observed in the New Mexico site, and probably results from aggressive weathering contributing to congruent dissolution of uranium isotopes. Alternatively, this could be an “age” effect. The New Mexico profile is considerably older ($\sim 250,000$ year old parent material) than the New Hampshire profile ($\sim 10,000$ years). The kinetics of preferential release of ^{234}U relative to ^{238}U and ^{238}U relative to ^{230}Th may not be rapid enough to develop measurable disequilibrium among these isotopes over the “age” of the NH47 profile. The $^{230}\text{Th}/^{238}\text{U}$ activity ratios show disequilibrium only at mid-depths of the core, 20–50 cm, where all nuclides show distinct peaks in their concentrations (Fig. 2).

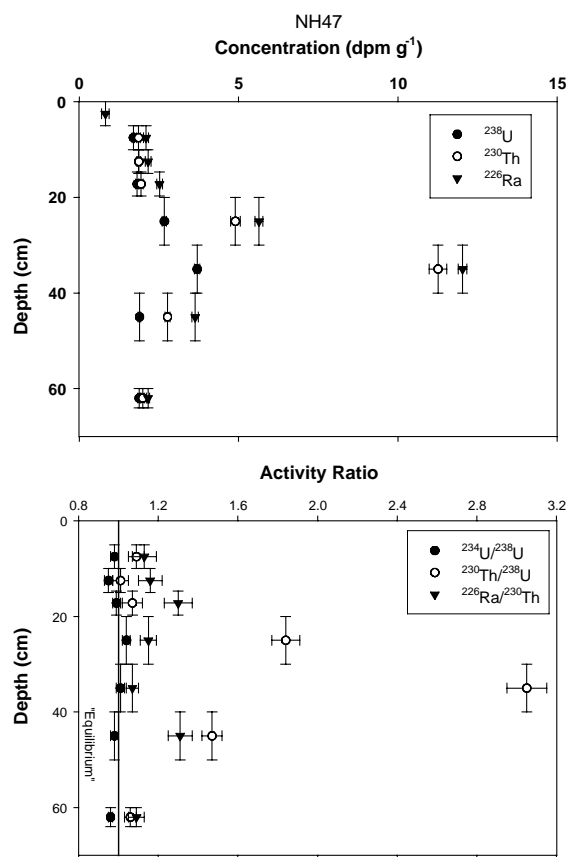


Fig. 2. Distribution of ^{238}U , ^{230}Th , ^{226}Ra , $^{230}\text{Th}/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$ and $^{226}\text{Ra}/^{230}\text{Th}$ with depth in a New Hampshire profile. The data show high concentrations of U, Th isotopes and significant excess of ^{230}Th over ^{238}U in mid-depths.

Spodosols are characterized by an ash-colored upper horizon consisting principally of weathering resistant minerals such as quartz and zircon, underlain by a horizon that has a high concentration of humic material, iron and aluminum. They are typically found in cold regions and are developed on parent material at the time of the last deglaciation. The NH47 profile suggests that intense and rapid weathering takes place in the upper 20 cm resulting in solution of most minerals. Sesquioxides and humic material precipitate from solution in the horizon of accumulation and scavenge trace elements in the process.

The pattern of distribution of ^{238}U decay products appears to be explicable in terms of this simple model. The U and Th concentrations in the surface ~ 15 cm can be accounted by their abundances in minerals more resistant to weathering. Potential sources for the high U and ^{230}Th in the 30–40 cm interval could be (i) scavenging from percolating solution, the ^{230}Th more efficiently than U. The near equal activities of ^{226}Ra and ^{230}Th would

suggest that the transport took place early in the soil forming process, and (ii) inherited from parent material.

Analogous to U and Th, Os also shows high concentration at mid-depth characterized by highly radiogenic $^{187}\text{Os}/^{188}\text{Os}$. The distribution of osmium and osmium isotopes cannot, however, be explained by its scavenging from percolating solution. As will be shown in the next section, the Os systematics strongly suggest that the parent material is inhomogeneous and the 30–40 cm interval contains some weathered organic rich sediment, probably of Paleozoic age. If the parent material is heterogeneous, it is difficult to infer much about vertical transport of U decay series nuclides and Th during soil formation.

The large deficiency of ^{234}U and ^{238}U with respect to ^{230}Th in the 30–40 cm interval suggests that significant U removal took place within the past 250,000 years either in the original regolith or during the past 10,000 years as the soil developed.

The U, Th and Os enriched layer in the mid-depth of this core is consistent with weathered organic rich sediment, although it appears that the enriched layer is notably lowest in organic carbon of the soil profile. Considering that this soil profile developed after the last glaciation ended (~10,000 years ago), and that the $^{230}\text{Th}/^{238}\text{U}$ activity ratios in the surface and deepest sections are near equilibrium, it seems to suggest that the origin of high ^{230}Th and ^{238}U in the mid-depths of the core is inherited from an organic rich parent material. The large excess of ^{230}Th over ^{238}U can be explained in terms of preferential removal of uranium from the organic rich sediments. This removal could have occurred prior to incorporation in the soil profile or is an ongoing process.

^{226}Ra Like the New Mexico soil profile, there is a clear excess of ^{226}Ra over that expected based on ^{230}Th values. The activity ratio $^{226}\text{Ra}/^{230}\text{Th}$ ranges from 1.07 to 1.30. As both sites show excess ^{226}Ra over ^{230}Th throughout the length of the cores, an explanation is required for the prevalence of this disequilibrium in the soil profiles for both a temperate and a semi-arid region. In the NH47 profile, the $^{230}\text{Th}/^{238}\text{U}$ disequilibrium though can be explained in terms of inheritance, it cannot account for the ^{226}Ra excess problem: the soil profile has had over 10,000 years to develop and the half-life of ^{226}Ra is only 1620 years.

Osmium In the New Hampshire core, the Os concentration peaks at 390 ppt in the depth range 30–40 cm, similar to U and Th isotopes (Table 2). In the 0–20 cm section, the Os values range from 12 to 47 ppt with the highest value in the surface to 5 cm section. The peak in Os concentration also coincides with the most radiogenic $^{187}\text{Os}/^{188}\text{Os}$ (Table 2). The elevated osmium concentration (47 ppt) of the top 5 cm is probably related to the high organic carbon content (44%) made predominantly of leaf litter. This organic matter and associated soil can

sequester Os resulting in its higher concentration at the surface.

The core is far less radiogenic ($^{187}\text{Os}/^{188}\text{Os} \sim 0.7$) in the top 20 cm compared to 20–64 cm depth, where it is significantly more radiogenic ($^{187}\text{Os}/^{188}\text{Os} \sim 1.84\text{--}2.27$).

The mid-depth highs in Os and $^{187}\text{Os}/^{188}\text{Os}$ can best be explained as inherited from a previously developed soil on a parent rock with high Os and $^{187}\text{Os}/^{188}\text{Os}$, such as an organic-rich sediments. The high Re and U concentrations required to give the strong radiogenic Os isotope signature and high ^{230}Th abundance in these sections is consistent with this explanation (Ravizza, 1991; Singh *et al.*, 2003).

The New Hampshire soil profile is developed on glacially mobilized prior soils on sedimentary rocks of Ordovician through Devonian age. It is not possible to determine the age of the hypothesized organic-rich parent material due to lack of data on Re and on the rapid and differential loss of Re and Os during weathering. However, using the peak $^{187}\text{Os}/^{188}\text{Os}$ of ~2.2 (Table 2), for ages of 140–320 Ma, the $^{187}\text{Re}/^{188}\text{Os}$ is calculated as ~400–700 (assuming an initial ratio between 0.25–0.60 and a half-life for ^{187}Re of about 4.6×10^{10} years; Williams, 2002). These values are typical of black shales of Paleozoic age (Ravizza, 1991).

The variation of $^{230}\text{Th}/^{238}\text{U}$ and $^{187}\text{Os}/^{188}\text{Os}$ in the New Hampshire profile (Table 2) shows that both $^{230}\text{Th}/^{238}\text{U}$ and $^{187}\text{Os}/^{188}\text{Os}$ peak at 30–40 cm. In surface layers where ^{230}Th is effectively in equilibrium with ^{238}U , the $^{187}\text{Os}/^{188}\text{Os}$ is ~0.65. The ^{230}Th excess and highly radiogenic $^{187}\text{Os}/^{188}\text{Os}$ in the mid-depths is a result of high concentrations of Re and U in the putative organic rich source material (Ravizza, 1991; Singh *et al.*, 2003). The major difference is in the deeper sections, where the Os isotope ratios continue to be highly radiogenic whereas the ^{230}Th effectively returns to equilibrium with ^{238}U . The lack of correlation between these isotope ratios at these depths may be due to downward transport of radiogenic Os. If this is the case, then material balance calculations would require that major fractions of Os in the 40–50 and 50–60 cm depths are of mid-depth origin.

Possible explanation for the ^{226}Ra - ^{230}Th - ^{238}U disequilibrium in both soil profiles

Some recent studies (Kurtz *et al.*, 2000) show evidence for migration and redistribution of Th in soil profiles, which has been attributed to its affinity to form organic complexes. The impact of this on the ^{230}Th - ^{226}Ra disequilibrium in the profiles analyzed is presently unknown. Muhs *et al.* (1990) in their study of ^{238}U - ^{230}Th - ^{226}Ra systematics in soil profiles from the US and Barbados report the existence of some soils which have ^{226}Ra excess over ^{230}Th throughout the profile, as observed in our study. One of these profiles from New Mexico developed on

alluvium had $^{226}\text{Ra}/^{230}\text{Th}$ activity ratios in the range of 1.05 to 1.25. This excess was explained in terms of addition of unsupported ^{226}Ra via airborne dust. Such a mechanism can also be invoked to explain the ^{226}Ra excess observed in this study, though the origin of unsupported ^{226}Ra in the airborne dust needs to be identified. Further, such a source has to be continuous with a uniform flux of about $0.02\text{--}0.03\text{ dpm cm}^{-2}\text{yr}^{-1}$ and percolate through the entire profile. The observation that ^{137}Cs is detectable deep in the New Mexico profile (Table 1) is an indication that in this region atmospheric dust could be percolating deeper in the soil, but whether the dust can provide the required flux of ^{226}Ra excess needs to be ascertained through analysis of rain and dust samples.

In the New Hampshire profile also there is requirement for additional source of ^{226}Ra to account for its excess over ^{230}Th . If atmospheric deposition is the source for this excess, then its transport mechanism within the soil profile has to be different from that in New Mexico. The observation that in the NH47 profile ^{137}Cs is retained in the top sections implies that the transport of the Ra is not by illuvation but probably through solution. The source of the ^{226}Ra may be throughfall resulting from the exudates from the trees as was shown to be the case for Sr and K in the Tesuque Watershed in New Mexico (Graustein, 1981).

Another, but unlikely explanation for the ^{226}Ra excess is the underestimation of ^{238}U and ^{230}Th concentrations relative to ^{226}Ra in the soils. U and Th were measured by acid dissolution whereas Ra by non-destructive γ -spectrometry. If the acid dissolution is incomplete due to presence of weathering resistant U-Th rich trace phases such as zircons, such underestimation can result. More rigorous inter-calibration needs to be done to address this.

CONCLUSIONS

The distribution patterns of U-Th series nuclides and Os in the two soil cores, one from New Mexico and the other from New Hampshire show clear differences. These are expected since the origin of the soil in each locale is different and the climatic conditions are also different. There are, however, also some common features in the distribution of the nuclides, although this does not necessarily mean identical causes for these features.

1. The New Mexico soil profile, assumed to be about 250,000 years old, has all studied members of the uranium decay chain out of equilibrium. The observation that the $^{234}\text{U}/^{238}\text{U}$ activity ratio is less than one for most of the core, except the bottom presumably carbonated enriched fraction, indicates that either the source of the soil was out of equilibrium or that the departure from equilibrium is maintained in emplaced soil during continuing pedogenic processes. If the age of the soil profile is

250,000 years then the excess of ^{226}Ra and ^{230}Th relative to ^{238}U must be sustained by importation from external sources. Based on our observations and the suggestion of others for neighboring areas, a potential source seems to be wind transported material enriched in ^{226}Ra and to a lesser extent ^{230}Th relative to ^{238}U . Possible sources are caliche or playa deposits enriched in the aforementioned nuclides. The transport through the soil profile is indicated to be of a continuous basis based on the presence of ^{137}Cs found throughout the soil profile. Although transport of a constant excess with depth is counter-intuitive, alternative explanations are more unlikely.

2. The New Hampshire profile is distinctive in that it is not a continuously varying system for any of the nuclides measured. In this profile, a layer at around 30 cm has all the properties of a weathered black shale. It is enriched in U and Os. This layer also has excess of ^{230}Th over ^{238}U and highly radiogenic $^{187}\text{Os}/^{188}\text{Os}$. Although the other layers in the core show some excess ^{230}Th over ^{238}U , the departure from equilibrium is clearly sharpest for this putative organic rich soil layer. In this glacial till deposit on which the current soil regime is being developed is clearly not a homogeneously deposited layer. Rather slivers of surrounding soils mobilized by the glacier that once covered this area make up the stack of different types of material forming the soil profile. Therefore, any attempt at treating the profile as being simply modified by contemporary weathering process acting on a homogeneous regolith is obviously flawed.

3. If atmospherically transported nuclides that we studied are mobilized through the soil profile then it is likely that other nuclides will also be transported to depth in the profile either by illuvation, as in New Mexico, or by solution, as in New Hampshire.

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