of maintaining a uniform power level of the tunable radiation through the microphone cell in the presence of the absorption by the gas. Thus, even up to NO concentrations high enough to give an absorption of $\sim 10^{-2}$ through the microphone cell, the signal output from the microphone cell will be linear with respect to NO concentration. The saturation and nonlinear behavior of the output signal is not expected to take place until we reach NO concentrations in excess of 10^4 ppm.

Our technique of determining NO pollution in air samples requires only ~ 1 cc of gas sample for an analysis that is capable of detecting 0.01 ppm of NO with a 4-second integration time, and thus this method can be adapted to real time measurement of NO pollution even at ambient levels. With longer integration times, the lower limit for NO detection can be improved. For detection of source pollution, significantly shorter integration times can be used. Many different pollutants can be detected with this technique and the method has a large dynamic range. We have already detected NO_2 in some experiments and we expect to investigate other pollutants with our technique.

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Alpha-Recoil Thorium-234: Dissolution into Water and the Uranium-234/Uranium-238 Disequilibrium in Nature

Abstract. *The rate of ejection of alpha-recoil thorium-234 into solution from the surface of zircon sand gives an alpha-recoil range of 550 angstroms. The alpha-recoil thorium-234 atoms ejected into the groundwater may supply excess uranium-234. In pelagic sediments, ejected alpha-recoil thorium-234 may contribute to the supply of mobile uranium-234 in the sedimentary column.*

A radioactive disequilibrium state between ^{238}U and ^{234}U has been observed by many workers both in seawater and in freshwater (*1*). Many samples of freshwater show enrichments of ^{234}U rather than deficiencies. The mechanism of the fractionation of ^{234}U with respect to its radiogenic parent ^{238}U in natural waters has been discussed in connection with the physiochemical nature of α-recoil atoms in the silicate lattice (*2*).

The α-recoil atoms in the silicate lattice are thought to be more easily leached out than the atoms that have settled into the lattice positions at the time of crystallization of the silicate. Thus it is plausible that the addition of excess ^{234}U atoms to freshwater is attributable to the leaching of α-recoil ^{234}U atoms in the weathering process of natural silicate. However, in laboratory leaching experiments on fresh igneous rocks or minerals, solutions containing ^{234}U have been found to contain less than 1.3 times the equilibrium amount of ^{238}U (*3*). Therefore, the process responsible for a disequilibrium state between ^{234}U and ^{238}U in nature with an activity ratio of ^{234}U to ^{238}U as high as 3 or 4 would require mechanisms other than the selective dissolution of α-recoil ^{234}U atoms. The process of dissolution of ^{234}Th atoms produced by the α-decay of ^{238}U atoms located near the surface of the solid silicate particles may be one of the other mechanisms responsible for the disequilibrium.

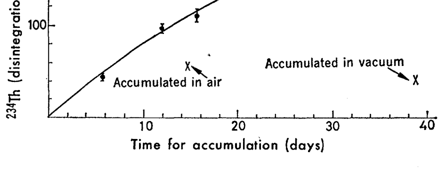

Fig. 1. Amount of ^{234}Th accumulated in the aqueous phase by the ejection of α-recoil ^{234}Th from the surface of the zircon powder suspended in the solution.

The observed increase in the amount of ^{234}Th in the aqueous phase of a system consisting of fine zircon powder and diluted nitric acid or sodium carbonate solution is shown in Fig. 1. The suspension containing 50 g of zircon powder (particles about 1 to 10 μm in diameter) was allowed to stand for a predetermined period of time. The amounts of nuclides leached out were measured in the solution after separation from the mineral powder and in the washing solution, 0.3*N* nitric acid. The uranium and thorium contents of zircon sand are 360 parts per million (ppm) and 131 ppm, respectively. The surface area of the 50 g of powder was estimated from microscopic observation of the particles to be 1.8×10^5 cm^2.

In this experiment, the size of the particles (1 to 10 μm) is large enough as compared with the range of the α-recoil atoms, and we can neglect the curvature of the surface of the particle. Thus the rate of supply *Q* of ^{234}Th atoms from the solid surface to the solution is given by

$$Q = \frac{1}{4} L S u \rho \lambda_8 \qquad (1)$$

where *L* is the α-recoil range of ^{234}Th in the silicate, *S* and ρ are, respectively, the surface area and the density of the silicate, *u* is the number of ^{238}U atoms in 1 g of silicate, and λ_8 is the decay constant of ^{238}U. The accumulated amount *A* of ^{234}Th in the solution after time *t* is given by

$$A = \frac{1}{4} L S u \rho \lambda_8 (1 - e^{-\lambda_4 t}) / \lambda_4 \qquad (2)$$

where λ_4 is the decay constant of ^{234}Th. The observed increase in the amount of ^{234}Th in the aqueous phase, which is shown in Fig. 1 (*4*), fits the calculated increase predicted by Eq. 2 on the basis of an α-recoil range of 550 Å. This range is in good agreement with the estimated range which has been discussed in connection with investigations of the fossil α-recoil tracks in silicate (*5*). The accuracy of this observed range depends primarily on the accuracy of the estimation of the surface area of the mineral powder and may have an error of about 10 percent.

Table 1. Amounts of dissolved nuclides in the aqueous phase in the suspension of 50 g of zircon powder. The ratio of volume to surface of the zircon powder is 5.9×10^{-5} cm; dpm, disintegrations per minute.

Composition of the aqueous phase	Time for accumulation (days)	Dissolved nuclides (dpm)				
		^{238}U	^{234}U	^{232}Th	^{230}Th	^{234}Th
0.1*N* HNO_3	12.2	5.5 ± 0.2	6.8 ± 0.2	1.6 ± 0.2	5.7 ± 0.2	97 ± 7
0.2*N* HNO_3	5.8	4.2 ± 0.1	5.0 ± 0.1	1.50 ± 0.05	4.5 ± 0.1	50 ± 3
0.1*N* HNO_3	38.4	7.9 ± 0.1	9.1 ± 0.1	1.77 ± 0.06	8.1 ± 0.1	216 ± 6
0.02*N* HNO_3	15.7	1.86 ± 0.06	2.16 ± 0.06	0.54 ± 0.03	1.65 ± 0.05	109 ± 8
0.2% Na_2CO_3	25.8	3.3 ± 0.1	3.7 ± 0.1	0.97 ± 0.08	3.11 ± 0.15	158 ± 12

Table 1 shows the amounts of dissolved nuclides in the aqueous phase for several suspensions. The amounts of the uranium nuclides were estimated by the use of a ^{232}U tracer and alpha spectrometry. The amounts of the thorium nuclides were estimated by the isotope dilution technique with the use of alpha spectrometry and beta-ray counting with a proportional counter.

In all suspensions for which data are shown in Table 1, excess ^{234}U was observed in the aqueous phase. It seems plausible that these excess dissolved ^{234}U atoms moved into the solution along the fossil tracks at the surface of the solid silicate. However, it is not known at this time to what extent this selective dissolution of ^{234}U contributes to the disequilibrium state between ^{234}U and ^{238}U in natural groundwater samples. In contrast to the rate of leaching of α-recoil ^{234}U, which may be affected by the unknown physiochemical nature of the α-recoil atoms in the silicate, the rate of dissolution of α-recoil ^{234}Th into solution depends only on the density and uranium content of the silicate, as indicated by Eq. 1. Thus it seems certain that the ejection of ^{234}Th from the solid silicate surface may occur in nature exactly as indicated by Eq. 1.

On the basis of the experimental data obtained from three red-clay cores of pelagic sediment, Ku (*6*) proposed a migration of ^{234}U in the sedimentary column. His diffusion model, with the assumption that about 30 percent of the ^{234}U generated within the core is free to diffuse, explained the vertical variation in the ratio of ^{234}U to ^{238}U observed. The quantitative explanation for the deficiency of ^{234}U in the sedimentary column on the basis of this diffusion theory supports the existence of a mobile fraction of ^{234}U in the column.

The dissolution of α-recoil ^{234}Th described here was observed in a mineral powder in solution. When the mineral powder was kept in air or in a vacuum, only a part of the α-recoil ^{234}Th from the surface could be dissolved after 4 hours of digestion with cold 0.4*N* HNO_3 solution (Fig. 1). However, when the mineral powder was kept in solution, the amount of dissolved ^{234}Th was independent of the degree of dispersion of the suspension. Even when the mineral powder was kept as a hard sediment, the amount of α-recoil ^{234}Th ejected into the aqueous phase was not affected. Thus in pelagic sediments almost all of the α-recoil ^{234}Th atoms that are ejected from the surface of sedimentary particles may be in the aqueous phase and may become free to diffuse.

When a disintegration of ^{238}U occurs in a particle with a radius R, the probability P of the ejection of α-recoil ^{234}Th atoms from the surface of the particle is given by

$$P = \frac{3}{4}\left[\frac{L}{R} - \frac{1}{12}\left(\frac{L}{R}\right)^3\right] \qquad (3)$$

where L is the α-recoil range of ^{234}Th in the particle. In the pelagic sediments the range of the α-recoil ^{234}Th atoms might be estimated to be about 900 Å on the assumption that the range of the α-recoil atom is inversely proportional to the density of the material in which the disintegration is taking place. From Eq. 3 one can conclude that 30 percent of the ^{234}Th atoms produced in the particles of pelagic sediments may be ejected into the aqueous phase when the particles have a diameter of 0.7 μm. It is plausible that the mobile fraction of ^{234}U in the diffusion theory of Ku (*6*) is supplied by the ^{234}Th fed from the sedimentary particles into the surrounding aqueous phase.

It seems certain that the excess ^{234}U in the underground water having a high activity ratio of ^{234}U to ^{238}U is supplied by the α-recoil ^{234}Th from the surface of the solid silicate. For instance, deep underground water at Tokyo City has a radioactivity attributable to ^{234}U of about 2 disintegrations per minute per 700 liters with an activity ratio of ^{234}U to ^{238}U equal to 4. When this underground water flows into the sand layer with a porosity of 40 percent and when the ratio of volume to surface of the sand is 10^{-2} cm, a residence time of about 600 years is sufficient to bring about the accumulation of the observed amount of ^{234}U in this water from the supply of ^{234}Th in the surface of sand with a uranium content of 1 ppm.

The radioactivity of ^{234}Th in this underground water was about 30 disintegrations per minute per 700 liters, which is only 1/30 of the calculated amount under the above conditions. However, the measured value may be explained by the fact that the pumping up of the underground water would collect mainly the water that has been reserved in a pebble-rich layer having a higher ratio of volume to surface than the fine sand layer. These preliminary results on underground water may lead to a way to investigate the movement and history of underground water.

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