

DETERMINATION OF URANIUM SERIES RADIONUCLIDE ^{231}Pa USING LIQUID SCINTILLATION COUNTING

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ABSTRACT. We use a method for determining naturally occurring alpha-active protactinium in rock samples in which ^{231}Pa is determined simultaneously with uranium, thorium and radium. The purpose of the measurement is to aid the interpretation of U-series data obtained in the context of natural analog studies on radionuclide migration. ^{231}Pa was separated from U and Th by ion-exchange chromatography and measured in a low-level, low-background liquid scintillation counter using pulse-shape analysis (PSA). PSA allows simultaneous measurement of α -active ^{231}Pa and its β -active yield tracer, ^{233}Pa . Simultaneous measurement ensures the reliability of the yield determination. The detection limit was 5.3 mBq for ^{231}Pa . The disequilibrium between ^{231}Pa and ^{235}U in a sample can be distinguished from equilibrium when the disturbance causing the disequilibrium is $<120,000$ yr. In migration analog studies around U deposits, where concentration of ^{231}Pa is well above the determination limit, our method can be applied to obtain information for interpreting U-series data.

INTRODUCTION

Study of the concentrations of uranium-series radionuclides in rock around water-bearing fractures adjoining uranium deposits offers a unique means to assess processes of waste radionuclide migration (see *e.g.*, Chapman, McKinley & Smellie 1984). Interpretation of the radioactive disequilibrium developed between the member radionuclides in one natural decay chain (Fig. 1) can provide information about the concentrations of radionuclides in another. Thus, comparison of the concentrations of protactinium (^{231}Pa) and ^{235}U in the 4N+3 chain can assist interpretation of the radioactive disequilibrium developed between ^{234}U and ^{230}Th in the 4N+2 chain.

The concentration of ^{231}Pa can be determined by measuring its alpha activity. However, the lack of suitable alpha-emitting tracers makes solid-state α spectrometry laborious in disequilibrium studies. To circumvent difficulties encountered in α spectrometry, we chose the liquid scintillation counting (LSC) method. In our LSC system, the nuclide and yield tracer (^{233}Pa) can be measured simultaneously, and measuring time is shortened considerably.

We describe here a new method for determining the U-series radionuclide, ^{231}Pa , in rock samples. This method is currently being applied in migration analog studies at Palmottu, Finland (Suksi, Ruskeeniemi & Rasilainen 1992). Studying ^{231}Pa should improve our understanding of the geochemical behavior of this element and aid in assessing its fate in nuclear waste.

METHODS

We used the Quantulus 1220TM, which is designed to measure low-level activities; background is reduced by careful selection of materials and by massive lead-copper-cadmium shielding. The Quantulus has an active shielding consisting of a liquid scintillator, and it is also equipped with a pulse-shape analyzer, capable of separating radioactive decay modes. The Quantulus 1220TM has two dual multichannel analyzers (MCA): a sample MCA that detects decay events in the sample, and a guard MCA that measures the interfering background (*i.e.*, cosmic muons and environmental gamma radiation). Through pulse-shape analysis (PSA), the sample MCA collects pulses caused by alpha and beta decays into different spectra (Schönhofer & Henrich 1985). Because of poor energy resolution of the LSC method for α particles, we used a high-resolution, solid-state α spectrometer (ORTEC) to confirm the effectiveness of the chemical separation.

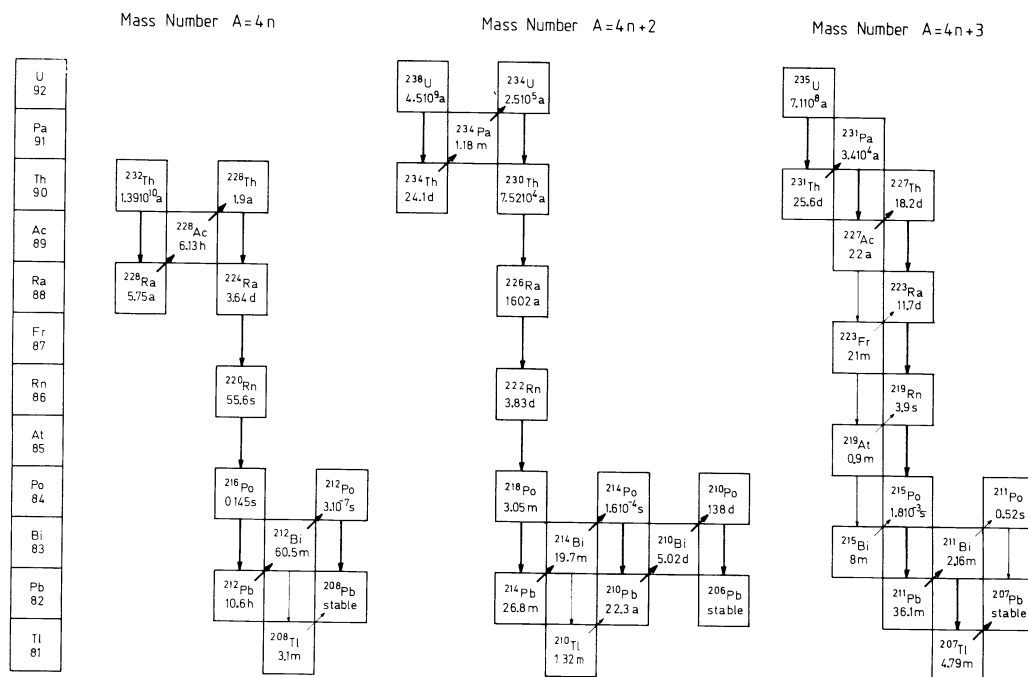


Fig. 1. Uranium decay series

We performed chemical separations and purifications by ion-exchange chromatography. Separations were made in polyethylene columns (BioRad Econocolumns). For anion exchange, we used Dowex 1×8 (100–200 mesh) resin in chloride or in nitrate form. The resin was pretreated with NaOH and HCl. Supor®-100 membrane filters (Gelman) of 0.1- μm pore size and 13-mm diameter were used to collect ^{231}Pa precipitates for α counting. We used Optiphase HiSafe™ 3 (Wallac), Lumagel® (Lumac/3M) and Ultima Gold™ XR (Packard) as liquid scintillators. The scintillation vials were pure polyethylene (Packard) and Teflonized polyethylene (Zinsser).

Protactinium has two β -active isotopes, of which ^{233}Pa , with its longer half-life (27 days), is the more suitable tracer for ^{231}Pa . The maximum energies of β particles of ^{233}Pa are 300 and 600 keV. Because the half-life of ^{233}Pa is only 27.0 days, an isotope generator was constructed for its production. ^{233}Pa was separated from its α -active mother nuclide, ^{237}Np ($t_{1/2} = 2.14 \times 10^6$ yr), by MnO_2 co-precipitation (Inoue, Tochiyama & Hamashima 1978), which was done twice to achieve sufficiently clean ^{233}Pa solution. In spite of the high mass of ^{237}Np compared with that of ^{233}Pa , the separation is effective and easily performed. We used solid-state α spectrometry to check the purity of the separated ^{233}Pa tracer solution. After a measuring time of one week, only a normal background level could be detected in the α spectrum of ^{233}Pa .

To develop and test the methods, we used uraninite that we assumed to be in radioactive equilibrium, because we had no suitable reference material certified for ^{231}Pa . We compared the ^{231}Pa activity in uraninite samples to that of ^{238}U . Activities of individual radionuclides in the decay chain are the same when radioactive equilibrium in natural decay series is established. Assuming a constant value of 0.00726 for the $^{235}\text{U}/^{238}\text{U}$ mass ratio, a value of 21.5 for the $^{238}\text{U}/^{231}\text{Pa}$ radioactivity ratio can be calculated when decay chains are in radioactive equilibrium.

After evaporation of the (8 M HCl + 0.3 M HF) eluent, the residue containing Pa was dissolved in 2 ml of 1 M HCl and transferred into the scintillation vial; 10 ml of scintillator was added and the mixture was allowed to stabilize in the counter overnight before measurement. For solid-state α spectrometry, the Pa fraction was co-precipitated with cerium hydroxide on a Supor®-100 membrane filter according to Sill (1987). After α counting, the filter was transferred to a scintillation vial and 2 ml of 1 M HCl; 10 ml of scintillator were then added. Figures 3 and 4 show the α spectrum of ^{231}Pa measured by LSC and with a solid-state α spectrometer, respectively.

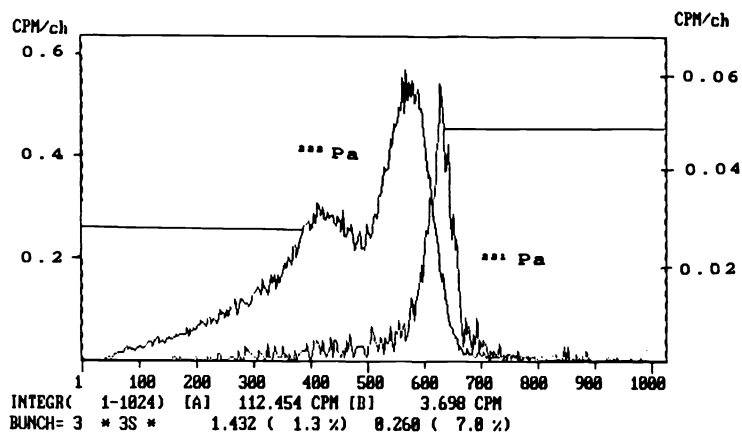


Fig. 3. α spectrum of ^{231}Pa and β spectrum of ^{233}Pa measured in LSC

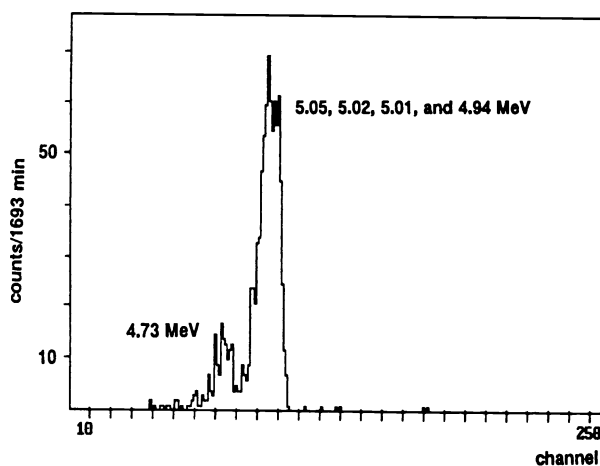


Fig. 4. α spectrum of ^{231}Pa measured by solid-state α spectrometer

We determined chemical yield of Pa as a simple ratio of the ^{233}Pa count rate in the sample and ^{233}Pa count rate in a standard. A new standard was prepared for each series of samples. Chemical yield varied between 50 and 90%. Figure 3 presents the β spectrum of ^{233}Pa .

Counting efficiency was calculated from Equation 1, and was determined on the assumption that, where PSA level is 1, all pulses are on the α side of MCA. Counting efficiency for the filter sample was $66 \pm 2\%$, and for the evaporated sample, $91.5 \pm 1.0\%$.

$$E\% = \frac{[A_{100}(\text{cpm}) - \text{Bkg}_{100}(\text{cpm})] \times 100}{A_1(\text{cpm}) - \text{Bkg}_1(\text{cpm})} \quad (1)$$

where $A_{100}(\text{cpm})$ = ^{231}Pa count rate, while PSA = 100
 $\text{Bkg}_{100}(\text{cpm})$ = background count rate, while PSA = 100
 $A_1(\text{cpm})$ = ^{231}Pa count rate, while PSA = 1
 $\text{Bkg}_1(\text{cpm})$ = background count rate, while PSA = 1.

RESULTS AND DISCUSSION

^{231}Pa can be separated in very pure form for counting. No signs of the other natural α -active nuclides were found in the ^{231}Pa α spectrum measured by solid-state α spectrometry (Fig. 4). The counting efficiency in LSC is >90% (average 91.5%). We determined precision of the method by analyzing a set of aliquots of a solution containing dissolved uraninite (Table 1); we assayed each counting sample three times. The same samples were also analyzed by solid-state α spectrometry. We compare the results in Table 2.

TABLE 1. Precision of the Method

Volume (ml)*	Activity (mBq ml ⁻¹)	Average (mBq ml ⁻¹)	Variance (%)
2	68.8 ± 3.2	70.0 ± 1.8	2.57
	69.0 ± 3.2		
	72.2 ± 3.2		
3	61.7 ± 2.3	61.8 ± 1.6	2.59
	60.3 ± 2.2		
	63.3 ± 2.3		
4	69.3 ± 2.5	70.3 ± 1.3	1.85
	69.8 ± 2.5		
	71.7 ± 2.5		
1.5	58.7 ± 3.0	61.7 ± 3.0	4.86
	61.8 ± 3.0		
	64.7 ± 3.2		
1.5	72.5 ± 3.0	73.0 ± 0.9	1.23
	72.3 ± 3.0		
	74.0 ± 3.3		
Average		67.3 ± 5.2	7.72

*Volume refers to aliquot size of the solution containing dissolved uraninite (UKTR/1)

We tested the method on uraninite samples from different localities where we expected ^{231}Pa to be in radioactive equilibrium with its parent U. Calculated $^{238}\text{U}/^{231}\text{Pa}$ radioactivity ratio is 21.5. The measured activity ratios (Table 3) indicated radioactive equilibrium between Pa and U. Measurement error in the $^{238}\text{U}/^{231}\text{Pa}$ activity ratio varied between 7 and 17%.

TABLE 2. Comparison of α spectrometry and LSC

Volume (ml)	α (mBq ml ⁻¹)	LSC (mBq ml ⁻¹)
2	73.8 \pm 5.0	70.0 \pm 1.8
3	74.7 \pm 1.2	61.8 \pm 1.6
4	80.8 \pm 1.3	70.3 \pm 1.3
1.5	71.5 \pm 1.3	61.7 \pm 3.0
1.5	57.5 \pm 0.3	73.0 \pm 0.9
Average	71.3 \pm 8.6	67.4 \pm 5.2

TABLE 3. Accuracy of Determination of Radioactive Equilibrium Between ²³⁸U and ²³¹Pa

Uraninite	²³¹ Pa (mBq ml ⁻¹)	²³⁸ U (mBq ml ⁻¹)	²³⁸ U/ ²³¹ Pa
R346	31.5 \pm 5.3	656 \pm 17	20.8 \pm 3.6
	30.8 \pm 5.2	635 \pm 15	20.6 \pm 3.5
15.10	167 \pm 28	3340 \pm 70	20.0 \pm 3.4
	174 \pm 29	3320 \pm 110	19.1 \pm 3.2
72.10	157 \pm 26	3870 \pm 130	24.7 \pm 4.2
	169 \pm 26	3610 \pm 130	21.4 \pm 3.8
UKTR/1	67.3 \pm 5.2	1340 \pm 10	19.8 \pm 1.5

The detection limit for ²³¹Pa in LSC is 0.29 cpm, which is equivalent to 0.005 Bq of ²³¹Pa. Corresponding values in solid-state α spectrometry are 0.071 cpm and 0.008 Bq ²³¹Pa. Thus, the precision of LSC is slightly better than that of α spectrometry, and the higher measurement efficiency results in a lower detection limit (L_q) (1σ), which was calculated from the following equation (Currie 1968)

$$L_q = 50 \times [1 + (1 + (\mu_b/25))^2] \quad (2)$$

where μ_b is the number of counts in the α spectrum of ²³³Pa over 500 min (LSC) or the number of background counts in 1440 min (0.00136 cpm for α spectrometry).

Measurement accuracy of radioactive disequilibrium between isotopes and their parents depends on how far the system is from radioactive equilibrium. In the samples examined, where U concentrations were high and radioactive equilibrium could be indicated, the error for the ²³⁸U/²³¹Pa activity ratio varied between 7 and 17%. If one takes the mean of the errors, any disequilibrium between ²³¹Pa and ²³⁵U in a sample can be distinguished from equilibrium if the sample age or the disturbance that caused the disequilibrium is <120 ka. To apply the method to samples containing normal environmental levels of this isotope, much larger samples would be needed. However, the recent progress in developing LS systems (especially for α particles), incorporating better energy resolution and lower background should improve the applicability of this method. To improve further the interpretation of U-series data, we have developed an LSC method for determining ²²⁶Ra (Saarinen & Suksi 1992).

CONCLUSIONS

An LSC-based method was developed for determining ^{231}Pa concentrations in rock. The method allows simultaneous measurement of an α -active ^{231}Pa and its β -active yield tracer, ^{233}Pa , rendering the chemical yield determination reliable and accurate. The detection limit for ^{231}Pa is 5.3 mBq. Counting times can be reduced considerably from those of solid-state α spectrometry, and a series of samples can be measured automatically.

ACKNOWLEDGMENTS

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