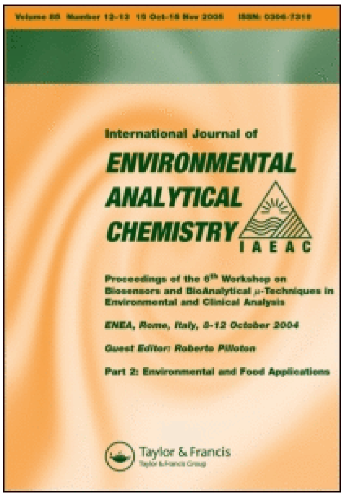

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Marine Sediments and Snow from Ross Sea Region (Antarctica) Dating by ^{210}Pb Method

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MARINE SEDIMENTS AND SNOW FROM ROSS SEA REGION (ANTARCTICA) DATING BY ^{210}Pb METHOD

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^{210}Pb is widely used to determine accumulation rates in order to obtain a time scale in environmental samples. The most accurate method uses the determination of ^{210}Pb via its grand-daughter ^{210}Po by alpha spectrometry. Unfortunately this method requires a complex wet-chemistry procedure to achieve the separation of ^{210}Po from its matrix. In this work a simplified procedure for the chemical separation of ^{210}Po is proposed and applied to three marine sediment cores and a 10 m snow core collected in Antarctica. The calculated sedimentation rates for marine sediments range from 0.053 to 0.071 cm y^{-1}. The mean annual accumulation rate for the snow is 16.6 cm y^{-1} w.e.. A comparison with literature data in the same region is given.

Keywords: ^{210}Pb; alpha spectrometry; radiodating; marine sediments; snow; Antarctica

INTRODUCTION

The constant changes or events occurring in the physical, chemical and biological systems are often recorded in various earth materials, but the recognised global source of environmental information is somewhat limited. They include marine sediments, lake and bog deposits, tree-rings, periglacial features and snow and ice deposits.

It is known that the period of greatest impact and most dramatic transformations due to human effect on the environment lies within the last 150 years. Marine sediments and snow deposits provide a baseline for reconstructing many aspects of this impact, so the assessment of detailed and accurate chronologies of

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deposits is of central importance. These are required not only for measurement of sedimentation rates but also for dating events and calculation of element fluxes.

The recently issued Protocol to the Antarctic Treaty on Environmental Protection (26 countries) recognizes the "unique opportunities in Antarctica for scientific monitoring of and research on processes of global as well as regional importance". Polar areas, high mountain districts, and desert lands are the most suitable fields for experimental investigation on the past and the present evolution of the climatic parameters, along with the probable anthropogenic induced influences, as these areas are the least affected by anthropogenic influence and pollution. Moreover, in the remote areas climatic parameters reach the maximum values, natural phenomena are remarkable and are exemplarily shown.

One of the most used methods of dating on a time scale of 100–200 years is by means of ^{210}Pb. This technique has been proposed by Goldberg (1961)[1] and was applied to the dating of lake sediments by Krishnaswami et al. (1971)[2]. This method has become very popular in dating recent sediments but was successfully applied to snow deposits too.

^{210}Pb is the first long-lived ($t_{1/2} = 22.26$ y) decay product of ^{222}Rn, the only gaseous radionuclide in the ^{238}U decay chain. Since ^{222}Rn is mainly outgassed from land surfaces (by the decay of ^{226}Ra) and has a half-life of 3.83 days, ^{210}Pb is primarily produced in the lower troposphere over continents. Soon after its formation ^{210}Pb becomes irreversibly attached to submicron aerosol particles[3]. ^{210}Pb is mainly removed (80 %) from the atmosphere by wet scavenging[4].

According to Oldfield and Appleby[5], ^{210}Pb resulting from the decay of ^{226}Ra present within the crustal matrices is defined supported ^{210}Pb, while the ^{210}Pb originating from the atmospheric input is referred to as unsupported or excess ^{210}Pb. ^{226}Ra in core samples is usually in secular equilibrium with supported ^{210}Pb, therefore when in the deepest sections constant ^{210}Pb activities are found, they can be taken as a measure of supported ^{210}Pb; this amount needs to be subtracted to the experimental value of ^{210}Pb in order to obtain the excess ^{210}Pb fraction which has to be used for radiodating.

The age of the matrix at any particular depth depends on the sedimentation rate and can be calculated from the excess ^{210}Pb activity according to the radioactive decay law:

$$A(x) = A(0)\, e^{-\lambda x/W}$$

where $A(x)$ = activity at depth x (Bq)

$A(0)$ = activity at depth 0 (Bq)

$\lambda = \ln 2/t_{1/2}$ (y^{-1})

W = sedimentation rate (cm/y)

x = depth (cm)

This approach is based on the hypothesis that excess ^{210}Pb (i.e., the atmospherically derived fraction) deposition rate is constant from year to year. In the case of undisturbed sedimentary environments there is a linear relationship between depth and the logarithm of excess ^{210}Pb with slope $-\lambda/w$. From the slope it is therefore possible to calculate the sedimentation rate. In the case that the amount of solids deposited yearly is constant, the core dating method is defined as "constant flux-constant sedimentation" (CF-CS).

^{210}Pb activity can be determined by three different techniques: alpha spectrometry of its granddaughter ^{210}Po ($E_\alpha = 5.3$ MeV), direct gamma spectrometry ($E_\gamma = 0.046$ MeV) and beta spectrometry of its daughter ^{210}Bi ($E_{max} = 1.16$ MeV).

There are at least four advantages related to the first one:

- alpha counting has a higher counting efficiency and a lower background than beta and gamma counting. For this reason the lowest detectable activity (LDA) is sufficiently lower to allow the determination ^{210}Pb in the snow samples too;
- the chemical separation of ^{210}Po from sediments and snow is relatively simple;
- polonium deposits spontaneously in acid solution onto a silver planchet;
- ^{209}Po (or ^{208}Po) can be used as a yield tracer in the chemical separation.

The aims of this paper were:

1. To propose a revised procedure for the determination of ^{210}Pb via its grand-daughter ^{210}Po in sediments based on the method described by Eakins and Morrison (1978)[6].
2. To apply this procedure, suitably modified, to a snow deposit.

In order to verify both procedures, three sediment cores and a firn core collected in the Ross Sea Region (Antarctica) throughout the Austral summers 1990–91 and 1993–94, respectively, were analyzed and dated.

EXPERIMENTAL

The ^{210}Pb determination via ^{210}Po can be summarized by the two following steps: the separation of ^{210}Po from the matrix and the spontaneous deposition of ^{210}Po onto a silver planchet. The application of this procedure requires the attainment of secular equilibrium between these radionuclides. As a rule, secular equilibrium is reached after 5–6 half-lives of the daughter radionuclide; in the case of polonium it means a delay of 5 times 138 days (~ 2 years) from the time of deposition.

Marine sediments

Flynn[7] was the first to report about the determination of low levels of ^{210}Po in environmental materials. The radionuclide was separated from the matrix by an acid leaching procedure; the same method, with a few variations, has been used by other authors [2,7]. Instead Eakins and Morrison[8] reported about an interesting separation of this radionuclide using the relatively low sublimation temperature of the polonium chloride. We modified this last method in order to obtain a faster and easier procedure applicable on a routine scale. The modified procedure used for sediments is summarized in Table I.

TABLE I Radiochemical procedures for the determination of ^{210}Pb via ^{210}Po in sediment (by Eakins and Morrison[6] modified) and snow

Sediments

1. Dry the sediment at 110°C for 12 hours. Then homogenize to a fine powder.

2. Take a 2 g aliquot in 50 ml beaker, add 5 ml of Hcl (12M) and stir. Add 0.1 Bq of ^{210}Po and stir.

3. Dry with 250 W IR lamp.

4. Transfer carefully into a 160 × 16 mm test tube. Push a plug of quartz wool down to the bottom to retain the sediment and to clean the walls. Insert a wet plug of quartz wool into the open end.

5. Insert the closed end of the tube for one-fourth into a horizontal tubular furnace and distill at 500°C for 30 min.

6. Remove the tube and cut off and discard the bottom containing the sediment. Push the wet quartz wool down the remainder of the tube into a 50 ml beaker and rising the tube with 50 ml of HNO_3 (15M) into the beacker. Boil for 10 min.

7. Filter off the quartz wool through a sintered glass filter funnel (No. 2 porosity)collecting the filtrate in a 50 ml beacker. Boil down to about 2 ml.

8. Add 10 ml of HCl (12M) and boil down to about 2 ml. Repeat the operation.

9. Dilute to about 35 ml. Add 0.1 g of ascorbic acid and 0.05 g of sodium citrate tribasic and stir.

10. Clean a 450 mm^2 silver disk with metal polish and wash in methanol. Cover one side of the disk with synthetic resin. Place the disk into the beaker and plate for 3 h at 90°C in a thermostated bath.

11. Remove the disk from the beaker, wash with water and methylated spirit.

12. Count the disk in the alpha spectrometer and record the areas at 4.88 and 5.30 MeV peaks.

Snow

1. Take a 200–300 g samples in a 600 ml teflon beaker and melt at room temperature.

2. Add 1 ml of HCl (12M) and 0.04 Bq of ^{209}Po and stir.

3. Concentrate by sub-boiling evaporation to 25 ml.

4. Transfer in a 50 ml teflon beaker with water washings to a final volume of about 35 ml.

5. See pts. 9 to 12 of the procedure for the sediments.

The main modifications involved are:

1. ^{209}Po (AEA Technology, Harwell, UK) is used instead of ^{208}Po as a tracer for the determination of the radiochemical recovery of ^{210}Po. ^{209}Po has an alpha energy of 4.88 MeV and it can be better resolved from the 5.30 MeV alpha emission of ^{209}Po with respect to the 5.11 MeV alpha particle of ^{208}Po.
2. The IR lamp drying has replaced the oven one which was more difficult due to the necessity to evaporate concentrated acid solutions.
3. The quantities of acids used in steps 6 and 8 are dramatically reduced, in order to decrease time and costs.
4. The spontaneous deposition of ^{210}Po onto a silver disk is simplified and the conditions are controlled more strictly. In particular the pH of the solution must be kept be between 0.5 and 2.0 in order to obtain the maximum recoveries. Sodium citrate (complexing agent) and ascorbic acid (reducing agent) are added in order to minimize the effects of the main interfering agents in the deposition process (Fe^{3+} and NO_3^-).

The radiometric measurement was performed by a Soloist™ Alpha Spectrometer with an Ion-Implanted-Silicon detector Ultra™ Ortec with an active area of 450 mm^2 (Efficiency > 25%). The vacuum chamber was operated at $p <$ 50 mTorr and the energy range selected was between 4 and 6 MeV. The alpha spectrometer was connected to a multichannel analyzer (Snip – Silena). The ^{210}Po activity (that means ^{210}Pb) was obtained from the ratio of the counts in the 5.30 MeV peak (^{210}Po) and 4.88 MeV peak (^{209}Po) and the level of ^{209}Po spike added. The counting time ranged between $9 \cdot 10^4$-$2.5 \cdot 10^5$ s, in order to have peak areas of at least 10^3 counts.

The precision of the method was calculated by 10 replicates of two sediment samples with a different amount of ^{210}Pb. The results are reported in the Table II.

TABLE II Results on analytical precision obtained by 10 replicates

Sample	*^{210}Pb activity via ^{210}Po (Bq/Kg)*	*std. dev. (%)*	*Radiochemical Recovery (%)*
PQ 18GS	102.3	3.1	62.4
PQ24GS	45.3	2.2	61.8

Sediment samples have been collected in the North-West Ross Sea during the 1990–91 Italian oceanographic expedition in Antarctica. Sampling sites are reported in Table III. Sampling has been carried out by a box corer and sub-sampled with polyethylene tubes (Φ = 54 mm, l = 400 mm). Cores have been preserved at 4°C and successively sectioned every 0.5 or 1 cm.

TABLE III Geographical position of sampling stations

Station	*Latitude S*	*Longitude E*	*Water depth (m)*	*Core length (cm)*
13	74° 03.72′	176° 48,78′	403	32
18	73° 25.93′	177° 43.57′	449	30
23	74° 25.69′	169° 35.38′	678	24

Snow

The procedure for snow samples is reported in Table I. Compared to sediments, the procedure is simpler because no separation from the matrix is required. In fact, the dating of snow is possible because the internal production of ^{210}Pb due to ^{226}Ra in the embedded dust, or ^{222}Rn in the air filling the pore space, can be neglected, as previously reported[9]. This means that ^{210}Pb measured exactly represents the unsupported fraction. The main problem in ^{210}Pb determination in Antartic snow samples is its low content (3–4 orders of magnitude lower than sediments, about 10^{-18} M), so some attention is required. Handling and treatment of samples were carried out under a Class-100 laminar flow bench-hood in order to minimize any environmental contaminations. Only teflon beakers, decontaminated according to standard procedures for trace analysis[10], were used.

In this case the radiometric determination requires longer counting times ($4 \cdot 10^5 - 5 \cdot 10^5$ s and more) in order to minimize the Lowest Detectable Activity (LDA) . Since the LDA has been defined[11] as:

$$LDA = \frac{1 + \sqrt{1 + 2bt}}{0.5Et}$$

where b = instrumental background (Bq)

t = countinty time (s)

E = counting efficiency

and since the instrument has a background of about 8 counts/day, it is possible to bring down the LDA increasing the counting time. The standard deviation as an estimate of method precision, calculated as described above, was 3.5%.

The firn core has been collected during the 1993–94 Italian Expedition in Antarctica. The sampling site was located at Hercules Nevè, about 200 km from the Italian Station at Terra Nova Bay (Latitude S 73° 07.57′, Longitude E 164° 58.20′, height 2990 m a.s.l.). The core was taken by using an all-plastic manual drill, 50 cm thick sections were stored at – 20°C until the day of analysis in two sealed polyethylene bags.

TABLE IV ^{210}Pb content in sediment cores studied

Core 13				*Core 18*				*Core 23*			
Sample	*Depth (cm)*	^{210}*Pbtot (Bq/Kg)*	^{210}*Pb ex (Bq/Kg)*	*Sample*	*Depth (cm)*	^{210}*Pbtot (Bq/Kg)*	^{210}*Pb ex (Bq/Kg)*	*Sample*	*Depth (cm)*	^{210}*Pbtot (Bq/Kg)*	^{210}*Pb ex (Bq/Kg)*
13.1	0.0–1.0	132.5	117.6	18.1	0.0–1.0	125.8	100.9	23.1	0.0–1.0	111.8	97.1
13.2	1.0–2.0	78.9	64.0	18.2	1.0–1.5	110.1	85.2	23.2	1.0–1.5	92.6	77.9
13.3	2.0–2.5	80.4	65.5	18.3	1.5–2.0	112.9	88.0	23.3	1.5–2.0	86.8	72.1
13.4	2.5–3.0	51.5	36.6	18.4	2.0–2.5	91.4	66.5	23.4	2.0–2.5	78.9	64.2
13.5	3.0–3.5	42.5	27.6	18.5	2.5–3.0	66.6	41.7	23.5	2.5–3.0	68.3	53.6
13.6	3.5–4.5	42.6	27.7	18.6	3.0–3.5	46.2	21.3	23.6	3.0–3.5	65.0	50.3
13.7	4.5–5.0	35.9	21.0	18.7	3.5–4.0	47.3	22.4	23.7	3.5–4.0	55.2	40.5
13.8	5.0–5.5	28.4	13.5	18.8	4.0–4.5	41.2	16.3	23.8	4.0–4.5	48.9	34.2
13.9	5.5–6.0	22.1	7.2	18.9	4.5–5.0	51.1	26.2	23.9	4.5–5.0	31.8	17.1
13.10	6.0–6.5	16.8	1.9	18.10	5.0–5.5	50.7	25.8	23.10	5.0–5.5	24.0	9.3
13.11	6.5–7.0	15.9	1.0	18.11	5.5–6.0	35.6	10.7	23.11	5.5–6.0	24.2	9.5
13.12	7.0–7.5	14.6		18.12	6.0–6.5	31.2	7.3	23.12	6.0–7.0	20.1	5.4
13.13	7.5–8.0	15.0	0.1	18.13	6.5–7.0	25.8	0.9	23.13	7.0–8.0	14.5	
13.14	8.0–8.5	15.3	0.4	18.14	7.0–7.5	25.1	0.2	23.14	8.0–8.5	13.5	
13.15	8.5–9.0	14.4		18.15	7.5–8.0	24.8		23.15	8.5–9.0	15.9	1.2
13.20	12.0-13.0	15.0	0.1	18.20	11.0-11.5	24.2		23.20	11.0-11.5	15.2	
13.25	16.5-17.0	14.6		18.25	13.5-14.0	24.5		23.25	15.5-16.5	14.5	

RESULTS AND DISCUSSION

Marine sediments

The total ^{210}Pb and the corresponding excess fractions are listed in Table IV. ^{210}Pb excess was calculated averaging the ^{226}Ra value in the deepest 5 sections showing a constant value and substracting it from the total ^{210}Pb. Plotting the natural logarithm of excess ^{210}Pb against depth, the slope of the stralight line is related to accumulation rate by the following expression, assuming Constant Flux-Constant Sedimentation model[12]:

$$s = \frac{\ln 2}{W_{t1/2}}$$

where s = slope in cm^{-1}
W= accumulation rate in cm y^{-1}
$t_{1/2}$ = half life in y

Accumulation rates are shown in Table V. Correlation coefficients ranged from 0.93 to 0.96. Accumulation rates obtained by alpha spectrometry are in agreement with those reported in the literature for the same area[13]. These low accumulation rates outline that sediment layers related to the last 150 year, correspond to about 8–11 cm, therefore environmental studies about possible anthropogenic effects in this region, should be confined only to the uppermost layers.

TABLE V Accumulation rates of sediment cores

	Core 13	*Core 18*	*Core 23*
Accumulation rate (cm/y)	0.053	0.071	0.063

Snow

Results of ^{210}Pb measurements in the firn core are shown in Table VI. Differently from sediments, ^{210}Pb does not decrease regularly with depth because each layer corresponds to a short-term variation of ^{210}Pb activity in the lower troposphere. Accumulation rate, calculated using the Constant Flux-Constant Sedimentation model, was 16.6 cm w. eq y^{-1}. This result is in good agreement with those reported by Udisti[14] (16.0 cm w. eq y^{-1}) in the same sampling site, using a dating method based on a combination of concentration profiles of three chemical parameters (H_2O_2, MSA and $nssSO_4^{2-}$) and also with Allen et al.[15] for a near area (18.2 cm w. eq y^{-1}). Based on these accumulation rates, 150 years correspond to about 25 m.

TABLE VI ^{210}Pb activity in the firn layers

Section	*Depth (cm)*	*Density (g cm^{-3})*	*Depth (cm w.eq.)*	*^{210}Pb (mBq Kg^{-1})*
FC2-1	0–14	0.38	2.6	13.0
	14–27	0.31	7.3	9.0
	27–47	0.35	12.8	8.1
FC2-2	47–67	0.36	19.8	11.8
	67–84	0.37	26.5	11.7
	84–95	0.37	31.7	9.4
FC2-3	95–114	0.39	37.4	
	114–134	0.35	44.6	12.2
FC2-4	134–181	0.37	56.8	
FC2-5	181–230	0.37	74.6	
FC2-6	230–248	0.39	87.2	9.0
	248–264	0.38	93.7	9.8
	264–279	0.38	99.6	6.7
FC2-7	279–329	0.41	112.7	
FC2-8	329–351	0.46	128.0	9.1
	351–372	0.38	137.1	6.9
FC2-9	372–422	0.43	151.9	
FC2-10	422–453	0.43	169.4	
	453–462	0.42	178.1	11.9
	462–473	0.44	184.9	7.4
FC2-11	473–505	0.47	194.8	
FC2-12	505–556	0.47	214.3	
FC2-13	556–606	0.47	238.1	
FC2-14	606–656	0.47	261.6	
FC2-15	656–709	0.47	285.8	
FC2-16	709–729	0.47	310.3	5.8
	729–744	0.46	326.9	4.9
	744–761	0.48	342.0	3.7
FC2-17	761–811	0.48	362.2	
FC2-18	811–838	0.46	380.4	7.2
	838–859	0.48	391.8	5.5

Depth is expressed in cm water eq. according to Lambert and Sanak[3]. Missing sections have been used by other research groups for the determination of different chemical parameters.

CONCLUSIONS

The procedure proposed for the determination of ^{210}Pb via ^{210}Po by alpha spectrometry demonstrates its reliability for both marine sediments and snow. For the latter one, the dating based on this method shows a remarkable agreement with a non-radioactive technique. The simplifications introduced as well as the analytical precision achieved, make this method one of the most utilizable for chronologies on a time scale of 100- 150 years.

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