

# DETERMINATION OF $^{226}\text{Ra}$ IN LAKE SEDIMENTS BY LIQUID SCINTILLATION COUNTING OF COCKTAIL-EXTRACTED $^{222}\text{Rn}$

KARL IRLWECK and GABRIELE WALLNER

Institute of Inorganic Chemistry, University of Vienna, Währingerstrasse 42, A-1090 Austria

**ABSTRACT.** Increasing environmental impact studies in recent years have induced renewed interest in  $^{210}\text{Pb}$  dating of young lake sediments.  $^{210}\text{Pb}$  ( $t_{1/2} = 22.3$  yr) is a decay product of  $^{226}\text{Ra}$  ( $t_{1/2} = 1622$  yr) in sediments as well as airborne decay products. Therefore, uppermost sediments contain  $^{210}\text{Pb}$  both supported and unsupported by  $^{226}\text{Ra}$  decay, and the relative proportion of  $^{210}\text{Pb}$  decreases with increasing age of the sediment. For best accuracy of this dating technique, it is important to measure the  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  on the same sediment samples. Our technique involves measurements of the  $^{210}\text{Pb}$  content in different layers of a sediment core. Liquid scintillation spectrometry applying alpha/beta pulse-shape analysis allows the measurement of  $^{226}\text{Ra}$  by extraction of the ingrown  $^{222}\text{Rn}$  into a mineral oil-based scintillator. We performed such measurements on sediment samples from different lakes. Our results show that the  $^{226}\text{Ra}$  content is usually in the range of 5 to 15  $\text{mBq kg}^{-1}$  of dry sediment. We have also observed much higher values, up to 120  $\text{mBq kg}^{-1}$ , depending on the geological setting of the lake under study.

## INTRODUCTION

Recently deposited lake sediments can be dated by measuring the  $^{210}\text{Pb}$  content in different layers of a sediment core. One must also distinguish between the fractions of "excess" or "unsupported"  $^{210}\text{Pb}$  from airborne Rn decay products and the "supported"  $^{210}\text{Pb}$ , which results from the decay of the natural  $^{226}\text{Ra}$  background of the sediment. Normally, this is done by analyzing the total  $^{210}\text{Pb}$  content of dried sediment down the sediment core until a relatively low and nearly constant value is found in the deeper layers deposited several  $^{210}\text{Pb}$  half-lives ( $t_{1/2} = 22.3$  yr) ago. This value is assumed to be the typical background of the upper layers of the core. The depth profile of the unsupported  $^{210}\text{Pb}$  can be obtained by subtracting this background value from the total measured  $^{210}\text{Pb}$  content of each layer. Such profiles can be evaluated to yield model ages of different deposits (Goldberg 1963; Krishnaswamy *et al.* 1971; Appleby & Oldfield 1978).

In this study, we determined the  $^{226}\text{Ra}$  content of each sediment sample, with respect to the  $^{210}\text{Pb}$  content, and assessed an upper limit of the supported  $^{210}\text{Pb}$  fraction directly. We describe our analytical method, designed especially for small amounts of sediment material (0.5–3 g dry weight); we employed alpha spectrometry and liquid scintillation (LS) spectrometry to determine  $^{210}\text{Pb}$  *via*  $^{210}\text{Po}$ , and  $^{226}\text{Ra}$  *via*  $^{222}\text{Rn}$  (+  $^{218}\text{Po}$  and  $^{214}\text{Po}$ ), respectively. We provide data that demonstrate characteristic differences of the natural background values as well as of the total  $^{210}\text{Pb}$  concentrations in sediments from lakes in different geological formations.

## METHODS

Figure 1 shows the analytical procedure for determining  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$ . The  $^{210}\text{Pb}$  is assayed by measuring its decay product,  $^{210}\text{Po}$ , assuming that radioactive equilibrium is established between both isotopes (Eakins & Morrison 1978). The dried sediment samples are treated in 35%  $\text{HNO}_3$  (20 ml  $\text{g}^{-1}$ ) for 3 h with a known amount of  $^{208}\text{Po}$  added as a spike; the slurry is evaporated repeatedly to dryness until all organic matter is oxidized. Then the material is converted to chlorides with concentrated or fuming hydrochloric acid. Then the solution is separated from insoluble residues, taken to dryness and dissolved in 1 M HCl (50 ml). The polonium deposits spontaneously onto a 1-cm-diameter copper planchet, which is stirred magnetically in this solution for 2 h at  $\sim 95^\circ\text{C}$ . The copper disk is cleaned by rinsing with distilled water and dried. We determined, by  $\alpha$ -spectroscopic measurement of one side of this disk, the  $^{210}\text{Po}$  and  $^{208}\text{Po}$   $\alpha$  activ-

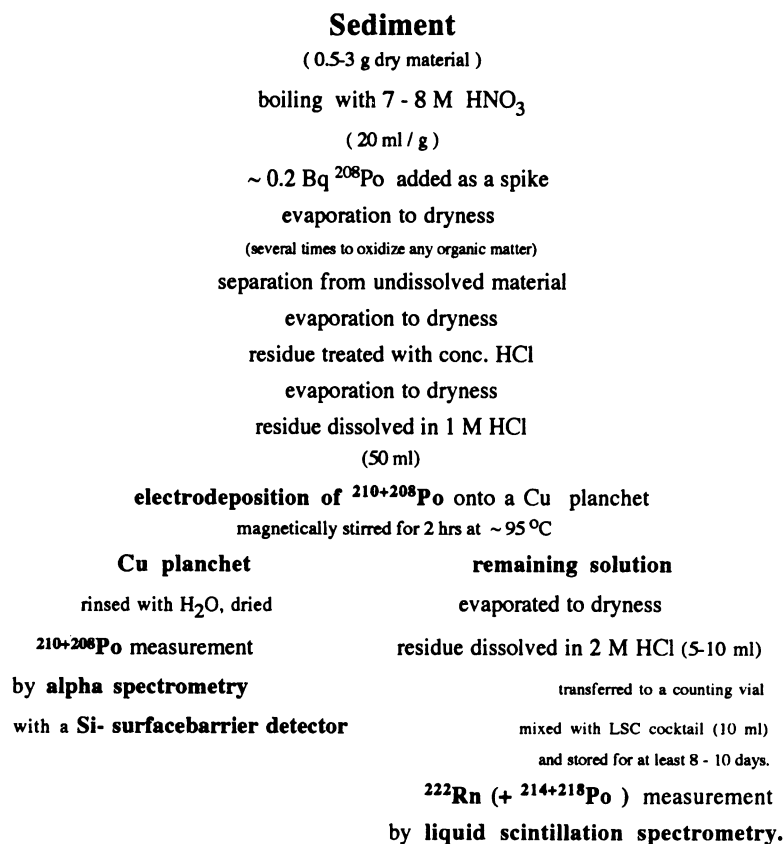


Fig. 1. Sequential analysis of <sup>210</sup>Pb via <sup>210</sup>Po and <sup>226</sup>Ra via <sup>222</sup>Rn

ities at energies of 5.30 and 5.11 MeV, respectively. We performed  $\alpha$  counting with a silicon surface-barrier detector and a multichannel pulse-height analyzer system using counting times of at least 30,000 sec. Figure 2 illustrates the energy resolution of such a spectrum, sufficient to separate the peaks of these Po isotopes. The radiochemical yield normally is between 30% and 45% measured exactly as <sup>208</sup>Po recovery. The minimum detectable <sup>210</sup>Pb content in sediments is about 0.5 mBq per sample, based on 3  $\sigma$  of the standard deviation of the background count rate.

The remaining solution was taken to dryness, dissolved again in 5–10 ml of 2 M HCl and transferred to a scintillation vial; we then added an immiscible mineral oil-based scintillator (New England Nuclear, Boston, Massachusetts, USA, NEF-957A). The vial was sealed and stored for at least two weeks and shaken occasionally. After ingrowth from the <sup>226</sup>Ra in the aqueous solution, <sup>222</sup>Rn was extracted into the scintillator phase, and measured, together with its decay products, <sup>218</sup>Po and <sup>214</sup>Po, by  $\alpha/\beta$  spectrometry and pulse-shape analysis (Oikari *et al.* 1987). Depending on the degree of radiochemical equilibrium reached between <sup>226</sup>Ra and <sup>222</sup>Rn, an apparent counting efficiency up to nearly 300% was achieved with regard to <sup>226</sup>Ra. This was confirmed by measuring a series of spiked samples. Non-equilibrium values were corrected as usual. These measurements were performed with a low-level Wallac 1220<sup>TM</sup> Quantulus LS spectrometer. Figure 3 shows typical spectra of two sediment samples from Badsee and the background of a chemical blank analysis. The overlapping  $\alpha$  peaks of <sup>222</sup>Rn (5.49 MeV) and <sup>218</sup>Po (6.00 MeV) are distinguished from <sup>214</sup>Po (7.68 MeV), a clear separation between the aqueous and the scintillator phase provided

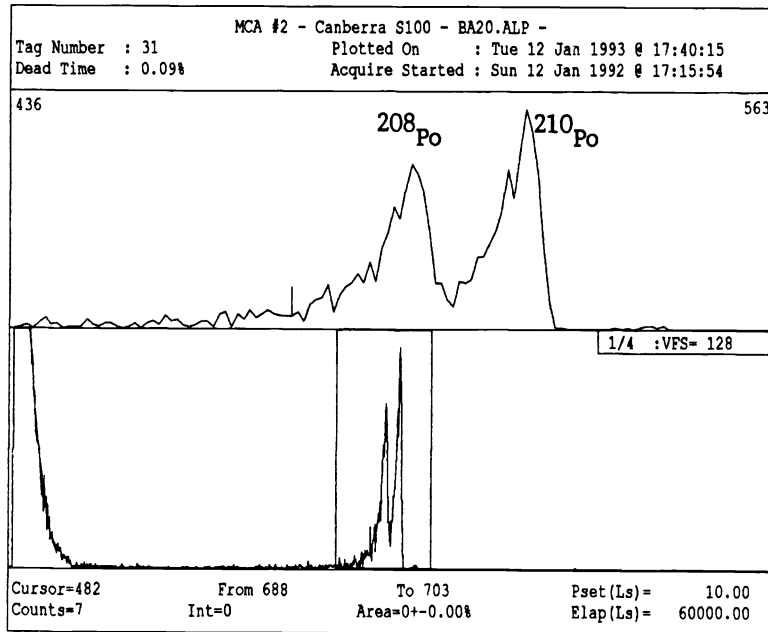
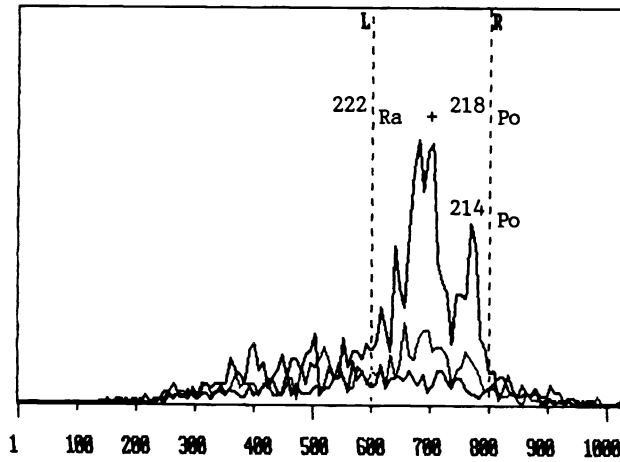


Fig. 2. Alpha spectrum of <sup>210</sup>Po separated from lake sediment after deposition onto a copper disk, measured with a silicon-surface barrier detector, counting time 60,000 sec. (Sediment: 1.00 g; <sup>208</sup>Po (spike) recovery: 40.0%; <sup>210</sup>Po: 99.4 mBq, total)

[A] 0.050 CPM/ch 246.82 min \222Rn\_24\0814501N.001 SP#12  
 [B] 0.050 CPM/ch 246.82 min \222Rn\_23\0814201N.001 SP#12  
 [C] 0.050 CPM/ch 493.61 min \222Rn\_19\0810501N.001 SP#12



INTEGR( 688- 888) [A] 1.066 CPM [B] 3.322 CPM [C] 0.537 CPM  
 BUNCH= 8 \* 3S = 0.197 ( 18.5 %) 0.348 ( 18.5 %) 0.099 ( 18.4 %)

Fig. 3. Alpha spectrum of cocktail-extracted <sup>222</sup>Rn and its daughter products by LSC; counting time 15,000 sec. A. Sediment sample BA/20; B. Sample BA/4; C. Chemical blank

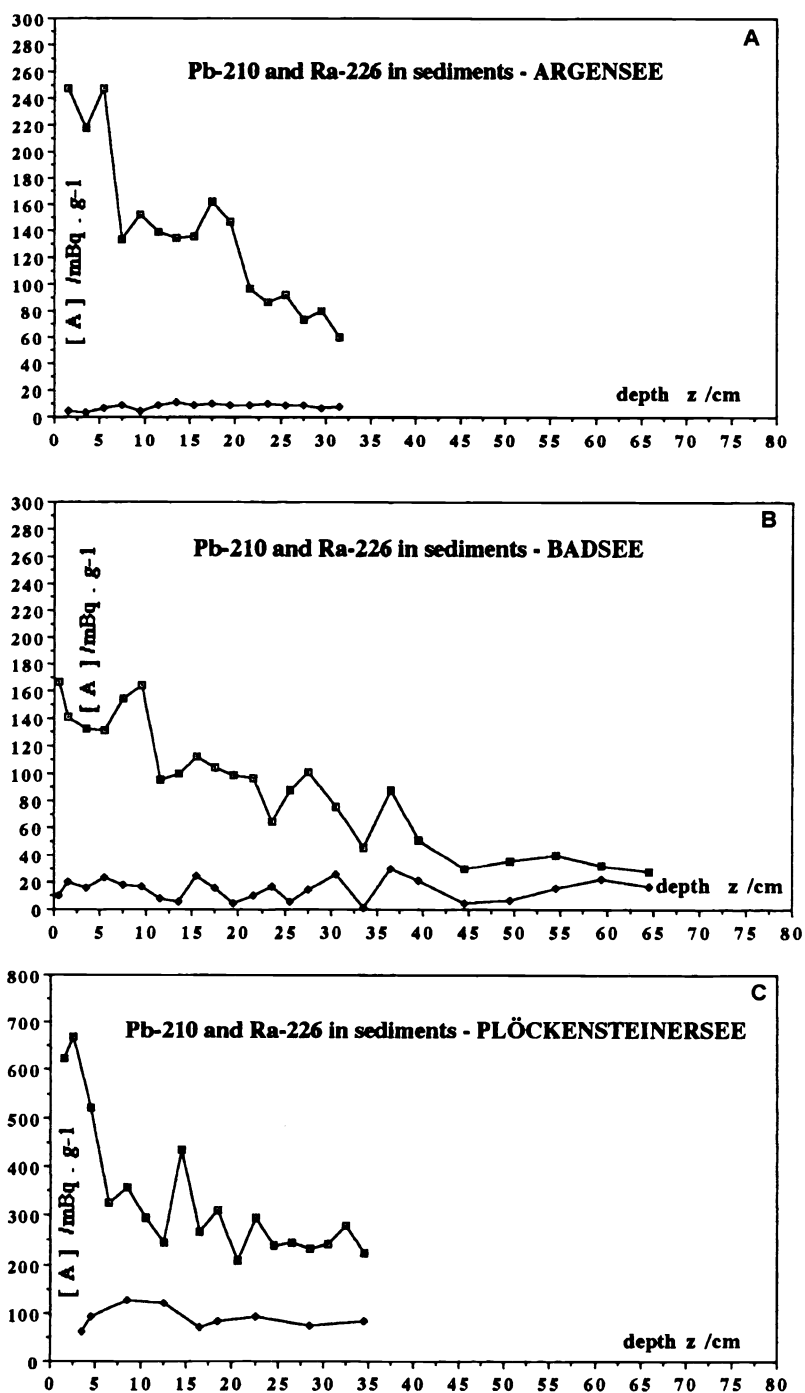


Fig. 4. Depth profiles of <sup>210</sup>Pb (□) and <sup>226</sup>Ra (◆) in sediment cores. Samples from: A. Argensee; B. Badsee; C. Plöckensteinersee

Using a counting time of 30,000 sec, a detection limit of 0.6 mBq  $^{226}\text{Ra}$  per sediment sample is obtainable.

## RESULTS

We present the results of investigations of three small lakes. Argensee and Badsee are located in Baden Württemberg, Germany, north of Lake Constance in a marsh landscape of a glacial moraine. Plöckensteinersee is situated in the Bohemian Forest in a granite formation with a relatively high background of natural radioactivity. The sediment cores were taken from the deepest areas of these lakes at depths of 7.2, 6.9 and 17 m, respectively. Figure 4 shows the measured concentrations of  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  in the sediments of these lakes. Comparison of data from these lakes reveals that the  $^{226}\text{Ra}$  content depends strongly on the lake's geological setting. Average values of  $7.8 \pm 2.1$  ( $n = 16$ ) and  $14.5 \pm 7.8$  ( $n = 24$ ) Bq  $\text{kg}^{-1}$  of dry sediment can be calculated for Argensee and Badsee, respectively. However, Lake Plöckensteinersee shows a clearly higher value of  $90 \pm 21$  ( $n = 9$ ) Bq  $\text{kg}^{-1}$ . As mentioned above, such values represent an upper limit for the supported  $^{210}\text{Pb}$  content, which can be taken as a first approximation of the mean value of the entire sediment column. In the upper layers of such cores, the total  $^{210}\text{Pb}$  content depends primarily on the sedimentation rate and annual supply of excess  $^{210}\text{Pb}$  from airborne Rn decay products. As seen from Figure 4, the normal core lengths of 30–40 cm were too short to reach the practically constant  $^{210}\text{Pb}$  concentration of the supported fraction in the deeper layers. In the case of Badsee (Fig. 4B), agreement between the supported  $^{210}\text{Pb}$  content determined by the  $^{226}\text{Ra}$  analyses and the measured total  $^{210}\text{Pb}$  content, within statistical uncertainty, is not achieved above ~60 cm depth. This means that only the layers below 60 cm are older than several half-lives of  $^{210}\text{Pb}$ , and the unsupported amount of  $^{210}\text{Pb}$  deposited there has decayed completely. However, our direct measurement of  $^{226}\text{Ra}$  concentration enables us to evaluate  $^{210}\text{Pb}$  profiles in much shorter cores.

## CONCLUSIONS

The measurement of  $^{226}\text{Ra}$  can be performed easily by LS spectrometry of  $^{222}\text{Rn}$  and its  $\alpha$  decay products after extraction into the non-aqueous phase of a mineral oil-based scintillation cocktail. The minimum detectable activity is about 0.6 mBq per sample. As little as 0.5 g of dry sediment material can be analyzed. Such  $^{226}\text{Ra}$  data provide an upper limit of the supported  $^{210}\text{Pb}$  content in lake sediments, and enable us to evaluate  $^{210}\text{Pb}$  profiles in short sediment cores of only 30–40 cm length, even in the case of large amounts of unsupported  $^{210}\text{Pb}$ .

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## REFERENCES

- Appleby, P. G. and Oldfield, F. 1978 The calculation of lead-210 dates assuming a constant rate of supply of unsupported  $^{210}\text{Pb}$  to the sediment. *Catena* 5: 1–8.
- Eakins, J. D. and Morrison, R. T. 1978 A new procedure for the determination of lead-210 in lake and marine sediments. *International Journal of Applied Radiation and Isotopes* 29: 531–536.
- Goldberg, E. D. 1963 Geochronology with lead-210. In *Radioactive Dating*. IAEA, Vienna, IAEA/STI/PUB 68: 121–131.
- Krishnaswamy, S., Lal, D., Martin, J. M. and Meybeck, M. 1971 Geochronology of lake sediments. *Earth and Planetary Science Letters* 11: 407–441.
- Oikari, T., Kojola, H., Nurmi, J. and Kaihola, L. 1987 Simultaneous counting of low alpha and beta-particle activities with liquid scintillation spectrometry and pulse-shape analysis. *International Journal of Applied Radiation and Isotopes* 38: 875–878.

