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Title: Mobility determination of lead isotopes in glass for retrospective radon measurements

Year: 2008

Version:

Please cite the original version:

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MOBILITY DETERMINATION OF LEAD ISOTOPES IN GLASS FOR RETROSPECTIVE RADON MEASUREMENTS

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Received on, 2007, revised on, 2007, accepted on, 2007

In retrospective radon measurements the 22 year half life of 210Pb is used as an advantage. The 210Pb is often considered to be relatively immobile in the glass after alpha recoil implanted by 222Rn progenies. The diffusion of 210Pb could however lead to uncertain wrong retrospective radon exposure estimations if 210Pb is mobile and can escape from glass, or lost as a result of cleaning, induced surface modification. This diffusion was studied by radiotracer technique where 209Pb was used as a tracer in a glass matrix for which the elemental composition is known. Using the RISOL technique the 209Pb atoms were implanted into the glass with an energy of 39 keV. The diffusion profiles and the diffusion coefficients were determined after annealing at 470 - 620 °C and serial sectioning by ion sputtering. In addition the effect of surface cleaning on diffusion was tested. From the Arrhenius fit the activation enthalpy was determined to be H = (3.2 ± 0.2) eV had characteristic of a sink implying loss of 209Pb in the very surface at high temperatures.

INTRODUCTION

It is estimated that radon in dwellings accounts up to 2% of all deaths from cancer in Europe [1]. This number is higher in the areas where higher concentrations of the natural uranium exists in the bedrock. To make accurate conclusions of radon induced fatalities it is important to have reliable method for measuring radon concentrations for a sufficient long time period. Starting from the 238U the radium decay series acts as a constant source of radioactive decay products. The half life of 1/2 = 3.8 d of the radon(222) gas allows 222Rn to diffuse out from the ground and to the dwellings. It is however not the radon itself that causes most of the exposure but the short lived alpha-emitting solid progenies of the inhaled radon [1].

Epidemiological surveys where radon retrospective measurements are used are based on surface traps such as glass [2, 3, 4, 5, 6] for determining the alpha recoil implanted radon progenies. Also substrates like CR-39 or other polymers is widely used for retrospective radon measurements, progeny detection and in epidemiological studies; see [7, 8, 9, 10] for example.

When 222Rn decays the radium series acts builds up after about an hour to in 210Pb. The long half life of 1/2 = 22 a of the 210Pb is what enables the retrospective radon measurements when the implanted 210Pb (or it’s progenies) concentrations into the glass can be determined reliably.

Most of the retrospective radon measurements based on the surface trap method does not however take into account the possibility of the diffusion of the 210Pb. Implantation depth of 210Pb from alpha decays of 218Po and 214Po is very shallow and ≤ 100 nm at the maximum [11, 12]. This can lead to erroneous results if the 210Pb is mobile and diffuses out from the glass. This is because most of the implanted 210Pb is concentrated very close to the surface [11, 12].

In retrospective radon measurements alpha activities of 2 Bq m -2 of 210Po can be measured [3]. Calculated from decay constants this polonium activity corresponds to about 4 × 107 210Pb at. cm-2. The diffusion processes where only very small concentration (107 - 1015 at. cm-2 ) of implanted atoms exists can only be studied by the radiotracer technique [13]. To measure the diffusion of 210Pb we used 209Pb as a radiotracer to mimic 210Pb as from the diffusion perspective they only differ by their mass which can be safely disregarded. This study further investigates the surface escape of the Pb and expands the reliability of the initial study [14] of the low concentration diffusion of Pb in glass.

METHOD

To measure diffusion by radiotracers at low concentrations the implanted isotopes need to have a half life between ~30 min and few tens of hours so that enough statistics from β -decays can be collected in short period
of time. At Jyväskylä a primary energetic beam from the K-130 cyclotron is guided to a solid target at the ion guide isotope separator on-line (IGISOL) [15, 16, 17] where the radioactive products are isotope separated and accelerated to a maximum energy of 40 keV for implantation. After the implantation the sample is thermally annealed in vacuum to induce diffusion. Subsequently, the concentration profile of implanted $^{209}\text{Pb}$ was serially sectioned onto thin mylar foils by a sputtering method [18].

After sputtering the activity on each section was measured and the total crater depth of the sputtered sample determined. For different temperatures the diffusion profiles are determined from the crater depth, number of foils and from the measured activity on each foil.

The mathematical form of the diffusion profiles can be deduced from Fick's law [19, 20, 21] (see Eq. 1). Prior to fitting, the measured profiles were corrected for radioactive decay during the measurement. Diffusion equation

$$C_{\text{Pb}}(x, t) = N \int_{0}^{\infty} \exp \left( -\frac{(x-x')^{2}}{4\lambda^{2}} \right) + R \cdot \exp \left( -\frac{(x+x')^{2}}{4\lambda^{2}} \right) \left[ C_{\text{Pb}}(x', t=0) \right] dx'. \quad (1)$$

relates the evolution of the concentration profile $C_{\text{Pb}}(x, t)$ with depth $x$ and time $t$ to the initial, as-implanted profile $C_{\text{Pb}}(x, t=0)$. $\lambda$ is the diffusion length.

In eq. (1) the shallow implantation depth from the surface has been taken account by $R (-1 \leq R \leq +1)$ which describes the surface boundary condition. $R = -1$ for a perfect sink while $R = +1$ corresponds to a perfectly reflecting boundary [21]. The as-implanted profile $C_{\text{Pb}}(x, t=0)$ was taken to have a Gaussian form where $x_{0}$ is the centroid of the as-implanted profile. Fig. 3 shows this to be a good approximation to our experimental data. When Eq. (1) is integrated it can be represented in the form:

$$C_{\text{Pb}}(x, t) = N \left[ \text{erfc} \left( -\frac{x_{0}}{2\nu} + \frac{\lambda}{2\nu^{2} + \lambda^{2}} \right) \exp \left( -\frac{(x-x_{0})^{2}}{2\nu^{2} + 4\lambda^{2}} \right) + R \cdot \text{erfc} \left( -\frac{x+x_{0}}{2\nu} + \frac{\lambda}{2\nu^{2} + \lambda^{2}} \right) \exp \left( -\frac{(x+x_{0})^{2}}{2\nu^{2} + 4\lambda^{2}} \right) \right] + B. \quad (2)$$

where $\nu$ and $x_{0}$ are taken from the as-implanted Gaussian and $N$, $\lambda$, $R$ and $B$ are free parameters.

The elemental composition of the soda-lime glass used in the experiment was measured using time of flight-elastic recoil detection (ToF-ERD) [22] analysis to be Ca 3%, Si 26%, Mg 3%, Na 8%, and O 60% respectively. The glass samples used were taken from the same batch (Menzel-Gläser 76×26×1 mm$^{3}$ sized microscope slides, article number 011101) as our preliminary study [14].

To test influence on cleaning on diffusion and loss of Pb from the glass surface two sets of samples were cleaned in different ways. One set of samples were treated in 99.5% acetic acid for >24 h prior to diffusion while another set was treated with a commercial window cleaner (Ajax Tm) and rubbed with cotton wool on
sticks for 20 minutes between implantation and thermal treatment.

The $^{208}\text{Pb}(d,p)^{209}\text{Pb}$ reaction was used to produce $\beta^{-}$ active $^{209}\text{Pb}$ [23] with $t_{1/2} = 3.253$ h. The 14 MeV deuterium beam was produced by the Jyväskylä cyclotron. Thin enriched $^{208}\text{Pb}$ was used as a primary target material in IGISOL (Fig. 1). The $^{209}\text{Pb}^{+}$ ions were implanted in the glass samples with an energy of 39 keV. According to SRIM-2006 [24] the lateral implantation depth was 23.0 nm with stragling (square root of variance) of 4.3 nm when elemental composition was as measured with ToF-ERDA and density of 2.5 g cm$^{-3}$ was used in the simulation.

After the implantation the activity in the sample was checked using a scintillation monitor to be sufficiently large to give a measurable activity over the whole measurement cycle (~4 h).

The samples were heat-treated in a quartz vacuum tube at 1-5 × 10$^{-5}$ Pa mounted in a tube furnace (Gero GmbH, type F) between 470 – 670 °C. The annealing time was 1 h except for the lowest temperature where this was extended to 4 h to improve measurement accuracy.

Timing was started when sample was slided in the oven and stopped when taking out. Temperature saturation was slowest for the lowest temperatures but the gradients at the beginning and in the end of the annealing were expected to cancel each other out to some degree. Next the samples were taken to the serial sectioning [18]. The ion source for the sputtering system was ECR plasma source "OSPrey" from Oxford Scientific. Gas feedstock for the ion gun was air and the acceleration voltage of 1 kV was used for the ion beam (Fig. 2). When the serial sectioning by sputtering to the mylar foil was completed the foil was taken out for activity measurement.

Activity of each foil section was measured with two large silicon detectors. Both detectors facing each other had an active area of 50×50 mm$^2$ and a thickness of 500 µm. Distance between the detectors was about 4-5 mm. Each detector was segmented to four quadrants. Since the sputtered fluence in the foil had diameter of ≈30 mm, detectors formed effectively 4$\pi$ detection angle. $\beta$-decay counts from $^{209}\text{Pb}$ were collected for 200 s for each foil section. Maximum count rate was less than 25 counts/second. Counting electronics had veto pulses to discriminate signals too close each other (~1 µs). By this veto double/multiple counts caused by electron scattering from quadrant to quadrant were rejected.

The depth of the crater formed during the sputtering was measured from 4-10 positions around the implantation spot with P-15 stylus profiler from KLA-Tencor. The vertical resolution of the profiler is better than 2 nm.

**ANALYSIS AND DISCUSSION**

The implantation depth $x_0$ measured from the Gaussian fit is 22.6 ± 0.2 nm which is close to SRIM simulation result. Figure 4 presents an Arrhenius plot of the diffusion coefficient $D = \lambda^2/t$. $\lambda$ is obtained from the Eq. (2) and $t$ is the annealing time.

The temperature dependence of $D$ follows the Arrhenius equation:

$$D = D_0 \exp \left( -\frac{H}{kT} \right) ,$$

(3)

here $D_0$ is the so-called pre-exponential factor, $H$ is the activation enthalpy, $k$ is Boltzmann’s constant and $T$ is temperature in Kelvin.

The fitted activation enthalpy was 3.2 ± 0.2 eV and $D_0$ in the order of 20 m$^2$s$^{-1}$. The largest uncertainty factor in the measurements was the background in the foil activity measurement. Background deviation of a few percent in the measurements cause noticeable changes to the diffusion length and this is the main cause of the scatter from a straight line in Fig. 4. Error bars for the $T^{-1}$ and $D$ in Fig. 4 correspond to the delay in temperature stabilization in the annealing and $^1$ Temperature is the mean of the measured values 40 minutes before the end of annealing and the error-bars represent standard deviation of these values.
to the diffusion data correlation to the fits (Fig. 3), respectively.

The diffusion length at the room temperature for $^{209}\text{Pb}$ extrapolated over a time period of 50 years is in the order of $10^{-22} - 10^{-24}$ m. This result confirms that $^{210}\text{Pb}$ is immobile in glass. This is a critical assumption in retrospective radon measurement by Samuelsen's method [3].

In contrast to our preliminary study the surface was found to be characteristic of a near-perfect sink ($R \approx -1$). This is confirmed by inspection of Fig. 3 where Pb is seen to be depleted in the diffused profiles in the 30 nm closest to the surface. This is not inconsistent with the data in our previous study [14, 21]. This means that if the $^{209}\text{Pb}$ is diffused to the surface, it will escape from the sample under the conditions studied. Even if this holds true at the room temperature it affects only the very surface layer because, as shown above, in the glass $^{209}\text{Pb}$ (and $^{210}\text{Pb}$) is immobile.

CONCLUSIONS

Diffusion coefficients of $^{209}\text{Pb}$ in glass were measured over the temperature range of 470 – 620 °C. The activation enthalpy was determined to be $3.2 \pm 0.2$ eV and the pre-exponential factor $D_0$ in the order of $20 \text{ m}^2 \text{s}^{-1}$. Extrapolation of these diffusion parameters to room temperature shows that Pb is completely immobile in the glass over a time scale of 50 years. We also did not find differences in diffusion coefficients between the untreated samples, and the samples subjected to cleaning treatment by soaking in acid or a combination of commercial window cleaner and abrasion. For retrospective radon measurements where long decay time of $^{210}\text{Pb}$ is used it can be confirmed that implanted $^{210}\text{Pb}$ concentration does not alter due to diffusion mechanism. Over the temperature range of the measurements the surface behaved as an near-perfect sink, indicative of evaporation of the implanted Pb that diffuses to the very surface.

ACKNOWLEDGEMENT

This work was supported by the Academy of Finland under the Finnish Center of Excellence Programme 2006-2011 (Project 213503).

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