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An Excess ^{226}Ra Chronology for Deep-Sea Sediments from Saanich Inlet, British Columbia

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Abstract

To further explore the efficacy of ^{226}Ra$_{(excess)}$ dating for deep-sea sediments, previously dated varve sediments from Saanich Inlet were investigated. Ages obtained using ^{226}Ra$_{(excess)}$ are comparable to the varve ages in the upper 20-25 m of the sedimentary record, but radiometric ages for those sediments older than *c.* 4000 yr BP are significant underestimates. This results from major changes in sedimentation within Saanich Inlet around 4000 yr BP linked to rising sea levels, with younger sediments characterised by a higher biogenic contribution resulting from the establishment of an anoxic fjord environment. The older sediments were deposited in a shallow water inlet characterised by variable Ra mass balance and non-radiogenic losses. Therefore, while ^{226}Ra$_{(excess)}$ can produce reliable dates, its application may be limited where the relative significance of authigenic and allogenic input and bottom water anoxia have been variable and where closed-system behaviour is compromised.

1 Introduction

1.1 Context

Freshwater and marine sediments can yield valuable data on past human and climatic changes over a range of timescales (e.g. Bowler et al., 2003; Elliot et al., 1995; Hays et al., 1976; Hughen et al., 1998; Jalut et al., 2000; Oldfield et al., 2003; Shackelton et al., 1990). However, without the ability to place an accurate timeframe around such changes, these records are likely to be of limited use in linking cause and effect, hence identifying the drivers of environmental change, and in constraining response times and operational timescales. Indeed, questionable chronologies limit detailed reconstructions of past vegetation and climate trends from sedimentary records (Anderson and Lozhkin, 2001). Over the period of the Holocene current dating techniques fail for a number of reasons. For example, the application of ^{14}C to date sediments can suffer from poorly-resolved reservoir effects (Geyh et al., 1999; Moore et al., 1998), resuspension of older marginal material and radiocarbon plateaus (Magny et al., 2003), all of which lead to problems in dating. While attempts have been made to use optically stimulated-luminescence (OSL) for dating lake sediments, e.g. Lang and Zolitschka (2001), a number of limitations are associated with its use in aqueous environments. In particular its application may be limited in lakes where allogenic inputs are low and authigenic sedimentation dominates. Equally, despite recent advances in chronological techniques there is still a need for ever better chronologies over the Holocene (Oldfield, 2003).

Where current dating methods fail, new dating techniques are required. Uranium-series radioisotopes provide tools with sufficient time resolution to study many earth processes that have occurred on timescales from days to 10^5 years (Bourdon et al., 2003). The successful utilization of such methods depends on a clear understanding of the mechanism by which the radioisotope(s) is/are incorporated into the sediments (Appleby et al., 1990), and the extent to which closed system behaviour prevails after deposition. Attempts have been made to establish chronologies and determine sedimentation rates using unsupported ^{226}Ra, or $^{226}\text{Ra}_{(\text{excess})}$, in a range of sedimentary environments, e.g. Eikenberg et al. (2001); Koide et al. (1976), Latham et al. (1986); Murray et al. (1992); Sturchio, (1990); Van Beek and Reyss, (2001). The use of $^{226}\text{Ra}_{(\text{excess})}$ offers considerable potential to date sediments over the Holocene due to its half-life of 1602 years. However, numerous assumptions have to be made regarding the behaviour of ^{226}Ra when applying $^{226}Ra_{(excess)}$, particularly with regard to its sediment-water transfer and its potential for post-depositional mobility (e.g. Fairclough et al., 2006; Murray et al., 1992).

For a new dating technique to develop beyond theory into application it is essential that it first be independently validated. One of the primary methods of achieving this is the dating of samples that have been dated previously using established techniques. Varved or laminated sediments consist of annually laminated sediments and offer the potential to reconstruct past climatic and oceanographic changes at a very high resolution (e.g. Blass et al., 2003; Brauer et al., 1999; Hang, 1997; Ludlam, 1984; Nederbragt and Thurow, 2001; von Rad et al., 1999; Tiljander et al., 2003; Troften, 2000). This high resolution puts varved sediments on a par with tree ring and ice-core records (Bornhold and Kemp, 2001). In an effort to develop a network of high resolution palaeoenvironmental sites from around the globe the ODP has undertaken sampling at a number of coastal anoxic basins including Santa Barbara Basin, California (Leg 146), Cariaco Basin, Caribbean (Leg 165), Saanich Inlet, British Columbia (Leg 169S) and Palmer Deep, Antarctic continental margin (Leg 178). Here we present the results of an age intercomparison study where ages determined for deep-sea sediments from Saanich Inlet using $^{226}Ra_{(excess)}$ are validated with reference to those obtained using established techniques, i.e. varve and ^{14}C dating. This validation is an essential step if $^{226}Ra_{(excess)}$ dating is to be used routinely, and sets the foundations for further hypothesis testing with respect to the mechanism(s) responsible for the preservation (or non-preservation) of $^{226}Ra_{(excess)}$ in the deep-sea sedimentary record.

1.2 Previous Applications of $^{226}Ra_{(excess)}$

The first attempts to use $^{226}Ra_{(excess)}$ as a dating tool were made almost 50 years ago by Petterson (1955). Koide et al. (1976) investigated the application of excess ^{226}Ra as a geochronological tool for dating marine sediments from the San Clemente Basin in Southern California. Planktonic diatoms, i.e. *Chaetoceros sp.* and *Rhizosolenia sp.*, were found to contain high concentrations of Ba and Ra. This may result in substantial amounts of Ra being transferred to sediments located in biologically productive areas.

Koide et al. (1976) identified two methods for calculating unsupported ^{226}Ra:

I. The assumption that the ^{230}Th comes to the sediment with an amount of ^{226}Ra that is in equilibrium with it.
II. The assumption that the ^{230}Th comes to the sediment without any ^{226}Ra but that with time ^{226}Ra grows in through the decay of this Th isotope.

Of the two, hypothesis I is the most probable in coastal locations as Th is likely to be present in the sediment as a particulate flux, which will largely be in equilibrium with its daughter products. Therefore, unsupported ^{226}Ra or ^{226}Ra$_{(excess)}$ can be calculated using the following equation:

$$\text{Excess } ^{226}\text{Ra} = \text{total } ^{226}\text{Ra activity} - \text{supported } ^{226}\text{Ra (total } ^{230}\text{Th activity)} \tag{Eqn 1}$$

Since the early work of Koide et al. (1976) ^{226}Ra$_{(excess)}$ has been applied as a chronological tool in a range of sedimentary environments, including: stalagmites (Latham et al., 1986); travertine (Eikenberg et al., 2001; Sturchio, 1990); barite (Van Beek and Reyss 2001; Van Beek et al., 2002) river sediments (Murray et al., 1992); and lake sediments (Fairclough, 1999; Fairclough et al., 2006).

Van Beek and Reyss (2001) found that ^{226}Ra activities decreased exponentially with depth in barite crystals extracted from central and western equatorial Pacific Ocean sediments. This is believed to represent the behaviour of a closed system with the data suggesting that it is possible to calculate reliable sedimentation rate estimates. Van Beek and co-workers applied these findings to Holocene sediments from the Southern Ocean where radiocarbon dating has proven to be problematical due to the need for sea-surface reservoir-age corrections (Van Beek et al., 2002). The technique was found to be useful for dating these sediments, although at depth the errors were large due to low ^{226}Ra activities that were close to the limits of detection.

Eikenberg et al. (2001) suggest that $^{226}Ra_{(excess)}$ is ideal for dating younger speleothem samples ranging from a few hundred years to about 7-8 kyr (or up to 5 half-lives). Furthermore, three major requirements have to be fulfilled in order for $^{226}Ra_{(excess)}$ dating to yield reliable results. These are: correct subtraction of a detrital, non-authigenic component; insignificant inherited, unsupported $^{230}Th_{(0)}$ in the precipitating authigenic material; and a constant initial concentration of $^{226}Ra_{(0)}$ in all samples independent on the time of system closure (Eikenberg et al., 2001). Fortunately Eikenberg et al. (2001) were able to fulfil the first two requirements as detrital input could be subtracted using a constant U/Th ratio and all samples started without significant amounts of inherited ^{230}Th. Although, the third dating requirement was not as easily resolved, by plotting a decay curve for $^{226}Ra_{ex}(t)/^{226}Ra(0)$ they found that 16 samples had a similar initial $^{226}Ra_{(0)}$ activity to their youngest sample.

Murray et al. (1992) found that there was a reasonable degree of similarity between $^{226}Ra_{(excess)}$ and thermoluminescence dates in river deposits from the Alligator Rivers, Australia. Here, an underlying condition is that the sediment is deposited with constant initial ^{226}Ra excess over ^{230}Th of R_o then, because the ^{226}Ra half-life is short compared with its parent, that excess will decay exponentially to a value R after time t:

$$\mathrm{R} = \mathrm{R_o}\ \mathrm{e}^{-lt} \tag{Eqn 2}$$

where l is the decay constant for ^{226}Ra. Where deposition is at a steady rate, s, with time then the accumulated depth $D = s\ t$. Therefore:

$$R = R_o \exp\left(-\frac{lD}{s}\right) = R_o\ e^{-KD} \tag{Eqn 3}$$

i.e. it is expected that the $^{226}Ra_{(excess)}$ depth profile will be exponential in form.

For this approach to work, a number of assumptions about the system are required: first, that there is a constant rate of sedimentation; secondly, that there is constant deposited ^{226}Ra and ^{230}Th concentrations in time; thirdly, that there is chemical immobility of ^{226}Ra and ^{230}Th since deposition; and, fourthly, that there is no significant bioturbation or other physical disturbances within the profile. Of these four assumptions the majority can be checked, however the constancy of ^{226}Ra supply will always remain an assumption (Murray et al., 1992). This approach is essentially similar to the constant rate of ^{210}Pb supply (CRS) model used in the application of ^{210}Pb dating (Appleby and Oldfield, 1992).

From work on a variety of fluvial sediments from Australian sites Olley et al. (1996) believe that using the analytical techniques available they would be unable to detect any excess ^{226}Ra after about 11 000 years since deposition as an initial ^{226}Ra excess of, say, 120 Bq kg^{-1} will have decayed to within 3% of equilibrium. The activity of ^{226}Ra was calculated as follows:

$$^{226}a_t = {}^{230}a + ({}^{226}a_0 - {}^{230}a)\, e^{-\lambda_{226} t} \qquad \text{(Eqn 4)}$$

where $^{226}a_0$ and $^{226}a_t$ are the activities of ^{226}Ra at time $t = 0$ and t, respectively, ^{230}a is the activity of ^{230}Th, and λ_{226} is the decay constant for ^{226}Ra (Olley et al., 1996).

Fairclough et al. (2006) successfully used an unsupported ^{226}Ra chronology to establish sedimentation rates for sediments from Hawes Water in northern England. The magnitude of the disequilibrium was found to be sensitive to changes in both the supply and initial activity of ^{226}Ra, both of which could be identified with reference to a profile of excess ^{210}Pb activity. Fairclough et al. (2006) also identified that where there is a significant disequilibrium between ^{230}Th and ^{234}U, a more exact relationship shows that excess ^{226}Ra may deviate from a simple exponential decay curve after just 5000 years. In sediments older than 5000 years the following equation may be required to calculate ^{226}Ra$_{(excess)}$ ages:

$$A_{226} = A_{234}\left(1 - e^{-\lambda_{226} t}\right) + \frac{\lambda_{226}\left(A_{230}^{0} - A_{234}\right)}{\lambda_{226} - \lambda_{230}}\left(e^{-\lambda_{230} t} - e^{-\lambda_{226} t}\right) + A_{226}^{0} e^{-\lambda_{226} t} \qquad \text{(Eqn 5)}$$

where A_{226} is the present activity of ^{226}Ra, A_{234} is the activity of ^{234}U (this may be regarded as constant as during the ^{226}Ra/^{230}Th equilibration period any unsupported ^{234}U will only decline by about 1%), A_{226}^{0} and A_{230}^{0} are the initial activities of ^{226}Ra and ^{230}Th respectively, *t* is the time since deposition, and λ_{226} and λ_{230} are the decay constants of ^{226}Ra and ^{230}Th.

It is, therefore, clear that the application of ^{226}Ra$_{(excess)}$ can be affected by the effects of: low initial activities of ^{226}Ra; detrital input; varying supply and/or initial activity; post-depositional mobility; and the fact that after just 5000 years BP the decay of ^{226}Ra$_{(excess)}$ may not be exponential. Furthermore, identifying the source of ^{226}Ra$_{(excess)}$ in the sediment in question may be crucial in understanding the extent to which the excess activity is a function of radioactive decay in a closed system. For example, where ^{226}Ra is incorporated in the sediment column in association with Ba, due to their close chemical similarities, the ^{226}Ra/Ba ratio may be used as a tool for establishing whether down-core variations in ^{226}Ra activities result from radioactive decay alone (Berkman and Ku, 1998). However, Grayson (2005) found that in lake sediments this ratio might be severely impacted by seasonal diagenesis, with evidence that Ba and ^{226}Ra are affected by the reduction and diffusion of Fe and Mn within bottom sediments, leading to the recycling of ^{226}Ra and Ba at the sediment-water interface. Therefore, in some circumstances downcore variations in the ^{226}Ra/Ba ratio may not be truly representative of the radioactive decay of ^{226}Ra. In addition, the ^{228}Th/^{232}Th activity ratio may be used as a check for Ra diffusion from the sediment column, in this case ^{228}Ra being used as a proxy for ^{226}Ra (Colley and Thomson, 1992).

The reductionist approach would seek to identify the physico-chemical carrier of ^{226}Ra$_{(excess)}$ activity. This generally requires lengthy sediment phase extractions or *in situ* measurement to establish, in this case, whether the mechanism for transferring and storing the ^{226}Ra$_{(excess)}$ in the sediment column is that of uptake by detrital particulates (Běnes et al., 1984, 1985, 1986), co-precipitation with calcium carbonate (Rihs et al., 2000) or barium sulphate (Paytan et al., 1996), adsorption in association with Mn oxides (Kadko, 1980), or biogenic complexation in opaline silica (Shannon and Cherry, 1971). Problems with phase extractions result from the specificity of the extraction (Boyle, 2001) and the low activity of the extracts (e.g. Plater et al., 1992), and may be of little value if the transfer mechanism in question leaves no evidence in the sedimentary record, e.g. post-depositional dissolution of diatom silica (Mayer et al., 1991). A more general approach may be adopted whereby 'allogenic' (detrital) and 'authigenic' (non-detrital) fractions are identified through inter-element correlations (e.g. Boyle, 2001) and through investigation of various U- and Th-series activity ratios (e.g. Plater et al., 1992). For example variations in the $^{234}U/^{238}U$ activity ratio can identify changes in the relative importance of the dissolved input of U over particulate supply to sediments, with a ratio in excess of 1 indicating a dominant contribution from authigenic sources, i.e. the dissolved phase. Similarly, a $^{230}Th/^{234}U$ activity ratio in excess of 1 indicates that detrital input is dominant (e.g. Osmond and Cowart, 1976). Changes in the proportion of detrital input to sediments can also be identified through the use of the $^{230}Th/^{232}Th$ activity ratio with detrital material commonly having a $^{230}Th/^{232}Th$ activity ratio of 1.0± 0.5 (Ku and Liang, 1984). Using inter-element correlations and U- and Th-series activity ratios in association with the $^{226}Ra/Ba$ ratio provides an empirical proxy for direct consideration of the radiogenic, allogenic and authigenic influences on the observed down-core trends in $^{226}Ra_{(excess)}$ activity

2. Site Description and Methodology

2.1 Core Location

Saanich Inlet is a relatively narrow anoxic fjord located on the coastline of Vancouver Island, British Columbia which has an average depth of 120 m and a maximum depth of 236 m. In the summer of 1996 the Ocean Drilling Program undertook a three-day cruise of the JOIDES resolution to core Saanich Inlet (Leg 169S). During two days of drilling, cores were collected from two sites within Saanich Inlet, 1033 (location 48°35.44'N, 123°30.20'W; water depth *c.* 227 m) and 1034 (location 48°38.00'N, 123°30.00'W; water depth *c*. 202 m).

Sediments are characterized by lamina 'triplets' comprised of grey silty mud deposited in late autumn and early spring, olive diatomaceous ooze deposited in late spring to early summer, and dark diatomaceous mud deposited in late summer to early autumn (Bornhold et al., 1998). The average varve thickness is 6 mm, ranging from 3 to 15 mm although Blais-Stevens *et al*., (2001) have identified a significant change in varve thickness at a depth of around 22 mbsf in core 1034, with an average varve thickness of 12 mm above this depth and 7 mm below.

These cores collected during 1996 were cross-correlated using a number of factors, with the main tool being the numerous massive intervals identified across the different cores at a range of depths. These massive intervals, or layers, are typically less than a few centimetres to a few decimetres in thickness and are essentially structureless diatomaceous muds and are possibly the result of past seismic activity within the region (cf. Blais-Stevens et al., 2001) . A light grey layer of ash of between 1 and 1.5 cm in thickness was also identified. This ash layer was interpreted as Mazama Ash with an age of 7645 cal yr BP, as determined by AMS radiocarbon dates (Bornhold et al., 1998). Throughout the two cores a total of 69 radiocarbon ages were determined thanks to the presence of plentiful amounts of charcoal, well-preserved plant debris and fish remains.

Using the depths and radiocarbon ages obtained by Bornhold et al. (1998) from sites 1033 and 1034, Nederbragt and Thurow (2001) used digital sediment colour analysis to construct a varve chronology for the last 6000 years. The massive layers were correlated across parallel holes using the distinct features found in the varve pattern below and above each massive layer. A good degree of similarity between the varve dates and the ^{14}C AMS dates was observed to at least 4000 yr BP, beyond this date the two records diverge. This coincides with major sedimentation changes within Saanich Inlet, with indistinct laminated sediments subject to bioturbation being deposited prior to 4270 yr BP, while from this date sediments gradually change upwards into laminated sediments that are generally unaffected by bioturbation (Blais-Stevens et al., 2001).

This change to distinctly varved sediments at around 4000 yr BP reflects a gradual decrease in oxygenation of bottom waters as sea level reached its present day position around this time, freshwater input was also no greater than today after this time (Blais-Stevens et al., 2001). As a result the character of sediments deposited since 4000 yr BP reflect present day conditions with laminations being distinct and generally thicker. Prior to 4000 yr BP the impacts of rising sea levels had a significant impact on the geomorphology of Saanich Inlet, Huntley *et al*. (2001) identified that this period was characterised by both marine transgressions and valley aggradation. However, since 4000 yr BP modern drainage patterns and oceanographic conditions have become established

Hebda (1995) reconstructed Holocene vegetation and climate records for British Columbia from pollen records and identified three main climate phases: the first was a warm dry period between ca. 9500-7000 BP; the second a warm moist period between ca. 7000-4500 BP; and, the third a moderate and moist period between 4500 and the present, with a cooling between 4500 and 3000 BP which may have resulted in increased moisture. Nederbragt and Thurow (2001) also suggest wetter periods were experienced between 6000 and 3250 yr BP, 2100 and 1750 yr BP and from 500 yr BP onwards. The change in climate had a distinct impact on vegetation, with modern forest developing between ca. 4500 and 4000 yr BP and modern vegetation arising between 4000 and 2000 yr BP. Therefore, the change in sedimentation at 4000 yr BP coincides with temperatures reaching similar levels to present day conditions, a switch to a wetter climate and a major shift in vegetation (Blais-Stevens et al., 2001; Hebda, 1995).

2.2 Research Design

The primary aim of this work is to establish whether $^{226}\mathrm{Ra}_{(\mathrm{excess})}$ exhibits a decrease in activity down-core in accordance with radioactive decay in a closed system. Similarly, the research focuses on the analysis of bulk samples, thus limiting the extent to which sediments need to be physically and/or chemically separated in order to obtain a reliable chronology. This approach is based largely on the findings of Fairclough (1999) and Fairclough et al. (2006) which demonstrate that the analysis of $^{226}\mathrm{Ra}_{(\mathrm{excess})}$ in bulk sediment samples is preferable to sequential extraction as no differential fractionation occurs as a result of the analysis technique (e.g. Bischoff and

Fitzpatrick, 1991). This approach is acceptable if the main carrier of the $^{226}Ra_{(excess)}$ activity in the sedimentary record is known or where, in this case, the integrity of the authigenic 'carrier' component, and its significance in relation to the contribution from allogenic detrital mineral matter, is to be evaluated.

Despite the above, we can assume that the main authigenic carrier of $^{226}Ra_{(excess)}$ in the sedimentary record concerned is biogenic silica. The dysaerobic conditions presently experienced in the bottom waters and the anoxic sediments within Saanich Inlet result from a combination of restricted water circulation, the presence of thermal stratification and generally moderate rates of organic matter accumulation which is typically marine in origin (Bornhold et al., 1998; McQuoid et al., 2001). Here, marine phytoplankton is the primary source of organic matter, with the majority of total organic carbon (TOC) deposited during the Holocene being derived from such phytoplankton; TOC has also exhibited a slight monotonic rise through the Holocene (McQuoid *et al*., 2001). In addition, the Si composition of the upper laminated sediments reflects the presence of biogenic Si and the organic matter is primarily derived from marine phytoplankton (Bornhold et al., 1998; McQuoid *et al*., 2001). This is, therefore, indicative of a significant authigenic source of sediment and, hence, $^{226}Ra_{(excess)}$ in association with diatom productivity.

Our research is also designed to investigate the efficacy of $^{226}Ra_{(excess)}$ dating across a gradient of significant environmental change in Saanich Inlet, driven primarily by relative sea level changing the environment of deposition from a well-mixed shallow tidal inlet to a seasonally stratified fjord characterised by anoxic bottom waters. This change is preserved in the sedimentary record as a gradual upward transition in the nature of sedimentation from indistinctly laminated sediments subject to bioturbation, deposited prior to 4270 yr BP, to laminated sediments that are generally unaffected by bioturbation. Although corresponding climate change at this time impacted on precipitation, catchment vegetation and, hence, the delivery of terrigenous allogenic sediment input to the Inlet, we consider this to be secondary to the impact of bottom water anoxia on the efficiency and integrity of authigenic $^{226}Ra_{(excess)}$ capture by biogenic silica,

2.3 Methodology

A total of 23 samples from Saanich Inlet were obtained from the ODP during 2002 (Table 1), the sample depths chosen to cover the full range of the $^{226}Ra_{(excess)}$ dating technique. It was intended that samples could be collected from specific varves; however difficulties in identifying individual varves, which typically range from 1 to 20 mm thickness, meant that it was not possible to sub-sample the cores at such a high resolution. Instead samples were taken covering several laminations and were based on depth with reference to the presence of correlated massive layers. Whilst it was not possible to identify how changes in the composition and/or grain size of individual varves impact on the use of the $^{226}Ra_{(excess)}$ dating technique, i.e. changes in Si content and diatom abundance, the use of bulk samples covering several laminations essentially excludes the impacts of inter-annual variations in sediment composition by providing a sequence of time-averaged data that permits comparison of samples from different depths where only long-term trends in sediment composition are prevalent. In essence, this is no different to radiocarbon dating of bulk samples where the organic matter concerned may have components of different age but that, together, have accumulated over the period of time covered by that particular sample.

2.3.1 Geochemical Analyses

Geochemical analysis was carried out using a Metorex XMET9200 XRF comprising a heavy element probe (Metorex HEPS 2431 ^{109}Cd) and a light element probe (Metorex LEPS 2172 ^{35}Fe). Estimations of accuracy were made using periodic measurements of a known set of standards, e.g. NIST SRM 2704 Buffalo River Sediment, by comparing the XRF results with the known values. Two sigma standard errors for each element are cited in Boyle (2000), and are c.20 mg/g for Si, 2.0-2.3 mg/g for Ca, K and Fe, 0.8-0.9 mg/g for S and Cl, 0.4-0.5 mg/g for Ti and Mn, 18-22 mg/kg for Pb, Sr, Zn and Zr, and 8 mg/kg for Rb. Solution techniques were used to measure Mn and Ba, with samples being digested using a HNO_3 digest heated for 1 hour at 90 ^{o}C. A SOLAR UNICAM 933 FAAS was used to measure Mn, whereas Ba was measured using ICP-OES at the Department of Soil Science at the University of Reading.

2.3.2 Dating Methodology

Fifteen of the samples obtained from the ODP underwent radiometric analysis using alpha-spectrometry; these covered an age range of 500 to 6000 yr BP (Table 1). When carrying out U-series analysis on solid samples complete dissolution and/or digestion is usually required (Lally, 1992). This was achieved by initially ashing the samples to remove any organic material before being refluxed in 60 ml aqua regia (45 ml HCl and 15 ml HNO_3) for between 1 and 2 hours. The supernatant was then removed and spiked with 0.2 ml ^{236}U and ^{229}Th and allowed to equilibrate. The remaining residue was digested using a HF:$HClO_4$ digest (30 ml HF and 10 ml $HClO_4$) brought to dryness under an infrared heat lamp; this stage was repeated at least twice. Once dry 10 ml of HNO_3 were added to the sample and brought to dryness to remove any fluoride complexes; this step was repeated. The remaining residue was digested in 5-10 ml HCl and added to the solution from the aqua regia extraction. The sample was allowed to equilibrate overnight and brought to dryness ready for chemical separation.

Chemical separation was used to isolate the radionuclide of interest from the stable elements and interfering natural and artificial radionuclides in the matrix. This was achieved through a combination of solvent extraction and ion-exchange (Figure 1). Although it is possible to separate Th, U and Ra using just ion-exchange, a solvent extraction step was added to increase the recovery of Th (Roberts, 1996). Samples were initially re-dissolved in 20 ml 8M HNO_3 and added to a separating funnel. Separate Ra, Th and U fractions were extracted using a combination of tri-n-butyl phosphate (TBP) and xylene. First TBP was added to the sample, with the Ra fraction being extracted in the 8M HNO_3. Xylene was then added to the organic phase to decrease the capacity of the TBP to retain both Th and U (Tomé et al., 2002). The Th and U fractions were then back-extracted using 5M HCl and H_2O respectively.

The Th fraction was then refluxed to remove any traces of solvent and passed through an anion-exchange column to remove any traces of U.

The Ra fraction underwent a more complex purification stage involving precipitation, anion exchange and cation exchange. To remove any traces of TBP the Ra fraction was passed through a filter and evaporated to dryness. Once dry the Ra fraction was redissolved and diluted using DD H_2O prior to the addition of a Pb carrier to form a precipitate, which was gently warmed and allowed to settle. The supernatant was removed and the precipitate redissolved and passed through an anion exchange column (Dowex 1X-8) and then a cation exchange column (Dowex X-12) to remove Pb, residual Th and Ac and then Ba; the time was recorded to indicate the start of ingrowth of ^{225}Ac as a tracer of ^{225}Ra. All three fractions were then brought to dryness, with a Na_2SO_4 carrier being added to the U and Th fractions prior to complete dryness to prevent loss onto the walls of the beakers.

Electrodeposition of the U, Th and Ra fractions onto small 20 mm diameter stainless steel discs was achieved using an electrodeposition cell with a platinum electrode based on that described by Talvitie (1972). The U and Th sources were deposited at a current of 1.2A for 1h using an ammonium sulphate electrolyte (4 ml H_2O and ~ 5 ml 1% H_2SO_4) (Hallstadius, 1984; modified from Talvitie, 1972). While this technique can produce yields of 99 and 98% for U and Th respectively, the yield for Ra is less than 1% (Hallstadius, 1984). Therefore, the Ra fraction was deposited in a propanol-based electrolyte at a current of 120 mA for 30 minutes (Fairclough, 1999). To allow for the ingrowth of ^{217}At and ^{213}Po yield monitors the Ra sources were left for 17 days prior to measurement (Martin and Hancock, 1992).

Measurement of the Ra, Th and U sources was carried out using Canberra Quad Alpha Spectrometers (Canberra Scientific Instruments, model 7404) with 450 mm^2 Passivated Implanted Planar Silicon (PIPS) detectors for a count-time of 300 000 seconds. Background counts were made using clean discs, while the efficiency and the energy calibration coefficients of each detector were calculated using a multi-element source (NPRL 477 containing ^{241}Am, ^{244}Cm and ^{237}Np). The Th and U activities were calculated using the

UTAGE programme (Ivanovich and Harmon, 1982 modified by Leonard) while ^{226}Ra activities were calculated using the RAD225 programme (Martin and Hancock, 1992). All results are quoted as Bq kg^{-1} with all errors being one standard deviation and based on counting statistics.

3. Results

Radionuclide activity (Figure 2) and metal content (Figure 3) data are presented as down-core plots. Both datasets demonstrate marked variations with depth, indicating change over time that may be in addition to those explained by radioactivity alone. In order to examine the impact that changing sea level and, hence, bottom water oxia/anoxia may have had on the nature of sedimentation and the integrity of the authigenic ^{226}Ra$_{(excess)}$, the results are subdivided to distinguish between those sediments older and those younger than 4000 yr BP; this division being based on the earlier observations that major changes in sedimentation, i.e. degree of lamination, occurred around this time and that the established varve and ^{14}C chronologies diverge at this point (Blais-Stevens et al., 2001; Nederbragt and Thurow, 2001).

3.1 U-Series Characteristics

The down-core U-series isotope plots clearly demonstrate significant variations with depth (Figure 2). The down-core changes in activity and activity ratios illustrate that activities of the three Th radioisotopes are only marginally lower in those sediments younger than 4000 yr BP, while the activities of the two U radioisotopes are more obviously higher (Table 2). To a certain extent, the down-core increase in ^{230}Th may be explained by the radioactive decay of ^{234}U (a 5% increase over the time interval concerned), but the common response of the Th isotopes, and higher activities of both ^{234}U and ^{238}U in the younger sediments (see Table 2), may be more indicative of a higher contribution from U-series radionuclides that are acquired from solution, i.e. U isotopes that are more readily dissolved than those of Th. Due to the relative concentrations of the dissolved and detrital phases, i.e. µg/l as opposed to µg/g, this impacts little on the overall activity trends but may be more readily expressed in the U/Th isotopic activity ratios. Consequently, there is no significant difference in the ^{230}Th/^{232}Th activity ratio of the older and younger sediments, i.e. the detrital component remains largely unchanged through the core, but the ^{234}U/^{232}Th, ^{238}U/^{232}Th and ^{230}Th/^{234}U activity ratios of the upper laminated sediments illustrate an enhanced authigenic contribution from dissolved U.

In those sediments younger than 4000 yr BP ^{226}Ra activities generally decrease with depth, with a few exceptions. Prior to 4000 yr BP, i.e. at a depth of *c.* 24 m, there is a reverse trend in ^{226}Ra activity and, indeed, ^{226}Ra$_{(excess)}$, and the ^{226}Ra/^{230}Th activity ratio. Whilst this may be interpreted as a decrease in ^{226}Ra$_{(excess)}$ due to radioactive decay in the upper sediment, the lower ^{228}Th activity relative to ^{232}Th is indicative of continued ^{228}Ra loss throughout the period of record.

3.2 ^{226}Ra$_{(excess)}$

The ^{226}Ra$_{(excess)}$ activity of the sediments was calculated by subtracting the ^{230}Th activity from the ^{226}Ra activity. To examine the decay of ^{226}Ra$_{(excess)}$ over time it is important that the present day activity is known, given as t_o. However, where the present day activity of ^{226}Ra$_{(excess)}$ is unknown, as in the case of the above, the activity of the earliest sample can be taken as t_0, as long as the age of this sediment has been established previously. In this case, the activity of the uppermost sample varve-dated at 528 yr BP was determined to be 20.88±6.1 Bq kg^{-1}. Using this activity, a decay curve was constructed using the $t_{½}$ of ^{226}Ra (1602 years), with an upper and lower limit based on the errors associated with ^{226}Ra$_{(excess)}$ at t_o (Figure 4). Due to the fact that the errors for both ^{226}Ra and ^{230}Th are quite high, the resulting error associated with ^{226}Ra$_{(excess)}$ is correspondingly high.

The ^{226}Ra$_{(excess)}$ activities of those sediments younger than 4000 yr BP correspond well with the trend driven by the decay of ‘initial’ ^{226}Ra$_{(excess)}$ activity. This systematic decrease in ^{226}Ra$_{(excess)}$ activity falls within the entire period of observed correspondence between the varve and ^{14}C ages (Nederbragt and Thurow, 2001), fitting within the window provided by the upper and lower errors associated with the initial activity. For most of the younger samples the calculated mean activity lies just below that expected from the initial activity. Only the sample from 23.79 m (3697 yr BP) has an activity below that expected. In contrast, all sediments older than 4000 yr BP characteristically demonstrate higher activities than would be expected given the initial activity of $^{226}Ra_{(excess)}$ at t_0. In the older sediments the activity of $^{226}Ra_{(excess)}$ actually increases with increasing depth rather than decreasing as would be expected due to radioactive decay.

The $^{226}Ra_{(excess)}/Ba$ ratio confirms the idea that the decreases in $^{226}Ra_{(excess)}$ in those sediments younger than 4000 year BP is driven by decay as the ratio generally decreases with depth (Figure 5). However, again in those sediments older than 4000 yr BP this ratio actually increases with depth, indicating a significant shift in the source of either Ba or ^{226}Ra between the older and younger sediments.

3.3 Metal concentration

Throughout the cores the majority of elements exhibit significant changes with depth, although many of the elements respond in a similar manner (Figure 3 and Table 3). Several of these changes coincide with variations in the U-series record, suggesting that U-series activities may be supply controlled, i.e. allogenic vs authigenic, and/or affected by geochemical processes related to the nature of the depositional environment.

A significant and apparently short-lived change in chemical composition can be identified at a depth of *c.* 30 m, with the concentrations of several elements decreasing significantly, with both Si and organic matter decreasing after this depth. A further significant decrease in the concentration of many of the elements occurs at *c.* 13 m, with only Pb Cu and Zn exhibiting significant increases. For a number of elements there is also a significant change in concentration at *c.* 11 m; however, this sample was taken from borehole B while those above and below were from borehole C. Therefore, this difference may result from the fact that the samples were taken from different cores in different holes.

Between approximately 19 and 22 m, where the sampling resolution is highest, the sediments show considerable variability in metal content. This coincides with the change to distinct laminated sediments and a change in average varve thickness and covers a period of 736 years. Significant variations also occur between *c.* 29 and 31 m, where the sampling resolution is again high. This indicates that significant short-term variations in the geochemical composition of the sediments occurred, but that the nature of variability is highly dependent upon the sampling resolution.

Those sediments older than 4000 yr BP and below a depth of *c.* 24m are characterised by higher Ba and Mn concentrations (Figure 3). These sediments also exhibit decreased Br, Cl and S concentrations, all of which are likely to be linked through their association with organic matter and potentially indicating an enhanced preservation of the marine influence on sedimentation in the sediments younger than 4000 yr BP. A contrast is also observed for Ti, Rb and Fe, and to a lesser extent K and Zr, concentrations, indicating a clearer association between lithogenic elements linked to detrital mineral matter in the lower, older sediments deposited in the well-mixed shallow tidal inlet. Significant shifts are also observed in the Mn/Ba and Ca/Ba concentration ratios at this age/depth, both of which are indicative of higher Ba contents in the lower part of the sediment column. This again supports an important shift in the source of Ba, and by association ^{226}Ra, between the older and younger sediments.

3.4 Calculating $^{226}\mathrm{Ra}_{(\mathrm{excess})}$ and $^{226}\mathrm{Ra}_{(\mathrm{excess})}$/Ba ratio Dates

Using the activity of $^{226}\mathrm{Ra}_{(\mathrm{excess})}$ at t_0, dates were calculated for each of the samples using the following equation:

$$t = -\frac{\ln \frac{a_t}{a_0}}{\lambda}$$

(Eqn 6)

where a_0 is the $^{226}\mathrm{Ra}_{(\mathrm{excess})}$ activity at t_0, a_t is the $^{226}\mathrm{Ra}_{(\mathrm{excess})}$ activity at depth t and λ is the decay constant for ^{226}Ra.

Equation six was also used to calculate dates for each sample using the $^{226}Ra_{(excess)}/Ba$ ratio, however in this instance a_0 is the $^{226}Ra_{(excess)}/Ba$ ratio at t_0, and a_t is the $^{226}Ra_{(excess)}/Ba$ ratio at depth t. In both cases t_0 is not zero but is in fact 528 yr BP, hence 528 years were added to each of the calculated ages. The dates produced using $^{226}Ra_{(excess)}$ and the $^{226}Ra_{(excess)}/Ba$ ratio were plotted against the varve ages produced by Nederbragt and Thurow (2001) with the diagonal lines representing a perfect match between the varve dates and the $^{226}Ra_{(excess)}$ dates and the $^{226}Ra_{(excess)}/Ba$ dates (Figure 6). For those sediments younger than 3500 yr BP the $^{226}Ra_{(excess)}$ ages clearly correspond well with the varve chronology (m = 1.1). As such, this indicates that they would also correspond well with the ^{14}C dates. In the older sediments the relationship between the varve and $^{226}Ra_{(excess)}$ dates diverges significantly. For the sample with a varve date of 3697, $^{226}Ra_{(excess)}$ overestimates the age, while for the remaining sediments with varve ages in excess of 4000 years old the $^{226}Ra_{(excess)}$ ages are severely underestimated, with what appears to be an almost systematic decrease in $^{226}Ra_{(excess)}$ age with increasing varve age. This is similar to the relationship observed between the varve dates and the ^{14}C dates by Nederbragt and Thurow (2001) although in that instance the varve dates were younger than the ^{14}C dates. The relationship between the varve dates and the $^{226}Ra_{(excess)}/Ba$ dates is similar to the $^{226}Ra_{(excess)}$ dates, although in this case the $^{226}Ra_{(excess)}/Ba$ and varve ages correspond less well (m = 0.415). Indeed, the two ages begin to diverge after *c.* 2400 years, with those between 3276 and 3697 being overestimates and again those after 4000 years being underestimates.

4 Discussion

It is evident from both the geochemical and U-series data that the nature of sedimentation and, in particular the contribution from authigenic $^{226}Ra_{(excess)}$ linked to biogenic silica, have been affected by the shift from shallow nearshore to varved sedimentation in an anoxic, seasonally stratified fjord at around 4000 yr BP (above a depth of 22 m). The variations in the U and Th isotopic activities and metal concentrations identified from the sedimentary record pose a number of questions when calculating $^{226}Ra_{(excess)}$ activities, particularly those associated with the major change in the depositional environment c.4000 yr ago. As already mentioned the characteristics of those sediments deposited during the past 4000 years reflect present day conditions, where the majority of organic matter is of marine origin and the $^{226}Ra_{(excess)}$ is likely to be derived from biogenic silica. Prior to this, lower sea level meant that the marine influence of sedimentation was more restricted, and the inlet was characterised by well-mixed oxygenated shallow waters and periodic wetting and drying (present tidal range 2.4-3.0 m). Hence, not only was the allogenic influx of terrestrial material higher, i.e. closer proximity to the shore, the significance and effectiveness of the biogenic $^{226}Ra_{(excess)}$ flux would have been compromised. Here, Key et al. (1985) note that radium mass balance in the estuary mixing zone is influenced by (i) conservative dissolved Ra in seawater, (ii) conservative dissolved Ra in river water, (iii) Ra that desorbs from suspended particulate matter, and (iv) the diffusive flux of Ra from the bottom sediments which is linked to salinity gradient, sediment composition and load, and dissolved Ra content (Moore and Scott, 1986). These factors will have been further complicated by the changes in climate, runoff and catchment vegetation, and hence terrestrial sediment delivery, that have been noted above.

4.1 Detrital vs. Authigenic Input

A broad scale change in the significance of allogenic terrestrial sediment influx to the inlet around 4000 yr BP may have impacted on the transport and mobility of U-series isotopes (cf. Plater et al., 1992). The chemical properties of both U and Ra dictate that both isotopes can be transported in the dissolved or particulate phase (Gascoyne, 1992; Langmuir, 1978; Lawrie et al., 2000; Moore and Edmond, 1984), whilst Th is less mobile and is generally transported in the particulate phase (Gascoyne, 1992; Langmuir and Herman, 1980; Moore and Edmond, 1984). As such a system dominated by terrestrial input is likely to have experienced higher detrital Th input than one dominated by authigenic marine sedimentation, this is particularly true for ^{232}Th

We observe that the older sediments have only marginally higher Th activities than the younger laminated sediments while the $^{230}Th/^{232}Th$ is not significantly different. Indeed, the fact that the ^{230}Th/^{232}Th activity ratios in both the older and younger sediments are within the range of 1±0.5 indicates a common detrital component. Similarly, the fact that the ^{234}U/^{238}U activity ratio does not change significantly from the older to the younger sediments indicates little variation in the source of the dissolved and particulate inputs over time. Here, we interpret the higher U isotopic activities and U/Th isotopic activity ratios as being indicative of an enhanced authigenic influence on sedimentation once the anoxic fjord had become established

The metal concentration data also support a shift towards an increased marine influence on sedimentation since 4000 yr BP, with an increase in Br, Cl, Si and organic matter being linked to an enhanced contribution from marine-derived organic matter. This concurs with the findings of McQuoid *et* al. (2001) who identified a gradual increase in %C_{org} with decreasing depth, however their end-member mixing estimates suggest a decreasing marine influence between *c*. 20 and 15 m after which the marine influence increases. Changes in biogenic silica were also found to parallel increases in organic matter, reflecting organic matter production being driven primarily by increased siliceous phytoplankton. Indeed, Bornhold *et al*. (1998) found that dissolved Si concentrations in the upper sediments averaged around 1100µM, which they suggest reflects the presence of biogenic Si. This shift to an anoxic marine environment after c.4000 yr BP clearly led to an increased and sustained ^{226}Ra$_{(excess)}$ via diatom silica uptake which was then able to operate as a closed system. Prior to this, the Ra budget is both temporally and spatially variable, and subject to post-depositional remobilisation, i.e. open-system behaviour.

4.2 Initial Input of ^{226}Ra

There is little distinction between the activities of ^{226}Ra in those sediments older than 4000 year BP and those younger. If the initial input of ^{226}Ra has remained constant over time then given the half-life of ^{226}Ra (1602 years) relative to its parent ^{230}Th (7.52 x 10^4 years), the ^{226}Ra activities within the older sediments should be lower. The fact that this is not the case, combined with the fact that Ba concentrations, as a chemical analogue, are generally higher in the older sediments, indicates that the supply of ^{226}Ra has not remained constant over time during the period of time when the inlet was a well-mixed shallow water environment. Here, it is postulated that the input of ^{226}Ra into Saanich Inlet was both higher, more variable and subject to considerable remobilisation prior to 4000 yr BP than between 500 and 4000 yr BP. Given the complexity of Ra mass balance in such shallow tidal environments, it is not possible to identify which process is responsible for the observed $^{226}Ra_{(excess)}$ trend, but it can be concluded that the $^{226}Ra_{(excess)}$ dating cannot be applied to such environments

4.3 ^{226}Ra/Ba Ratio

The above variation in the supply of ^{226}Ra to the older sediments of Saanich Inlet undermines the use of the $^{226}Ra/Ba$ ratio to establish whether or not decreases in ^{226}Ra are driven by decay. The significant variations in the $^{226}Ra_{(excess)}/Ba$ ratio confirm a shift in the source of Ra and Ba at *c.* 4000 yr BP, and that this change marks a transition to a more consistent and closed system (Figure 5). Within the sediments younger than 4000 yr BP both the $^{226}Ra/Ba$ and $^{226}Ra_{(excess)}/Ba$ ratios decrease with depth, suggesting the observed decreases may well result from the radioactivity decay of ^{226}Ra over time. In contrast, within the sediments older than 4000 yr BP the $^{226}Ra/Ba$ and $^{226}Ra_{(excess)}/Ba$ ratios increase with age indicating considerable Ra mobility relative to Ba during deposition, and most probably post-depositionally. Again, this cannot be investigated further but it is at least possible to refer to the current understanding of Ra in estuarine systems to illustrate the highly variable nature of Ra flux and preservation within the sedimentary record at this time. The suggestion that the increased flux of Ra in the older sediments is detrital in origin is not clearly supported by either the U-series or metal concentration data. Indeed, even if there were such increases in allogenic terrestrial influx, the ^{226}Ra would be likely to be in secular radioactive equilibrium with ^{230}Th, and then subsequently remobilised through diagenesis.

4.4 Potential Non-Radiogenic Post-Depositional ^{226}Ra Loss

One aspect as yet unconsidered in the apparently successful dating of the upper 25m of the sedimentary record deposited during the last 4000 years is the apparent post-depositional loss of Ra through non-radiogenic processes. Here sediments may have been subject to considerable bioturbation prior to the onset of deep water anoxia, which might well have impacted on the post-depositional mobility of ^{226}Ra. The observed ^{228}Th/^{232}Th activity ratios in the range of 0.8 to 0.2 and are indicative of ^{228}Ra loss, most likely through diffusion. By analogy, this implies that the sediments would have acted as a closed system to the ^{226}Ra$_{(excess)}$ since deposition, and that the observed down-core decrease in ^{226}Ra$_{(excess)}$ and the ^{226}Ra$_{(excess)}$/Ba ratio in the upper part of the sedimentary record might equally be explained by diffusive losses of ^{226}Ra. Whilst it is appropriate to suspect this, it is somewhat coincidental that: (i) the ^{226}Ra$_{(excess)}$ ages correspond so well with the varve and ^{14}C chronologies; (ii) the switch in the down-core behaviour of ^{226}Ra$_{(excess)}$ corresponds to changes in other radionuclides and metals; and (iii) that the loss of ^{228}Ra continues through the core, even where the ^{226}Ra$_{(excess)}$ begins to increase with depth. In this case, we suspect poor resolution of the low-activity ^{228}Th spectrum relative to background activity on the detectors is the cause of the apparent ^{228}Th/^{232}Th disequilibrium.

4.5 ^{226}Ra$_{(excess)}$ Dating

It is apparent that ^{226}Ra$_{(excess)}$ can produce reliable dates similar to those of the previously and independently established varve chronology (Figure 6). Indeed, the similarity between the dates obtained using ^{226}Ra$_{(excess)}$ and the varve dates for the past 3600 years is very encouraging. However, not all of the sediments appear to be suitable for dating using ^{226}Ra$_{(excess)}$ with the ages for those sediments older than 4000 years old being severely underestimated.

The data presented here suggest that the application of ^{226}Ra$_{(excess)}$ as a dating tool may be compromised in shallow tidal environments where Ra flux is highly variable and site specific, and where the opportunity for the closed system behaviour of Ra is limited. It is only in the relative deep fjord environments where both the authigenic and allogenic fluxes of ^{226}Ra and ^{230}Th are relatively constant during deposition and where anoxia favours closed system behaviour of $^{226}Ra_{(excess)}$ in association with diatomaceous silica. Fortunately changes in the supply and preservation of $^{226}Ra_{(excess)}$ can be identified using the approach outlined above. Thus, it is possible to identify those sediments that would be unsuitable for dating.

4.6 Implications for the Applicability of $^{226}Ra_{(excess)}$

Although $^{226}Ra_{(excess)}$ was able to produce relatively accurate dates, the errors associated with both Th and Ra activities, and subsequently $^{226}Ra_{(excess)}$, were often relatively large. There are two main sources of error. The first occurs as a consequence of the low ^{226}Ra and ^{230}Th activities in aqueous environments, which is primarily related to their chemical properties. The second relates to the procedures used to separate and measure ^{230}Th and, perhaps more importantly, ^{226}Ra. This suggests that for $^{226}Ra_{(excess)}$ to be reliably used to date sediments not only do activities of ^{226}Ra have to be reasonably high, but a number of the problems associated with separation and measurement also need to be overcome.

It became evident when using $^{226}Ra_{(excess)}$ to calculate ages for the Saanich Inlet samples that the calculation of accurate activities is critical. Indeed, in the case of the $^{228}Th/^{232}Th$, this is also true for the higher energy alpha-particles emitted by ^{228}Th. Errors in the calculation of ^{226}Ra and ^{230}Th activities significantly affected ages calculated using $^{226}Ra_{(excess)}$. To reduce these errors good recoveries are essential as is the use of long count times, as these can reduce the statistical uncertainties.

5 Conclusions

The application of $^{226}Ra_{(excess)}$ to date sediment samples from Saanich Inlet has proved successful, with dates calculated using $^{226}Ra_{(excess)}$ being comparable to dates obtained for the last 4000 years or so using both a varve chronology and ^{14}C.

It is not appropriate to assume constant initial $^{226}Ra_{(excess)}$, particularly spanning a period of known environmental change where the nature of sedimentation changes both physically and chemically. The higher and more robust marine authigenic component in those sediments from Saanich Inlet younger than 4000 yr BP resulted in a more consistent $^{226}Ra_{(excess)}$ thus making dating an effective tool for dating sediments deposited in a relatively deep water anoxic inlet. The preceding shallow water tidal inlet was characterised by highly variable Ra flux and, in all likelihood, open-system behaviour post-depositionally. Hence, where supply varies over both space and time it is not possible to assume constant initial $^{226}Ra_{(excess)}$ at time t_0 to calculate ages. As such, while offering the potential to date sediments over the Holocene, the application of $^{226}Ra_{(excess)}$ is sensitive to changes in sedimentation over time, and is prone to error where ^{226}Ra activities are low.

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Tables

Table 1: Table showing the sample ID assigned by ourselves and the hole, core, interval, bottom and top depth and metres below sea floor (mbsf) provided by the ODP, the massive layers between which each sample was found and the calculated varve dates given by Nederbragt and Thurow (2001). Samples denoted in bold are those analysed using alpha-spectrometry

Our ID	Hole	Core, section	Top (cm)	Bot (cm)	Depth (mbsf)	Varve Age	Between massive layers	Comments
1	**A**	**1H-6**	**99**	**101**	**8.49**	**1111**	**6-7**	
2	**B**	**3H-1**	**116**	**118**	**11.26**	**1720**	**12-13**	
3	B	4H-2	82	84	21.92	3416	22-23	
4	**C**	**1H-3**	**103**	**105**	**4.03**	**528**	**1-2**	
5	**C**	**2H-3**	**126**	**128**	**10.46**	**1255**	**8-9**	
6	**C**	**2H-5**	**90**	**92**	**13.1**	**1508**	**10-11**	
7	**C**	**2H-5**	**97**	**99**	**13.17**	**1508**	**10-11**	
8	**C**	**3H-3**	**56**	**58**	**19.26**	**2540 – 2943**		**Within ML 19**
9	C	3H-3	78	80	19.48	2943	19-20	
10	**C**	**3H-3**	**102**	**104**	**19.72**	**2943**	**19-20**	
11	**C**	**3H-3**	**127**	**129**	**19.97**	**2943**	**19-20**	
12	**C**	**3H-4**	**3**	**5**	**20.23**	**3072**	**20-21**	
13	**C**	**3H-4**	**87**	**89**	**21.07**	**3276**	**21-22**	
14	**C**	**3H-4**	**93**	**95**	**21.13**	**3276**	**21-22**	
15	**C**	**3H-6**	**59**	**61**	**23.79**	**3697**	**24-25**	
16	**C**	**4H-1**	**79**	**81**	**25.99**	**4129 – 4310**	**31-33**	**Just below 31**
17	C	4H-2	46	48	27.16	4129 – 4310	31-33	½ way between 31 & 33
18	C	4H-3	98	100	29.18	4587	33-34	Just below 33
19	C	4H-4	65	67	30.35	4587	33-34	Just above 44
20	C	4H-4	78	80	30.48	4863	34-35	
21	C	4H-4	91	93	30.61	5563	36-37	Just below 36
22	C	4H-4	98	100	30.68	5563	36-37	
23	C	5H-1	17	19	34.87	6047		Within ML 40

Table 2: Average activities and standard deviations for the various U-series isotopes and activity ratios, divided into those sediments older than and those younger than 4000 years BP (varve age).

	All Sediments		<4000 years BP		> 4000 years BP	
	Average Activity ($Bq\ kg^{-1}$)	St Dev.	Average Activity ($Bq\ kg^{-1}$)	St Dev.	Average Activity ($Bq\ kg^{-1}$)	St Dev.
^{238}U	62.11	13.10	68.34	11.59	52.78	9.57
^{234}U	69.28	16.25	76.18	15.62	58.94	11.60
^{232}Th	15.38	2.37	14.36	1.83	16.92	2.39
^{230}Th	17.68	3.05	17.08	3.21	18.58	2.82
^{228}Th	8.94	3.41	7.28	2.98	11.43	2.44
^{226}Ra	27.96	3.85	27.90	4.54	28.04	2.90
$^{234}U/^{232}Th$ AR	4.59	1.21	5.31	0.89	3.52	0.74
$^{238}U/^{232}Th$ AR	4.13	1.02	4.80	0.65	3.13	0.46
$^{234}U/^{238}U$ AR	1.11	0.08	1.10	0.08	1.12	0.10
$^{230}Th/^{232}Th$ AR	1.16	0.22	1.19	0.19	1.13	0.27
$^{230}Th/^{234}U$ AR	0.27	0.08	0.24	0.08	0.32	0.07

Table 3: Table showing mean concentrations of the various elements measured using XRF, FAAS and ICP-OES and mean organic matter content for those sediments younger and those older than 4000 years BP and the ratio between the two

	Mean Concentration <4000 yr	Mean Concentration >4000 yr	Ratio <4000 yr />4000 yr
Si	268.67	257.59	1.04
Al	34.55	36.23	0.95
Ti	2.95	3.15	0.94
Ca	8.05	7.85	1.03
K	7.74	8.20	0.94
Fe	31.32	34.49	0.91
Mn	0.49	0.54	0.91
S	10.79	9.85	1.10
Cl	29.83	23.06	1.29
Cu	67.30	61.12	1.10
Zn	67.99	54.91	1.24
Br	178.52	143.81	1.24
OM	8.95	8.70	1.03
Ba	47.98	65.00	0.74
Mn/Ba	0.01	0.01	1.22
Ca/Ba	0.17	0.12	1.42

Figures

Figure 1: Ra, Th and U separation scheme using a combination of solvent extraction and ion exchange (Martin and Hancock, 1992; Holm, 1984)

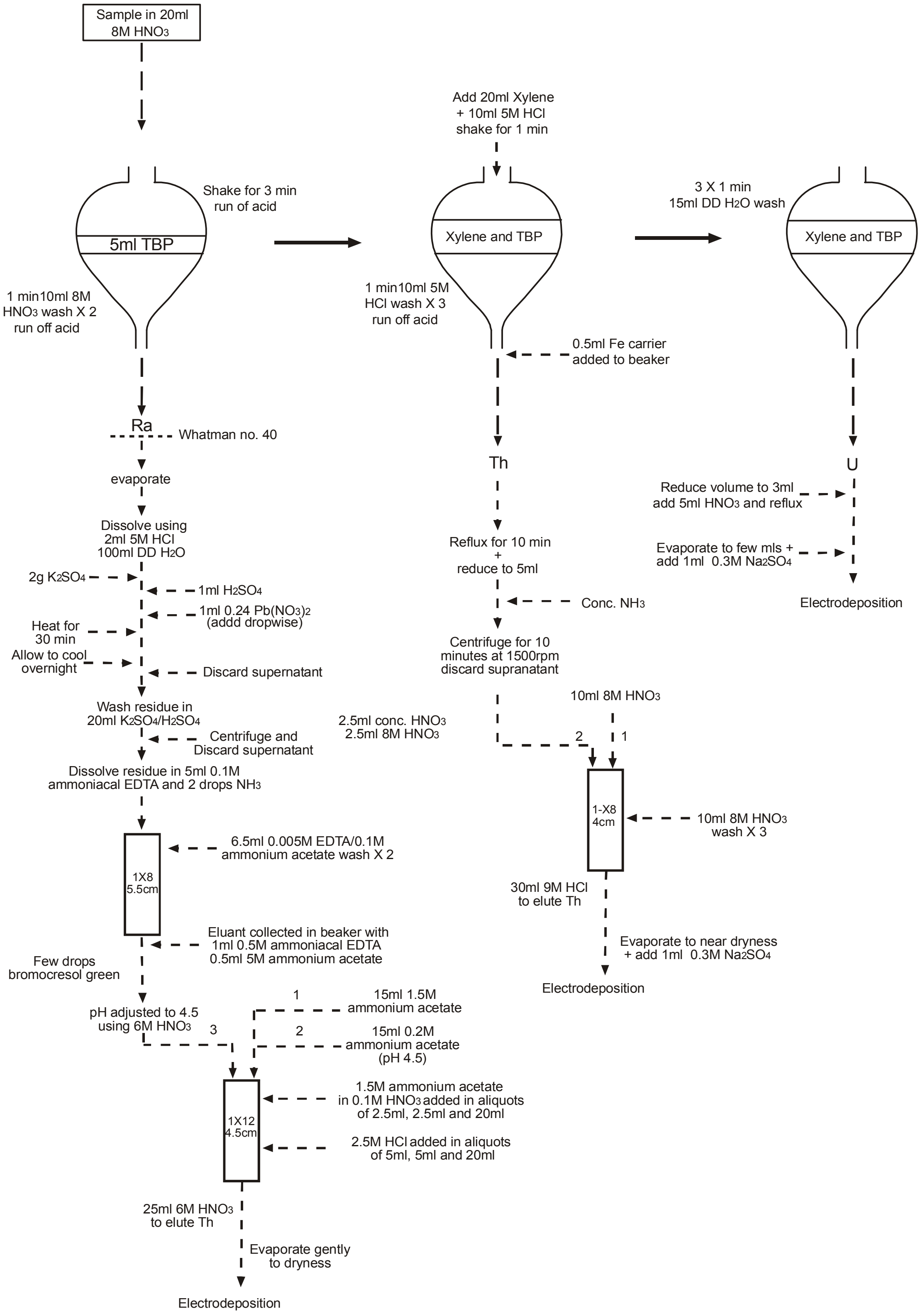

Figure 2: Down-core activities of ^{238}U, ^{234}U, ^{232}Th, ^{230}Th, ^{228}Th, ^{226}Ra, unsupported ^{226}Ra and the ^{226}Ra/^{230}Th, ^{234}U/^{238}U, ^{230}Th/^{232}Th, ^{230}Th/^{234}U and ^{228}U/^{232}Th activity ratios, solid triangles represent those sediments younger than 4000 yr BP, while the hollow triangles represent those sediments older than 4000 yr BP.

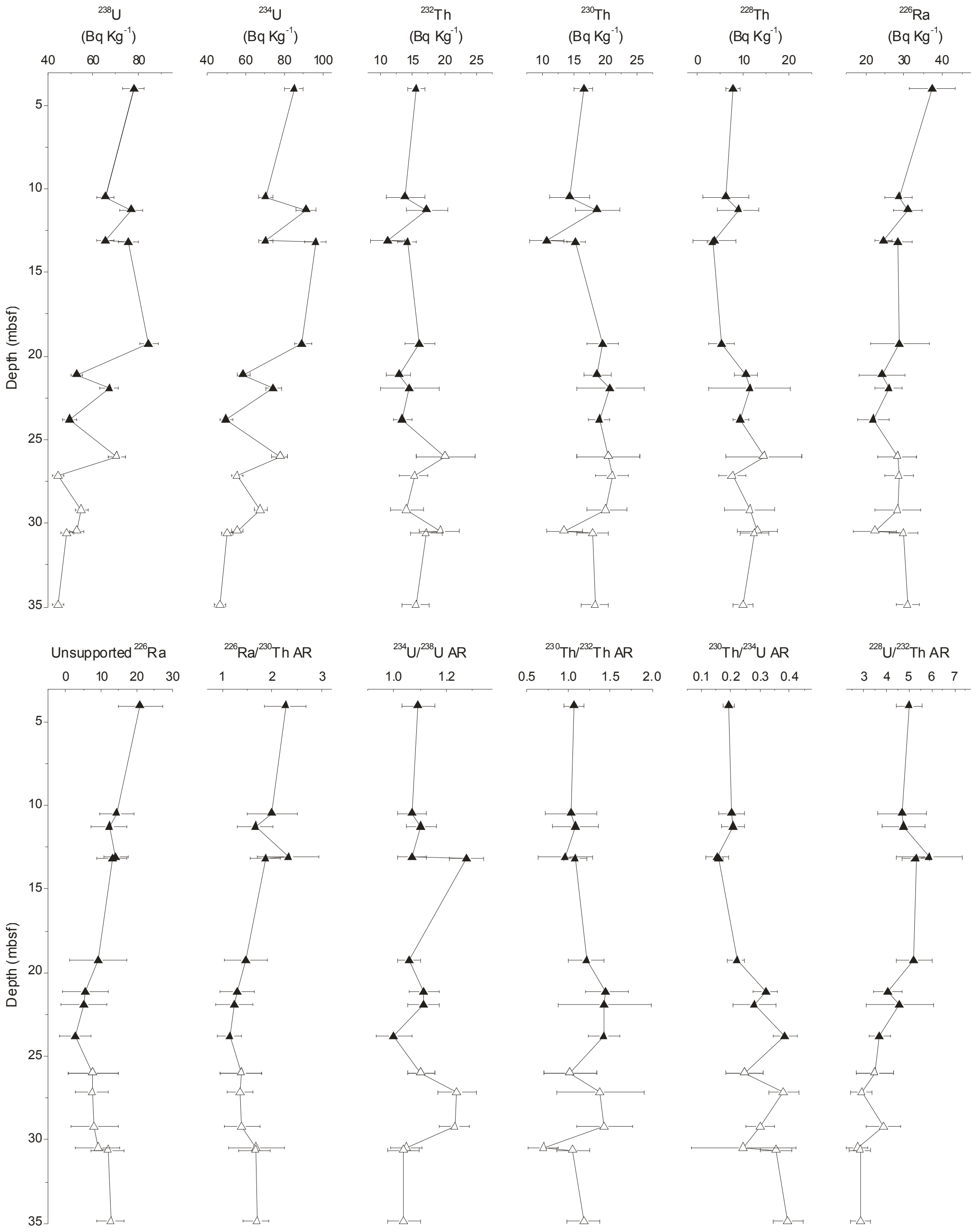

Figure 3: Down-core geochemical variations for Saanich Inlet. Solid triangles represent sediments younger than 4000 yr BP, while hollow triangles represent sediments older than 4000 yr BP. This division is based on the fact that Nederbragt and Thurow (2001) observed significant variations between varve and ^{14}C ages in sediments older than 4000 yr BP

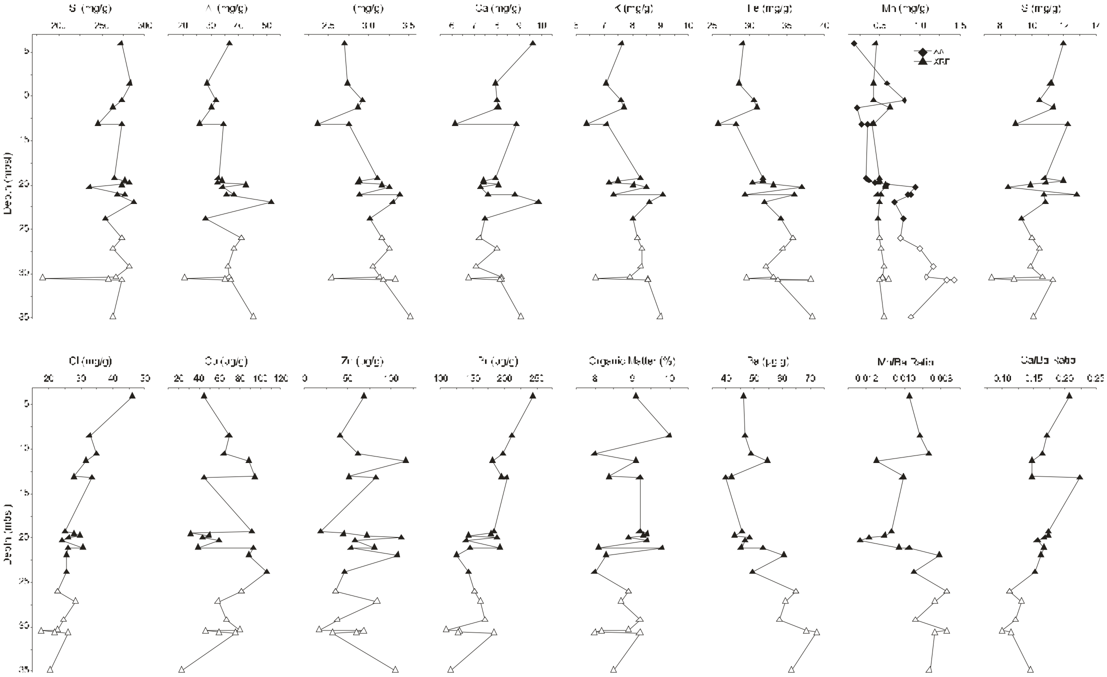

Figure 4: $^{226}Ra_{(excess)}$ activities against varve dates, solid triangles represent those sediments younger than 4000 yr BP, while the hollow triangles represent those sediments older than 4000 yr BP. The solid black line represents the expected decay of ^{226}Ra over time based on a starting activity at t_0 of 20.88 Bq Kg^{-1}. The upper and lower dashed lines represent the decay based on the upper and lower error of the activity at t_o.

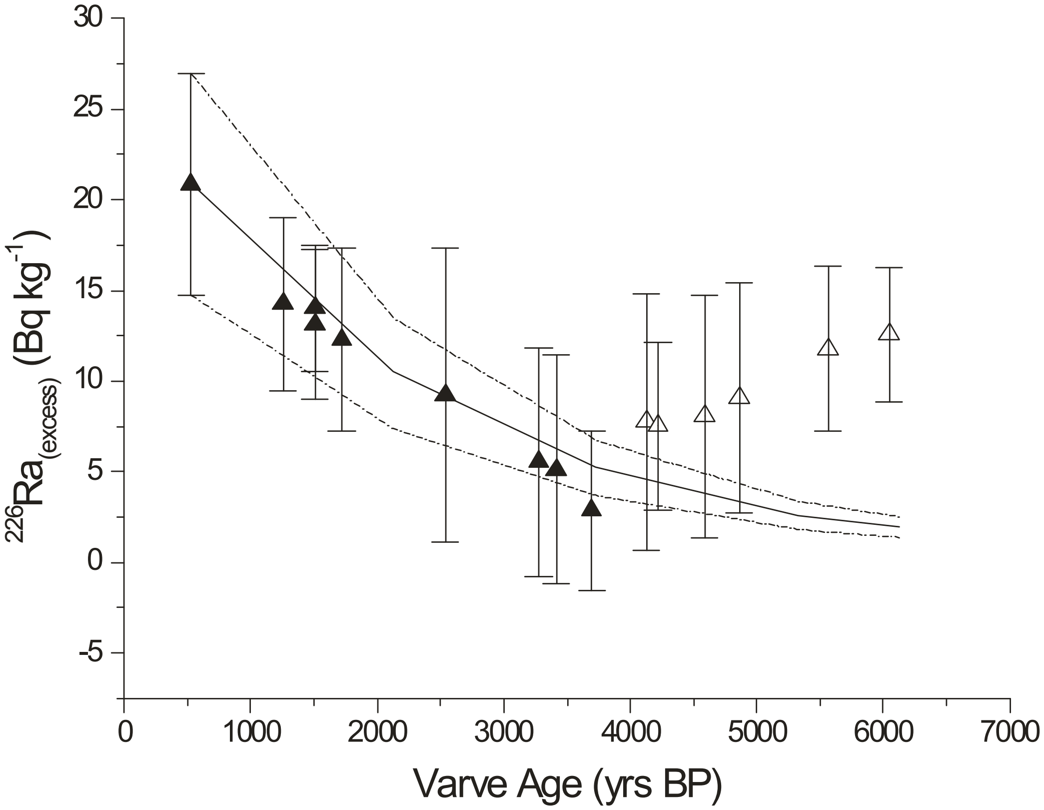

Figure 5: $^{226}Ra_{(excess)}/Ba$ ratios against depth (mbsf), solid triangles represent those sediments younger than 4000 yr BP, while the solid squares represent those sediments older than 4000 yr BP.

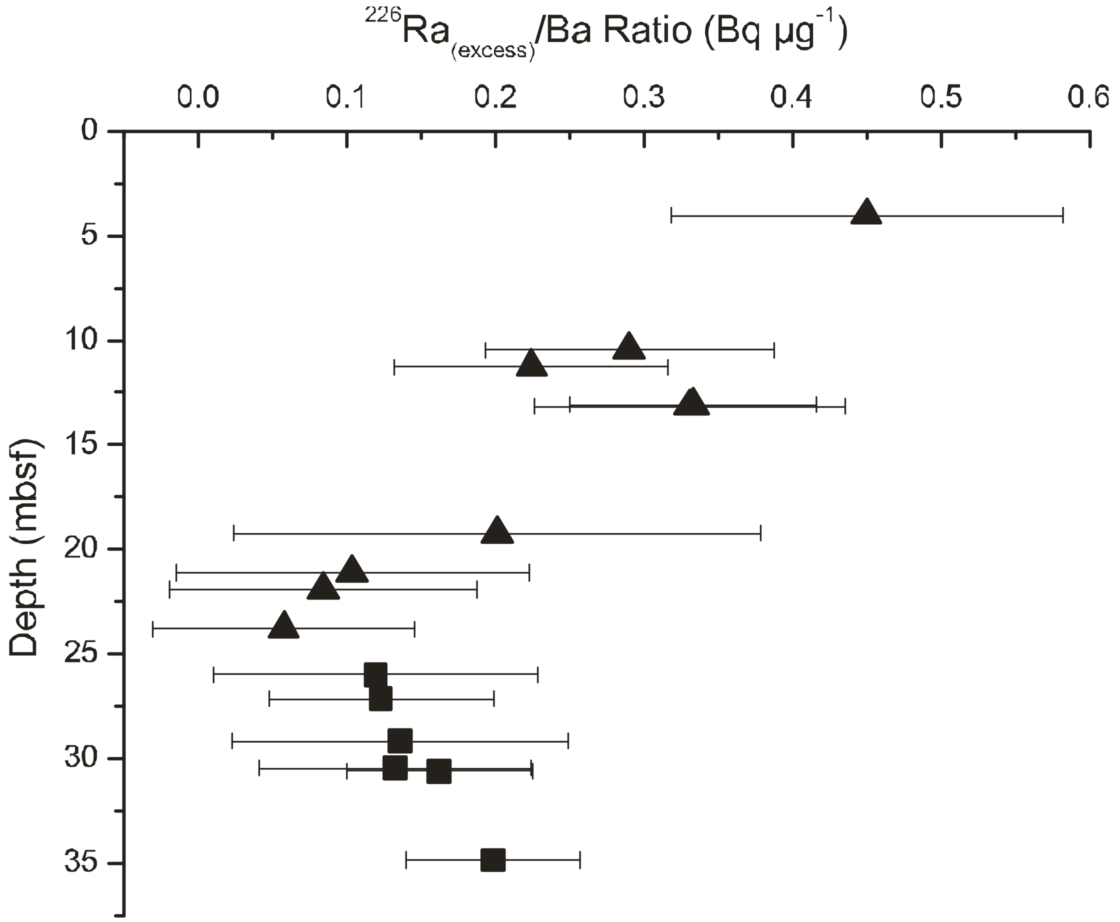

Figure 6: Varve dates plotted against ages calculated using $^{226}Ra_{(excess)}$ left and the $^{226}Ra_{(excess)}/Ba$ ratio (right), solid triangles represent those sediments younger than 4000 yr BP (varve age) and solid squares represent those sediments older than 4000 yr BP (varve age). The diagonal line represents a perfect match between the two dates.