

Control on ($^{234}\text{U}/^{238}\text{U}$) in lake water: A study in the Dry Valleys of Antarctica

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Accepted 5 September 2005

Abstract

The ($^{234}\text{U}/^{238}\text{U}$) ratio in surface waters is generally higher than secular equilibrium due to nuclide recoil during alpha-decay of ^{238}U . The size of the deviation from secular equilibrium contains information about the environment in which the water is found. This potential tool for environmental reconstruction has previously been studied in rivers, groundwater, and sediment pore-water. Here we conduct a first assessment of the controls on ($^{234}\text{U}/^{238}\text{U}$) in lakewaters. Thirty-three waters from glacial melt, streams, and lakes of the McMurdo Dry Valleys (Antarctica) were analysed for U concentration and isotope ratio. Glacial melt has a low U concentration and a ($^{234}\text{U}/^{238}\text{U}$) identical to seawater, suggesting that U in Antarctic ice is largely sourced from sea-salt aerosols. Stream waters have higher U concentration (0.009 to 1.282 ppb) and ($^{234}\text{U}/^{238}\text{U}$) (1.280 to 1.832) due to chemical weathering of sediment in stream channels and ^{234}U recoil from this sediment. Average ($^{234}\text{U}/^{238}\text{U}$) is 1.502, close to the average of observations from other surface waters worldwide. The absence of groundwaters in the Dry Valleys indicates that reasonably high ($^{234}\text{U}/^{238}\text{U}$) ratios do not require groundwater sources of U, so care should be taken before using high ($^{234}\text{U}/^{238}\text{U}$) as an indicator of groundwater inputs to stream waters. Lakewaters have U concentrations ranging from 0.027 to 46 ppb (i.e. up to 14 times the seawater concentration) and ($^{234}\text{U}/^{238}\text{U}$) from 1.05 to 4.50. Young lakes have ($^{234}\text{U}/^{238}\text{U}$) which reflects the sources of U. In one case (Lake Joyce) a ($^{234}\text{U}/^{238}\text{U}$) lower than seawater may suggest U sourced from melting of old ice in which ^{234}U excess has partially decayed. In older lakes, ($^{234}\text{U}/^{238}\text{U}$) is significantly higher than that in the inputs due to addition of recoil ^{234}U from sediments underlying the lake. The size of the deviation from secular equilibrium can only be explained, however, if recoil from a large area of sediment is considered. This is reasonable for the two lakes with particularly high ($^{234}\text{U}/^{238}\text{U}$) (Bonney, Vanda) which are both relicts of much larger lakes present during the last glacial period. On the basis of this study, the addition of recoil ^{234}U to lake water is expected to be a general feature, and to cause a noticeable increase in ($^{234}\text{U}/^{238}\text{U}$) for lakes with a U residence time of more than a few thousand years.

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Keywords: Uranium isotopes; Dry Valleys; Antarctica; Weathering; Lake chemistry

1. Introduction

Radioactive ^{234}U is formed from the decay of long-lived ^{238}U via two short-lived intermediate isotopes. The supply of ^{234}U is therefore limited by decay of ^{238}U , suggesting that the two uranium nuclides should have identical radioactivity in natural materials. Natural

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waters, however, typically have ($^{234}\text{U}/^{238}\text{U}$) ratios (where round brackets are used to denote an activity ratio) significantly greater than 1.0 due to the physical process of alpha-recoil during the energetic decay of ^{238}U (Chabaux et al., 2003).

This deviation from secular equilibrium encodes information about the environment in which the waters are found and can be a powerful tool with which to understand modern and past conditions. ($^{234}\text{U}/^{238}\text{U}$) in river waters, for instance, has been shown to respond to changes in physical erosion and rainfall (Robinson et al., 2004b) possibly allowing these environmental parameters to be reconstructed for past times. In groundwaters, ($^{234}\text{U}/^{238}\text{U}$) is used as part of a suite of U-series tracers which are used to assess the age of waters and the movement rate of chemical species (Porcelli and Swarzenski, 2003). Similar techniques have also been used to assess flow rates through marine sediments (Henderson et al., 1999). Such approaches require an understanding of the processes controlling ($^{234}\text{U}/^{238}\text{U}$) in the setting being studied. In particular, the relative importance of ^{238}U and ^{234}U addition to the water versus their chemical and radioactive removal must be understood. Such knowledge exists, or is being developed, for many types of natural waters, but understanding of the processes controlling ($^{234}\text{U}/^{238}\text{U}$) in lake waters is poor.

This study assesses the controls on ($^{234}\text{U}/^{238}\text{U}$) in lakes from the McMurdo Dry Valleys in Antarctica (from now on referred to as the Dry Valleys) together with the rivers and glacial melt waters which feed them. Despite their remoteness, the lakes of the Dry Valleys have been extensively studied, most recently to assess the adaptation of life to harsh environments and the potential for life on other planets (Doran et al., 1998). A significant body of work exists on the chemistry of the lakewater, including major and minor element data (Lyons et al., 1998), and a range of isotope systems such as Sr (Jones and Faure, 1978), Cl (Lyons et al., 1999) and the rare gases (Poreda et al., 2004). The Dry Valley lakes offer a number of advantages for a study of lake processes. Apart from the large body of prior research, they also represent an extreme end-member lake environment. Although they will not provide information about the full range of lake processes, they are good case examples of their type. They have also been demonstrated, from previous U/Th chronology, to exhibit high and variable ($^{234}\text{U}/^{238}\text{U}$) (Hendy, 2000). Dry Valley lakes are therefore an appropriate setting to conduct the first systematic study of uranium isotopes in lakewaters.

2. Samples and regional setting

The McMurdo Dry Valleys are located in the Transantarctic Mountains along the western coast of the Ross Sea (Fig. 1). They experience a hyper-arid polar desert environment with mean annual temperatures below $-20\text{ }^{\circ}\text{C}$ (Doran et al., 2002) and precipitation of less than 10 mm/yr. The area is devoid of macro-flora, although various algal communities are found. Glacial melt-water forms during a brief two-month period in summer and most ablation ($\approx 30\text{ cm/yr}$) is by sublimation (Chinn, 1980). Despite the harsh environment, small lakes with liquid water exist throughout the region. Most occur in closed basins and have perennial ice cover greater than 3 m in thickness. During summer, a narrow band of this ice can melt around the lake edges, forming a moat.

The presence of saline groundwaters in the region has been suggested (Cartwright and Harris, 1981) but oxygen and hydrogen isotope studies demonstrate the absence of meteoric groundwaters as a volumetrically important contributor to lake waters (Friedmann et al., 1995; Hendy, 2000; Matsubaya et al., 1979). Significant inputs of thermal groundwaters are also ruled out by temperature profiles which reach a maximum in the deep waters of the lake and decrease downwards into the sediment at gradients well explained by diffusion of solar heat from the lakes (Wilson and Wellman, 1962).

Lakewaters are derived, instead, from summer melting of glaciers, sometimes directly into the lakes, but more commonly at a distance with water flow in seasonal streams. Such stream flow occurs in discrete channels with little or no base flow (Nezat et al., 2001). Despite the low temperatures and lack of rainfall, the channelised run-off and the exposure of fresh mineral surfaces by freeze–thaw activity lead to reasonably high rates of chemical weathering within the stream channels (Nezat et al., 2001).

A total of eleven Dry Valley lakes were sampled for this study. Four of these have a complex history worthy of individual discussion, while the others are described only briefly. An extensive literature on the hydrography and chemistry of the Dry Valley Lakes exists and has been thoroughly summarized by Hendy (2000), a paper on which the following summary relies heavily.

- i. Lake Vanda is situated in the low point of the Wright Valley and has a surface area of $\approx 16\text{ km}^2$. It is fed by the Onyx River, at 28 km the longest stream in Antarctica, which receives most of its water from the pro-glacial Lake Brownworth to the East, with additional small contribu-

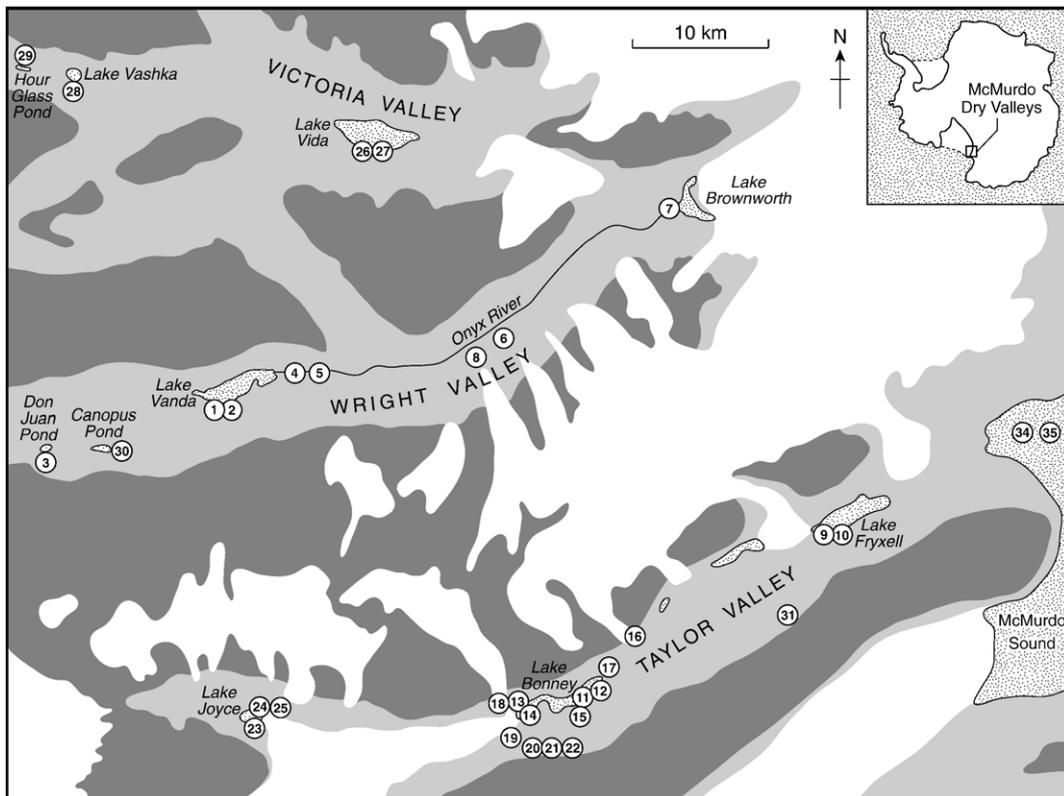


Fig. 1. Schematic map of the McMurdo Dry Valleys region. Dark and light grey represent areas above and below 1000 m respectively; white represents major permanent glaciers; stippled areas represent water (generally ice covered). Sample locations are numbered — see Table 1 for details and results of each numbered sample. The map represents an area 70 km across.

tions from melting of alpine glaciers during its flow westward. For this study, samples were analysed from the Onyx River where it outputs Lake Brownworth, at its midpoint, and where it enters Lake Vanda, as well as a sample from the melting Bartley Glacier which flows into the Onyx River. Lake Vanda is ≈ 73 m deep with permanent ice cover. It is highly stratified with a salt-rich lower layer diffusing upwards into fresher waters (Wilson, 1964). The length scale of this diffusion suggests that Lake Vanda was a shallow, highly saline lake which reflooded about 1200 years ago (Hendy, 2000; Wilson, 1964). The quantity and chemistry of the salt in this bottom layer indicate that it was not derived from the Onyx River but is a relict feature requiring considerable time to accumulate (Green and Canfield, 1984). One sample from the surface waters, and one from near the bottom were analysed in this study. Shorelines up to 480 m above the present surface of Lake Vanda demonstrate the past presence of a significantly larger lake filling much of the Wright Valley (Hall et al., 2001). Chronology of

these “Glacial Lake Wright” shorelines indicates that its level fluctuated during the last glacial period, before lowering abruptly at ≈ 8 ka (Hall and Denton, 1995). Close to the present Lake Vanda lies Don Juan Pond, a smaller water body which was also sampled. This is a highly saline ice-free pond which probably derived its salt in a similar fashion to Lake Vanda, and would have been part of Glacial Lake Wright during the last ice age (Hall et al., 2001).

- ii. Lake Fryxell lies at the eastern end of the Taylor valley (Fig. 1) and, compared to the other Dry Valley lakes, is close to the coast. It has a depth of ≈ 20 m and, like Lake Vanda, is strongly stratified with an increase in salinity in the bottom, although only to about 3% of the salinity seen in Lake Vanda. Modelling of the upward diffusion of salt suggests a reflooding of the lake about 1000 years ago (Lawrence and Hendy, 1985), a similar time to that for Lake Vanda. Unlike Vanda, however, the quantity and composition of salt in Lake Fryxell suggest that present stream inputs (from nearby alpine glacial melt) could have supplied the

Table 1

U concentrations and ($^{234}\text{U}/^{238}\text{U}$) for surface waters of the Dry Valleys (Location of listed samples are shown in Fig. 1)

No.	Sample	Type	Year	($^{234}\text{U}/^{238}\text{U}$)	^{238}U conc. (ppb)
<i>Lake Vanda system</i>					
1	Vanda moat west	Lake	2002	2.189 ± 0.003	0.047 ± 0.001
2	Vanda deep (68 m)	Lake	2002	4.320 ± 0.003	16.100 ± 0.020
3	Don Juan Pond	Lake	1999	1.963 ± 0.019	1.200 ± 0.115
4	Onyx River — inlet Lake Vanda	Stream	2002	1.497 ± 0.019	0.009 ± 0.001
5	Onyx River — inlet Lake Vanda	Stream	1999	1.474 ± 0.029	0.062 ± 0.001
6	Onyx River — midpoint	Stream	1999	1.358 ± 0.054	0.038 ± 0.002
7	Onyx River — outlet Lake Brownworth	Stream	1999	1.382 ± 0.119	0.011 ± 0.001
8	Bartley glacial melt water	Glacial melt	1999	1.146 ± 0.022	0.044 ± 0.000
<i>Lake Fryxell system</i>					
9	Fryxell surface	Lake	1999	1.390 ± 0.011	1.558 ± 0.033
10	Fryxell Delta Stream moat	Lake	1999	1.297 ± 0.019	0.038 ± 0.001
<i>Lake Bonney system</i>					
11	Bonney — East Lobe moat	Lake	1999	1.808 ± 0.071	0.027 ± 0.001
12	Bonney — East Lobe surface	Lake	1999	2.745 ± 0.006	1.085 ± 0.002
13	Bonney — West Lobe surface	Lake	1999	3.053 ± 0.004	1.385 ± 0.003
14	Bonney — West Lobe bottom	Lake	1999	4.520 ± 0.003	46.630 ± 1.390
15	Hughes Stream East	Stream	2002	1.522 ± 0.003	0.183 ± 0.000
16	Taylor Stream North	Stream	2002	1.699 ± 0.003	1.282 ± 0.002
17	Taylor Stream South	Stream	2002	1.832 ± 0.003	0.502 ± 0.001
18	Rhone Stream	Stream	2002	1.280 ± 0.012	0.022 ± 0.001
19	Calkin Stream	Stream	2002	1.787 ± 0.003	0.183 ± 0.001
20	South Side Blood Falls	Sub-glacier	2002	4.859 ± 0.003	4.199 ± 0.005
21	Blood Falls (ice)	Sub-glacier	2002	4.467 ± 0.003	0.281 ± 0.001
22	Blood Falls Dripping	Sub-glacier	2002	4.492 ± 0.003	0.181 ± 0.001
<i>Lake Joyce system</i>					
23	Joyce surface	Lake	1999	1.051 ± 0.003	0.913 ± 0.004
24	Joyce inlet (moat)	Lake	1999	1.070 ± 0.012	0.171 ± 0.002
25	Joyce bottom	Lake	1999	1.078 ± 0.002	14.930 ± 0.120
<i>Other lakes</i>					
26	Vida East moat	Lake	1999	1.342 ± 0.010	0.152 ± 0.001
27	Vida West moat	Lake	1999	1.397 ± 0.011	0.108 ± 0.001
28	Vashka moat	Lake	1999	1.279 ± 0.028	0.104 ± 0.002
29	Hour Glass Pond moat	Lake	1999	1.258 ± 0.023	0.084 ± 0.000
30	Canopus Pond	Lake	1999	1.202 ± 0.002	13.960 ± 0.140
31	Nussbaum Riegel Pond	Lake	1999	1.417 ± 0.010	2.103 ± 0.039
32	Trough Lake surface	Lake	1999	1.204 ± 0.007	1.844 ± 0.019
33	Trough Lake bottom	Lake	1999	1.194 ± 0.007	0.505 ± 0.006
<i>Seawater</i>					
34	McMurdo Sound seawater 1	Seawater	1999	1.146 ± 0.004	3.148 ± 0.053
35	McMurdo Sound seawater 2	Seawater	1999	1.144 ± 0.007	2.828 ± 0.106

salt budget in only a few thousand years (Green et al., 1988). Two samples from the surface of Lake Fryxell were analysed in this study.

- iii. Lake Bonney lies at the opposite, western, end of the Taylor Valley with the Taylor Glacier bounding it to the west. Again, it is a well stratified lake with an increase in bottom salinity suggesting reflooding early in the Holocene (i.e. earlier than Vanda and Fryxell). Bonney is more salty even than

Vanda, with the salts reflecting a long and complex history (Hendy et al., 1977). It is ice covered, and is divided into an eastern and western lobe separated by an underwater saddle. The eastern lobe dried completely sometime after reflooding and, although now full again, has a different water chemistry as a consequence. Surface water from under the ice were analysed from both lobes, together with a moat sample from the eastern lobe,

and a sample from the deep salty layer in the western lobe. Bonney receives the majority of its water from melting of the Taylor Glacier, including highly saline iron-rich waters flowing from under the glacier at “Blood Falls” (Black et al., 1963) which appear to represent reworking of evaporite material from an earlier period of the lake’s history (Lyons et al., 2005). In addition, melt water is received from several nearby alpine glaciers. Samples of Blood Falls and of these glacial melt-water-fed streams were analysed (Table 1). Like Lake Vanda, Bonney was part of a considerably larger lake during the last ice age. Shorelines in the Taylor valley indicate that the valley was filled completely with “Glacial Lake Washburn” which drained at ≈ 8 ka, probably due to removal of an ice dam at the seaward end of the valley.

- iv. Lake Joyce lies to the northern side of the Taylor Glacier and is probably dammed by it. It is more than 50 m deep, with permanent ice cover and salinity stratification. This lake has not been as heavily studied as others in the region, but its salt content is low relative to Vanda and Bonney (reaching a salinity of only $\approx 3\%$ at depth) so, at the present rate of input from Taylor Glacier, it could have accumulated its entire salt budget in a few thousand years (Green et al., 1988). Samples of surface water from below the ice, of the melted moat, and from the somewhat salty deep layer were analysed.
- v. Other lakes. In the north of the studied regions are three small water bodies: Lake Vida; Lake Vashka; and Hourglass Pond, all of which are largely frozen to the base. Samples from the summer moat were analysed from each of these. Canopus and Nussbaum Riegel Ponds, two small frozen ponds in the Wright and Taylor Valleys respectively were also sampled, as was the little-studied Trough Lake lying some distance to the South (and not shown on Fig. 1). These other lakes do not feature the salinity stratification seen in the four major lakes.

In summary, samples were taken which capture the full range of water types found in the Dry Valleys. These include glacial melt waters and waters from the summer streams in the region. They also include samples from the major types of lakes found including: small non-stratified ponds; stratified lakes with a short salt accumulation history and consequently intermediate salt content (Fryxell, Joyce); and stratified lakes with a long accumulation history and very high salt content (Vanda, Bonney).

3. Analytical techniques

A total of 33 250 ml water samples were collected during January 1999 and January 2002. Unfiltered waters were collected in pre-rinsed new HDPE bottles and were not acidified in the field. Samples described as “moat” (Table 1) were collected from the ice-free edge of lake surfaces. Those described as “surface” were collected through a hole cut into lake ice cover. Samples were recovered from depth in some lakes by lowered a weighted tube to the specified depth and pumping water upwards. Two McMurdo Sound seawater samples were also collected from close to the coast.

In the laboratory, samples were acidified to pH 2, left overnight and aliquoted to provide 150 ml samples for U analysis. A ^{236}U spike and 1 mg of Specpure Fe were added and, after allowing for equilibration for at least 24 h, U was co-precipitated with Fe oxyhydroxide by addition of NH_3 . Uranium was separated from the precipitate by standard ion-exchange procedures (following Edwards et al., 1986). Full procedural blanks measured on 150 ml of 18 M Ω water taken through this process (i.e. providing an overestimate of the blank) were <0.1 ng and therefore typically represent $<1\%$ of measured U.

Purified U samples were aspirated at ≈ 50 $\mu\text{l}/\text{min}$ in 2% HNO_3 , via a Cetac Aridus nebuliser, into a Nu Instruments Multi-Collector ICP Mass Spectrometer (MC-ICP-MS). ^{234}U was collected in one of three ion-counting channels, while ^{235}U , ^{236}U , and ^{238}U were collected synchronously in high-side Faraday collectors. Twenty five ratios, each of 10 s, were collected for each sample. Mass bias and ion-counter gain were assessed by measurement of the CRM145 U standard between each analysis (following Robinson et al., 2002). In samples where sufficient U was present, solution concentration was adjusted to provide a 2×10^{-11} amp ^{238}U beam, similar to that of the standard. At this beam size, measured $^{238}\text{U}/^{235}\text{U}$ of samples provided confirmation that samples and standards exhibited identical mass bias. ($^{234}\text{U}/^{238}\text{U}$) was calculated from measured $^{235}\text{U}/^{234}\text{U}$ (or $^{238}\text{U}/^{234}\text{U}$ where the ^{235}U beam was too small) using half lives of 4.4683×10^9 for ^{238}U (Jaffey et al., 1971) and 2.4525×10^5 for ^{234}U (Cheng et al., 2000). U concentrations were calculated from the measured $^{238}\text{U}/^{236}\text{U}$.

4. Results

The two seawater samples had values of 1.144 and 1.146, identical to seawaters measured elsewhere (Chen et al., 1986; Robinson et al., 2004a). This confirms the accuracy of the measurement technique for natural

water samples. U concentrations are lower than typical for open-ocean seawater, an unsurprising result given that these samples represent summer coastal water with a significant contribution from melted sea and land ice.

Melt water flowing directly from a melting alpine glacier in the Wright Valley (Bartley Glacier) has a U concentration of 0.044 ppb and a ($^{234}\text{U}/^{238}\text{U}$) of 1.146, identical to that observed in seawater (Robinson et al., 2004a). Eleven measured stream samples have a wide range of U concentration from 0.009 to 1.282 ppb, and a range of ($^{234}\text{U}/^{238}\text{U}$) from 1.280 to 1.832 averaging 1.502 (Table 1; Fig. 2). These ($^{234}\text{U}/^{238}\text{U}$) values are comparable to those reported in the literature for rivers and streams around the world which average 1.484 ($n=132$; Fig. 2).

The eighteen lake samples exhibit U concentrations which range by more than three orders of magnitude from 0.027 to over 46 ppb. In general, concentrations are lowest in moat samples, slightly higher in under-ice surface waters, and much higher in the salty deep waters. ($^{234}\text{U}/^{238}\text{U}$) in these lake samples also show a wide range, from 1.05 (i.e. less than the seawater ratio) to higher than 4.5. The high end of this range represents some of the highest values ever measured for surface waters (Fig. 2). For Lake Bonney, the highest ($^{234}\text{U}/^{238}\text{U}$) values are found in the western lobe and may be associated with the high values also observed in the Blood Falls samples which range up to 4.86.

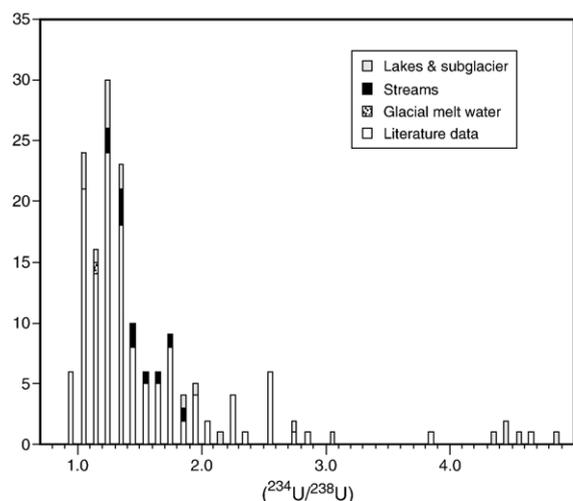


Fig. 2. Histogram of surface water ($^{234}\text{U}/^{238}\text{U}$) values. White data represent 132 measurements taken from the literature (e.g. Chabaux et al., 2003; Kronfeld and Vogel, 1991; Vigier et al., 2001) which average 1.484. New data from the Dry Valleys are shown by type. Note that stream samples have values within the range of samples from elsewhere, while some lakewater samples have extremely high values.

5. Discussion

5.1. Control of ($^{234}\text{U}/^{238}\text{U}$) in Dry Valley Streams

Uranium in glacial melt water in the Dry Valley region is likely to be of marine sea-salt origin. This is indicated by the Bartley Glacier sample which has ($^{234}\text{U}/^{238}\text{U}$) identical to that of seawater. This is not surprising for Antarctic glacial ice because the lack of significant areas for generation of mineral aerosols precludes the inclusion of significant detrital material in glacial ice. In other regions, where atmospheric dust loading is higher, glacial melt water might be expected to have higher U concentrations and more variable ($^{234}\text{U}/^{238}\text{U}$).

During transport in stream channels, melt waters accumulate additional U from the rocks they flow over. This is indicated by the fact that, in general, stream waters have higher U concentrations than the glacial melt water. It is also shown by the three samples taken from the Onyx River in a single year (1999) which show a systematic increase in U concentration downstream. Such an increase in solute concentration has been noted for major ions in the Onyx River (Green and Canfield, 1984) and reflects the chemical weathering of minerals in the stream channels (Nezat et al., 2001).

Melt waters preferentially accumulate ^{234}U during transport due to alpha recoil from rocks in the stream channels. This process leads all measured streams to have ($^{234}\text{U}/^{238}\text{U}$) higher than glacial melt water. Measured ($^{234}\text{U}/^{238}\text{U}$) values are not particularly high, however, when compared to values elsewhere on Earth (Fig. 2). This is initially surprising because riverine ($^{234}\text{U}/^{238}\text{U}$) is known to be high when rainfall is low, and/or when physical weathering is high (Robinson et al., 2004b). The Dry Valleys have low rainfall, and are likely to experience high physical weathering due to glacial grinding and freeze–thaw processes. Yet stream ($^{234}\text{U}/^{238}\text{U}$) values average only 1.502 — lower than the average for arid rivers in South Africa (1.974, (Kronfeld and Vogel, 1991)) or for the South Island of New Zealand with high rates of physical erosion (2.014, (Robinson et al., 2004b)). This feature is most readily explained by the fact that there is no run-off at all from most of the land surface. Only rocks in stream beds come into contact with waters and these see a reasonably large amount of water during an annual cycle. The absence of base-flow also reduces the amount of rock interacting with the waters as they flow. The high local run-off gives rise to high rates of chemical weathering in the stream channels themselves

(Nezat et al., 2001) equal to or higher than that observed in more temperate settings.

Stream water ($^{234}\text{U}/^{238}\text{U}$) as high as 1.832 is seen even in the complete absence of groundwater inputs, suggesting that the uranium isotope ratio is not a reliable tool with which to assess groundwater inputs to surface waters. The use of ($^{234}\text{U}/^{238}\text{U}$) for this purpose has been suggested based on data from Himalayan rivers (Chabaux et al., 2001) and streams draining Mount Cameroon (Riotte et al., 2003). Although these studies have indicated the importance of groundwaters in some settings, the Dry Valleys data clearly show that stream-water ($^{234}\text{U}/^{238}\text{U}$) can be increased to reasonably high values without any groundwater addition, indicating that care must be taken before using ($^{234}\text{U}/^{238}\text{U}$) as a tracer of groundwater inputs. This conclusion is in agreement with a previous study in New Zealand which indicated that very high ($^{234}\text{U}/^{238}\text{U}$) values found in streams were not explained by groundwater inputs (Robinson et al., 2004b).

5.2. Controls on U concentration and ($^{234}\text{U}/^{238}\text{U}$) in Dry Valley Lakes

In the closed-basin lakes of the Dry Valleys, U concentration is increased, as for other elements, by input in melt waters, and the subsequent sublimation of ice. U is removed principally by carbonates formed by occasional growth of algal mats (Hall and Henderson, 2001) and during evaporation. Other evaporite minerals have low U concentrations so their formation leads to only slight U removal. Removal of U does not appear to balance input so the lakes are not in steady state and their U concentrations increase as they age. Lakes with a long history, such as Vanda and Bonney, therefore have particularly high U concentration (up to 14 times higher than seawater).

Most of the smaller lakes in the Dry Valleys, and of the surface waters in larger lakes, have ($^{234}\text{U}/^{238}\text{U}$) values that can be explained simply by inflow of stream water. Lakes Vida and Vashka, for instance, have values which are close to the average for stream water in the area. And the moat of Lake Bonney has a value close to that of the Calkin stream which flows into this moat. There are notable exceptions to this trend, however. Lake Joyce has ($^{234}\text{U}/^{238}\text{U}$) consistently lower than streams in the region, lower even than seawater. And the saline waters found in Lake Vanda, Lake Bonney, and Don Juan Pond all have ($^{234}\text{U}/^{238}\text{U}$) much higher than can be explained by stream inputs.

The low values in Lake Joyce may relate to the direct input of waters from melting of old glacial ice,

rather than from stream flow as seen for other lakes in the area. One possibility is that U, originally derived from sea-salt aerosols, has had significant time for excess ^{234}U decay to occur during transit of the Taylor Glacier from the Taylor Dome, where the snow is accumulating.

The high ($^{234}\text{U}/^{238}\text{U}$) values seen in Lake Bonney appear, at first sight, to be related to the high values found in Blood Falls, flowing from under Taylor Glacier. No such input exists for Don Juan Pond nor Lake Vanda, however, so it is more likely that the high ($^{234}\text{U}/^{238}\text{U}$) in Blood Falls represents recycling of relatively recently buried Lake Bonney salt. The very high ($^{234}\text{U}/^{238}\text{U}$) value would seem to preclude the salt being of significant age as this would allow time for decay of the excess ^{234}U . If Blood Falls is merely recycled recent lake water, then the question remains: what causes the unusually high ($^{234}\text{U}/^{238}\text{U}$) values in the salty lakes of the Dry Valleys?

The source of additional ^{234}U to these salty lake waters cannot be groundwaters, which are absent in this setting (Friedmann et al., 1995; Hendy, 2000; Matsubaya et al., 1979; Wilson and Wellman, 1962). An alternative is that the source is a sudden pulse of ^{234}U from damaged sites in minerals exposed during deglaciation at the end of the ice age. But this explanation is unlikely because, rather than being ice covered at the last glacial, these valleys were filled with large lakes. Furthermore, ($^{234}\text{U}/^{238}\text{U}$) values for carbonates formed in these glacial lakes are high, indicating that the extreme values have been a long-lived feature. The most likely scenario, therefore, is that the high ($^{234}\text{U}/^{238}\text{U}$) is explained by addition of recoil ^{234}U from the sediments underlying the lakes. The importance of such recoil ^{234}U for seawater has been known for some time (Ku, 1965) where it is thought to support about half the observed ^{234}U excess. High ($^{234}\text{U}/^{238}\text{U}$) values in the Dry Valleys are always found in waters thought to have a long history of salt accumulation.

5.3. Addition of ^{234}U from lake bottom sediments

In the absence of physical breakdown of mineral grains in the lake-bottom sediment, ^{234}U cannot be released from damaged lattice sites and must, instead, be directly recoiled from minerals by decay of ^{238}U (and subsequent rapid decay of ^{234}Th and ^{234}Pa). Such alpha recoil addition of ^{234}U to the lake is a physical process that is described by the equation (modified from Henderson et al., 1999):

$$^{234}\text{U}_{\text{gain}} = ^{238}\text{U}_{\text{sediment}} \cdot \lambda^{238} \cdot f \quad (1)$$

where $^{234}\text{U}_{\text{gain}}$ is the total ^{234}U added to the lake (mol/yr); $^{238}\text{U}_{\text{sediment}}$ is the total amount of U contained in the sediment body which interacts with the lakewater (mol); λ^{238} is the decay constant of ^{238}U (a^{-1}); and f is the fraction of ^{234}U that is ejected from the sediment into the lake upon decay of ^{238}U . Removal of U from lakewater will not fractionate the isotopes so the only way to decrease excess ^{234}U (mol/yr) in the lakewater is by radioactive decay which is given by:

$$^{234}\text{U}_{\text{loss}} = ^{238}\text{U}_{\text{lakewater}} \cdot \lambda^{238} \cdot \left[\left(\frac{^{234}\text{U}}{^{238}\text{U}} \right) - 1 \right] \quad (2)$$

where $^{238}\text{U}_{\text{lakewater}}$ is the total amount of ^{238}U in the lakewater (mol); and $(^{234}\text{U}/^{238}\text{U})$ is the activity ratio of U.

The maximum possible $(^{234}\text{U}/^{238}\text{U})$ in lakewater is achieved when sufficient time has elapsed (≈ 4 half lives of ^{234}U) that the rate of ^{234}U addition by recoil is equal to the loss of ^{234}U from excess decay. From the above two equations above this value is given by:

$$\left(\frac{^{234}\text{U}}{^{238}\text{U}} \right)_{\text{max}} = \frac{^{238}\text{U}_{\text{sediment}}}{^{238}\text{U}_{\text{lakewater}}} \cdot f + 1. \quad (3)$$

By inserting reasonable values for $^{238}\text{U}_{\text{sediment}}$, $^{238}\text{U}_{\text{lakewater}}$, and f into this equation, we can assess whether values as high as those seen in the Dry Valley lakes can be explained by recoil addition of ^{234}U . Here we use this approach to assess the maximum $(^{234}\text{U}/^{238}\text{U})$ possible due to recoil in these salty lake waters.

$^{238}\text{U}_{\text{sediment}}$: U concentrations in Dry Valley sediments are not generally higher than the crustal average of 2.4 ppm (based on extensive U-series chronology of such sediments, including unpublished work by the authors). The maximum thickness of such sediment that can exchange with the lake can be no more than 8 m. This value is derived from the relationship $t=L^2/D_{\text{eff}}$ where t is the timescale of interest (which cannot be more than the ≈ 4 half lives required for recoiled ^{234}U to have decayed before diffusing to the lake); L is the distance diffused; and D_{eff} is the diffusion coefficient of U in typical sediments ($\approx 2 \times 10^{-8} \text{ cm}^2/\text{s}$; Henderson et al., 1999). This suggests an upper limit on $^{238}\text{U}_{\text{sediment}}$ of 7.6 μmol per cm^2 of lake floor.

$^{238}\text{U}_{\text{lakewater}}$: Taking Vanda as an example, this lake has a deep salty layer which reaches upwards 13 m from the bottom (Fig. 3). Given the linear salinity gradient seen in this layer, the assumption of a constant ratio between U concentration and salinity, and a measurement of U concentration close to the bottom of this layer, indicates an average U concentration of 10.7 ppb. This equates to $^{238}\text{U}_{\text{lakewater}}$ of 0.06 μmol per cm^2 of lake floor.

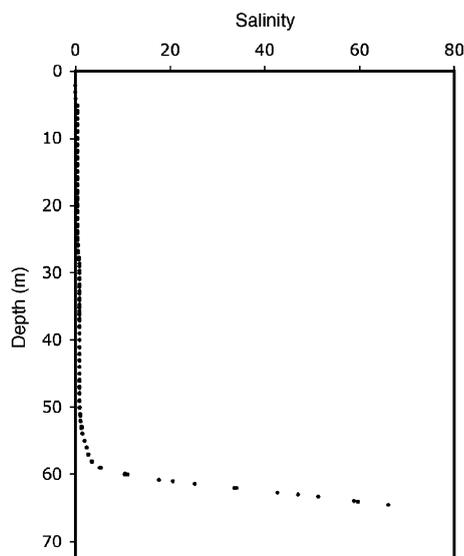


Fig. 3. The salinity profile for Lake Vanda as measured in 2002. Data taken from 8 CTD casts to various depths. The deepest cast extended to 73 m which is the deepest point of the lake (and is represented by the bottom of the figure) but salinity was off scale for the bottommost 9 m. Assuming a continuing linear increase in salinity to the bottom at the gradient observed from 60 to 68 m depth suggests a bottom salinity of 180, more than five times that of seawater.

f : is controlled by the size of the mineral grains in the sediment, the recoil distance, and the distribution of ^{238}U within the grains. In the simplest case of a uniform distribution, spherical grains, and ignoring re-implanting into adjacent grains it is given by $f=(r^3 - (r - \alpha)^3 / 4r^3)$ where r is the mean grain radius in the sediment (by mass), and α is the recoil distance (Henderson et al., 1999). The recoil distance in zircon is 0.055 μm , but is inversely related to density and is likely to be $\approx 0.080 \mu\text{m}$ in more typical crustal minerals. Average grain size of the sediments in Dry Valleys Lakes is around 30 μm (Sleewaegen et al., 2002). Assuming a minimum grain size of 10 μm provides a maximum value for f of 0.006 (i.e. only 0.6% of the ^{234}U is recoiled from the mineral grains).

Inserting these three values into Eq. (3) provides a maximum $(^{234}\text{U}/^{238}\text{U})$ of 1.8, a ^{234}U excess only one quarter that observed in the salty deep layer of Lake Vanda. An additional source of ^{234}U is therefore required. This is most likely to be derived from areas of the valley not presently under the lake. At times in the past both Lake Vanda and Lake Bonney were part of much larger lakes which covered large portions of the Wright Valley and Taylor Valley respectively. At these times, the total amount of U in the two lakes was probably not significantly different from that today, but the surface area of sediment from which the lake would accumulate recoil ^{234}U would have been approx-

ciably bigger. The unusually high ($^{234}\text{U}/^{238}\text{U}$) seen in these lakes probably reflects the average size of the lakes over several half lives of ^{234}U , rather than the present size of the lakes.

This explanation might also go some way towards explaining the very high ^4He concentrations observed in the western lobe of Lake Bonney (Poreda et al., 2004). Study of rare gases in the two lobes of Lake Bonney has demonstrated that the eastern lobe has been ice free recently, while the western lobe cannot have been ice free for at least the last 100,000 years (and probably longer) (Poreda et al., 2004). The water in this lobe must therefore have remained isolated from the atmosphere during reduction of lake size at the end of the glacial period. The addition of ^4He from a large area of Taylor Valley sediment could explain the very high observed ^4He values which, otherwise, require unusually rapid loss of He from the sediments underlying present Lake Bonney.

5.4. Implications for other lakes

Vanda and Bonney are closed lakes which have accumulated their salts over a long period. The process of ^{234}U addition that these lakes experience is nevertheless likely to operate in all lakes, even those with relatively short U residence times. For most lakes, the residence time of U is significantly shorter than the ≈ 1 Ma required for lakewater ($^{234}\text{U}/^{238}\text{U}$) to reach the equilibrium value (Eq. (3)). To assess the effect of recoil on lake ($^{234}\text{U}/^{238}\text{U}$) therefore requires consideration of the rate of increase of ($^{234}\text{U}/^{238}\text{U}$) caused by the constant addition of ^{234}U from the sediment, and the increasing ^{234}U decay. The evolution of ($^{234}\text{U}/^{238}\text{U}$) with time is given by (Henderson et al., 1999):

$$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_t = \left[\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_{\text{max}} - \left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_{\text{initial}} \right] \cdot (1 - e^{-\lambda t}) + \left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_{\text{initial}} \quad (4)$$

This equation indicates that lakewater ($^{234}\text{U}/^{238}\text{U}$) increases from an initial value (i.e. the value imparted on it from the combination of its U inputs) to the maximum value following an exponential trajectory, similar to that of a U-series system approaching secular equilibrium. Armed with an assessment of the maximum ($^{234}\text{U}/^{238}\text{U}$) for a lake (based, for instance, on the U content of the lake and the grain size and U concentration of the sediment) this equation can be used to assess the increase in ($^{234}\text{U}/^{238}\text{U}$) occurring as U

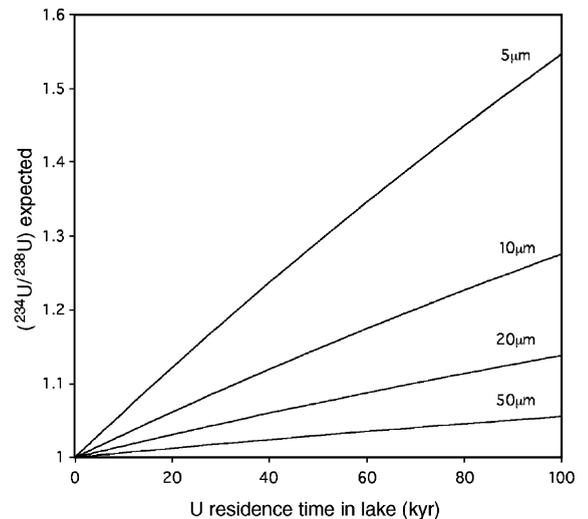


Fig. 4. Illustrative figure showing possible values of lakewater ($^{234}\text{U}/^{238}\text{U}$) with residence time of uranium. The rate of increase is controlled by the half life of ^{234}U , and by the maximum value of ($^{234}\text{U}/^{238}\text{U}$) expected for the lake in question (Eq. (3)). Calculated ($^{234}\text{U}/^{238}\text{U}$)_{max} in the figure above is based on an 8 m layer of sediment containing 2.4 ppm U, and a lake containing $10 \mu\text{g}/\text{cm}^2$ U (i.e. equivalent to 100 m water depth at 1 ppb U). Curves represent expected ($^{234}\text{U}/^{238}\text{U}$) for different average sediment grain sizes (assuming spherical grains). Although all the values used for these calculations will vary from lake to lake, the general conclusion is robust — lakes in which U resides for more than a few thousand years will experience a significant increase in ($^{234}\text{U}/^{238}\text{U}$) from addition of recoil ^{234}U .

resides in the lake. An example (Fig. 4) indicates that for U residence times of more than a few thousand years, the addition of recoil ^{234}U from sediments can cause a significant increase in lacustrine ($^{234}\text{U}/^{238}\text{U}$). Lake ($^{234}\text{U}/^{238}\text{U}$) is therefore a reflection of both the composition of U inputs to the lake, and of the residence time of U in the lake.

6. Conclusions

This study has assessed the controls on U concentration and, particularly, ($^{234}\text{U}/^{238}\text{U}$) of waters found in the Dry Valleys of Antarctica. This is a region without groundwater so the high ($^{234}\text{U}/^{238}\text{U}$) seen in some samples indicate that groundwaters are not required to cause large ^{234}U excesses in natural surface waters. ($^{234}\text{U}/^{238}\text{U}$) in glacial ice is identical to that in seawater, suggesting that sea-salt aerosol is the major source of U to ice in Antarctica. Streams in the Dry Valleys show ($^{234}\text{U}/^{238}\text{U}$) higher than seawater and similar to stream values elsewhere. This reflects the addition of recoil ^{234}U from sediments in the confined stream channels of the region. Lakewaters in which the U residence time is short have ($^{234}\text{U}/^{238}\text{U}$) which reflects

the sources of U. For one such lake (Joyce) the inputs have ($^{234}\text{U}/^{238}\text{U}$) significantly lower than seawater which might be explained by melting of old ice in which ^{234}U excess has partially decayed. In lakes where U has had a longer residence, ($^{234}\text{U}/^{238}\text{U}$) is significantly higher than the present lake inputs, ranging up to nearly five times the secular equilibrium value. These values can be explained by addition of recoil ^{234}U from sediments, but only if recoil from a large area of sediment is considered. This explains why the two lakes (Vanda, Bonney), which are relicts of much larger glacial lakes, are those to show the highest ($^{234}\text{U}/^{238}\text{U}$). The addition of recoil ^{234}U to lake water is expected to be a general feature, and to cause a noticeable increase in ($^{234}\text{U}/^{238}\text{U}$) for lakes with a U residence time of more than a few thousand years.

Acknowledgements

This paper is one in a series discussing ($^{234}\text{U}/^{238}\text{U}$) in Earth surface materials which start with those published while one of us (GMH) was a graduate student with Keith O’Nions. GMH thanks Keith for inspiration and guidance then, and in the years following. Also thanked are Nick Belshaw and Chris Atkinson for help in the lab; Ben Reynolds and Berry Lyons for helpful reviews; and Chris Hendry for provision of some of the waters analysed here. [SG]

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