## Noble Gas Radioisotope Constraints on Water Residence Time and Solvent Sources in Lake Bonney

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### THESIS

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### SUMMARY

A noble gas radionuclide analysis of perennially ice covered West Lake Bonney was performed in order to determine water residence time and ice cover timing. Bulk gas samples were collected at four depths in the lake. Krypton and argon gases were selectively isolated from the bulk gas and measurements of <sup>81</sup>Kr, <sup>85</sup>Kr and <sup>39</sup>Ar were made. Radiokrypton and radioargon analyses yielded lower limit ages of 78 to 285 years, significantly younger than expected based on previous dating efforts. It was determined that these new data do not invalidate previous work, but instead offer new insight into the timing of the most recent episode of direct communication between the atmosphere and West Lake Bonney waters.

# TABLE OF CONTENTS

INTRODUCTION1
SITE DESCRIPTION
HISTORY OF TAYLOR VALLEY LAKES
HOLOCENE LACUSTRINE HISTORY OF LAKE BONNEY8
SAMPLING AND ANALYTICAL9
DATA MODELING10
RESULTS
DISCUSSION
TOTAL ARGON MODEL
CONCLUSIONS17
REFERENCES:
APPENDIX: TOTAL ARGON MODEL R-STUDIO CODE23
VITA26

# LIST OF TABLES

TABLE	<u>PAGE</u>
I. PERCENT BULK GAS INVENTORIES (DRY BASIS) OF SAMPLES COLLECTED	) BY
EDGAR AND RELEVANT BULK GAS RATIOS	12
II. NOBLE GAS RADIONUCLIDE CONCENTRATIONS FOR WLB. RADIOKRYPT	'ON
CONCENTRATIONS MEASURED BY ATTA-3; <sup>39</sup> AR CONCENTRATIONS MEASURED	URED
BY LOW LEVEL COUNTING	15

# LIST OF FIGURES

<u>FIGURE</u> PAGE
1. MAP OF DRY VALLEYS REGION, ANARCTICA. (A) STAR INDICATES LOCATION
OF ROSS ISLAND AND THE DRY VALLEYS. (B) SATELLITE IMAGERY SHOWING
RELATIVE LOCATION OF TAYLOR VALLEY AND LAKE BONNEY TO ROSS
ISLAND. (C) SATELLITE IMAGERY OF LAKE BONNEY AND THE SIX
NEIGHBORING GLACIERS
2. MODELED TOTAL AR CONCENTRATIONS VERSUS AR CONCENTRATIONS
REPORTED IN POREDA ET AL. (2004) GENERATED USING A STEADY STATE BI-
DIRECTIONAL DIFFUSION MODEL WITH A FIXED CONCENTRATION FOR 10 M
DEPTH; D <sub>AR</sub> = 0.091 M2/YEAR, INITIAL CONDITIONS [AR] = ASW; BOTTOM FLUX
IS 0.350 CCSTP M <sup>-2</sup> YEAR <sup>-1</sup> . TIME REQUIRED TO REACH MODERN VALUES IS 63
YEARS
3. MEASURED <sup>85</sup> KR AND <sup>39</sup> AR AGE DEPTH PROFILES FOR WLB FROM TABLE 2.
DASHED LINES REPRESENT MEASUREMENTS GREATER THAN THE ADJACENT
<sup>85</sup> KR DATA POINTS
4. WLB DENSITY PROFILE GENERATED WITH DATA FROM 2011 CTD CASTS

### INTRODUCTION

Noble gas radionuclides can be used for determining water residence times in groundwater, lakes, oceans and glaciers, despite their extremely low atmospheric abundances (Loosli et al., 1989; Smethie et al., 1992; Collon et al., 2004; Sturchio et al., 2004; Corcho Alvarado et al., 2007; Jiang et al., 2012; Buizert et al., 2014). In lakes, the dominant source of these radionuclides is the atmosphere via dissolution at the air-water interface (Kipfer et al., 2002). The resultant radioisotope concentrations at depth are controlled by solubility equilibrium, turbulent and molecular diffusivities, radioactive decay, and addition from subsurface sources, and they can provide information about hydrologic history and water source mixing processes. Hydrologic changes in the Dry Valleys of Antarctica are a sensitive proxy for regional climate change, as minor climatic changes can have significant impacts on the lakes (Doran, 2002). The history of ice-covered, density-stratified West Lake Bonney, Taylor Valley, Antarctica is not well known, but determining the time of ice cover formation in this lake would provide a major constraint on its evolution. We explored a novel approach to understanding the paleolimnologic evolution of West Lake Bonney (WLB) by using measurements of the noble gas radionuclides  ${}^{81}$ Kr (t<sub>1/2</sub>=2.29x10<sup>5</sup> yr),  ${}^{39}$ Ar (t<sub>1/2</sub>=269 yr) and  ${}^{85}$ Kr (t<sub>1/2</sub>=10.76 yr) to constrain timing of the last episode of atmosphere-lake surface gas exchange.

Chlorine-36 and <sup>4</sup>He methods have been used to reconstruct the evolution of Lake Bonney with some difficulty, in part due to the unique physical and chemical properties of the lake (Lyons et al., 1998b; Poreda et al., 2004). The <sup>36</sup>Cl data produced model ages between 780 kya and 1.62 Mya and helium isotope analyses suggested that WLB has been an ice-covered water body for over 1 Ma (Lyons et al., 1998b; Poreda et al., 2004). We sought to test these earlier

interpretations with measurements of noble gas radionuclides. Noble gas radionuclides are ideal tracers as they are chemically inert and the sources are well known (Collon et al., 2004).

Krypton-81 is a cosmogenic radionuclide ( $t_{1/2}=229,000$  yr) that resides predominantly in the atmosphere as a natural product of proton- and neutron-induced spallation of <sup>82</sup>Kr, <sup>83</sup>Kr, <sup>84</sup>Kr and <sup>86</sup>Kr (Baglin, 1993). Three independent measurements of <sup>81</sup>Kr/Kr atmospheric abundance provided a mean ratio of  $5.2 \times 10^{-13}$  and indicate spatial homogeneity and a temporally constant initial isotopic abundance (Loosli and Oeschger, 1969; Kuzminov and Pomansky, 1983; Collon et al., 1997). The long half-life, well-known production processes, and chemically inert nature of <sup>81</sup>Kr make it an ideal isotope for dating water residence times between  $5 \times 10^4$  and  $2 \times 10^6$  years (Collon et al., 2004). Therefore, if WLB has had an ice cover for the past 0.8 to 1.6 Myr as suggested by previous studies, then exchange of Kr between the lake water and the atmosphere should have ceased at the time of formation of the ice cover, and the <sup>81</sup>Kr/Kr ratio in WLB water should have decayed for at least three or more <sup>81</sup>Kr half-lives (~720 kyr), i.e., to <1/8 that of the modern atmosphere.

Argon-39 is another cosmogenic radionuclide ( $t_{1/2}=269$  yr) produced primarily by cosmic-ray induced  ${}^{40}$ Ar(n,2n)<sup>39</sup>Ar reactions in the atmosphere (Stoenner RW et al., 1965). Argon is chemically inert, making  ${}^{39}$ Ar an ideal isotope for dating water residence times between about 50 and 1,000 years (Collon et al., 2004). Unlike  ${}^{81}$ Kr, however, there is a secondary terrestrial source for  ${}^{39}$ Ar though the reaction  ${}^{39}$ K(n,p) ${}^{39}$ Ar that can be substantial and can complicate dating efforts (Yokochi et al., 2012). The third noble gas radionuclide that we measured is  ${}^{85}$ Kr ( $t_{1/2}=10.76$  yr), which is produced naturally, by spallation of  ${}^{86}$ Kr and  ${}^{84}$ Kr, as well as anthropogenically as a fission product of nuclear fuel reprocessing (Meyer et al., 1980; Kutschera et al., 1994; Collon et al., 2004). Since the 1950s, atmospheric abundance of this isotope has increased by a factor of  $10^6$ , corresponding to a present atmospheric abundance  $^{85}$ Kr/Kr ratio of about  $2x10^{-11}$ , due to the use of nuclear technology (Collon et al., 2004). With its short half-life of ~11 years,  $^{85}$ Kr is an ideal isotope for dating water that has recently equilibrated with the atmosphere, and is useful for identifying atmospheric contamination in samples of much older waters (Collon et al., 2004).

#### SITE DESCRIPTION

Taylor Valley, Antarctica is one of three major valleys in the McMurdo Dry Valleys region of southern Victoria Land (76°30'-78°30' S, 160°-164° E) [Figure 1]. This region exhibits exceptional aridity with between 3 mm and 50 mm of precipitation annually (Fountain et al., 2010). Mean annual ice ablation rates between 64 and 99 cm render most of the surface free of snow and ice cover (Dugan et al., 2013). The dark sediments exposed at the surface of the valley reduce the albedo sufficiently to increase mean summer temperatures by 5-7° C and reduce mean winter temperatures by up to 5° C as compared to similar coastal regions (Chinn, 1993). Summer temperatures in Taylor Valley can approach 10°C; winter temperatures can be as low as -60°C and mean annual temperature is about -18°C (Doran, 2002). The dominant control on summer climate is solar radiation which is likely the reason that summer ablation is both highly variable and as much as an order of magnitude greater than winter ablation (Dugan et al., 2013). Winter climate variability is dominated by katabatic events lasting up to a few days and originating on the polar plateau. These events can increase temperatures by 30°C and decrease relative humidity by 30% over a period of 3 or more days with variable rates of change (Nylen, 2004).



Figure 1 - Map of Dry Valleys region, Anarctica. (A) Star indicates location of Ross Island and the Dry Valleys. (B) Satellite imagery showing relative location of Taylor Valley and Lake Bonney to Ross Island. (C) Satellite imagery of Lake Bonney and the six neighboring glaciers.

Taylor Valley, like other valleys in the region, was glacially carved and contains perennially icecovered lakes made up mostly of glacial meltwater. It contains three major lakes, the largest of which is Lake Bonney (elevation ~60 masl), having an area greater than 4 km<sup>2</sup> and a total length of 7.1 km (Chinn, 1993). Lake Bonney is divided into two lobes, East Lake Bonney (ELB) and West Lake Bonney (WLB), by a shallow (~18 m) sill. WLB is a 40 m deep, enclosed, closedbasin, stratified, partly hypersaline lake that maintains a perennial ice cover between 2.5 m and 5 m thick (Chinn, 1993). The west lobe of Lake Bonney receives significant annual input from eleven ephemeral streams and is occupied at one end by the tongue of Taylor Glacier, which contributes 42-90% of total annual input (Poreda et al., 2004). There is evidence that subglacial discharge also contributes to the hypolimnion of WLB (Doran unpublished data; Warrier et al., 2015). The unique combination of cold temperatures, resulting in limited melting of lake and glacial ice in summers, and extreme aridity, resulting in limited precipitation and high ablation rates, allow the Taylor Valley lakes to maintain a perennial ice cover (Chinn, 1993). In the austral summer, melting lake ice forms a moat around the lake perimeter that allows for limited exchange with the atmosphere, and allows a small amount of glacial meltwater to flow under the ice. Two important topographic highs exist in Taylor Valley. The first is the Nussbaum Riegel, a 200 m ridge that divides the valley into two segments referred to as upper and lower Taylor Valley. Lake Bonney resides in upper Taylor Valley. The second is Coral Ridge, a 100 m rise at the valley mouth near the Ross Sea. Taylor Valley soils maintain a permafrost layer between 300 and 600 m thickness (McGinnis and Jensen, 1971; Decker and Butcher, 1980). Groundwater input to the lakes of Taylor Valley is associated with the soil active layer, ground ice and snow melt input and is about four orders of magnitude smaller than glacial meltwater input (Levy et al., 2011). The water tracks and seeps associated with this input are a significant solute source for the lakes, however, and may exceed solute input from glacial streams despite their relatively minimal contribution to lake level (Levy et al., 2011). Five glaciers (Sollas, Hughes, Calkin, Matterhorn, Rhone and Taylor) feed meltwater into Lake Bonney.

#### HISTORY OF TAYLOR VALLEY LAKES

The first lakes in Taylor Valley may have originated as early as 4.66 Ma B.P. when the region emerged isostatically from the Ross Sea, trapping seawater in outlet glacier depressions, though no evidence for lakes dating to this time exists (Summerfield et al., 1999). The oldest direct evidence for lakes in West Antarctica are subglacial diatom assemblages that date to 2 Ma B.P. (Scherer, 1991). Little to no geologic evidence exists to interpret hydrologic changes from 2 Ma

until the onset of late Wisconsinan glaciations (~400 ka BP). From late Wisconsinan into the Holocene, relative warmth resulted in diminished aridity, increased inland precipitation, the expansion of Taylor Glacier eastward as far as the present position of Lake Fryxell, and the retreat of grounded ice sheets in the McMurdo Sound (Higgins et al., 2000a). The most recent occurrence of Taylor Glacier expansion is recorded in glacially derived algal carbonate clasts collectively known as the Bonney Drift which date to MIS stage 5 (69-134 ka B.P.) (Higgins et al., 2000b). Older reworked algal clasts in the Bonney Drift have been dated to MIS stage 7 (177-257 ka B.P.), MIS stage 9 (249-341 ka B.P.), MIS stage 11 and older (379 to >400 ka B.P.) providing substantial evidence for Taylor Glacier expansion during interglacial periods (Higgins et al., 2000b). During relatively cool periods, increased aridity led to the retreat of Taylor and other alpine glaciers and the westward expansion of grounded ice sheets from the McMurdo Sound into Taylor Valley. There are two competing interpretations of the magnitude of the most recent grounded ice sheet expansion, commonly known as Ross Sea I. The first interpretation describes Ross Sea I as expanding as far as the present position of Lake Fryxell (Higgins et al., 2000a). The second describes the expansion extending as far as the Nussbaum Riegel (Toner et al., 2013). In both cases, Ross Sea I dammed meltwater from local glaciers flooding inland Taylor Valley to about 300 masl and formed a Glacial Lake Washburn that either resided in both upper and lower Taylor Valley or just the Bonney Basin (Higgins et al., 2000a; Toner et al., 2013). Both interpretations agree, however, that Ross Sea I occurred between 8400 and 24000 <sup>14</sup>C years B.P.(Denton et al., 1989; Hall et al., 2000).

Chronology of the decline of Glacial Lake Washburn near the end of the Wisconsinan was described by Higgins et al. (2000b) based on <sup>14</sup>C dating of preserved algal mats in perched deltas and various lacustrine deposits. Vostok and Dome C ice core  $\delta^{18}$ O data suggest an abrupt

increase in precipitation around 15 kyr B.P. indicating a change in climate regime (Jouzel et al., 1987). This date agrees well with the estimated age of Ross Sea I maximum inland position of between 12.7 and 14.6 ka B.P. (Hall and Denton, 2000). This change in climate regime may have been the impetus for the renewed expansion of Taylor Glacier, retreat of the Ross Sea I lobe, and the elimination of a grounded ice sheet by 5370 <sup>14</sup>C yr B.P. (Hall and Denton, 2000). The subsequent draining of Glacial Lake Washburn reduced lake levels in upper Taylor Valley to the elevation of the Nussbaum Riegel and to Coral Ridge in lower Taylor Valley. Further lake level drawdown was driven by reduced meltwater input and evaporative processes (Wagner et al., 2006), and led to the formation of the modern glacial configuration known as Alpine I (Hall et al., 1993).

Toner et al. (2013) used evapoconcentrated salts and soil soluble salt content as proxies for stable paleolake levels, and ground penetrating radar (GPR) data to examine the internal structure of terraces along the valley walls which had been historically identified as deltas.

Evapoconcentration is the process by which leached salts along the margin of a water body are redistributed along the shoreline into the soil up to 30 m away from the water body by capillary forces (Barrett et al., 2009). This water later evaporates in the soil and, in this instance, leaves residual salts bound to the <2 mm soil fraction (Barrett et al., 2009; Toner et al., 2013). Toner et al. (2013) found that in the Bonney Basin, a marked decline in soluble salt content occurred at 300 m elevation and reasoned that this evidence, along with the confirmation of deltaic structures in terraces of Bonney Basin (Hall et al., 2000), demonstrated that the basin was leached of salt content by paleolakes up to 300 m elevation. At 116 m, the lower Nussbaum Riegel threshold, and 86 m elevations the study's highest recorded values for soil soluble salt content indicate that prolonged evapoconcentration occurred due to stable lake levels (Toner et al., 2013). Toner et

al. (2013) interpreted this to indicate that a glacially dammed lake with high stands between 116 m and 300 m elevation would be unstable due to historically large fluctuations in meltwater input and adjacent glacial movement and would not maintain a stationary level for enough time to develop a substantial evapoconcentration signature. The findings of Toner et al. (2013) generally agree with previous paleolake studies of Bonney Basin, but provide a new view of the scale of Lake Washburn. This soil salinity approach yielded an interpretation of paleolake activity in eastern Taylor Valley distinct from that of Hall et al. (2000). Only 20% of the terraces in eastern Taylor Valley analyzed by GPR have the characteristic foreset stratigraphy of deltas (Toner et al., 2013), some of which were used to provide paleolake ages by Hall and Denton (2000). Examination of soil revealed sharp increases in salt content at 120 m and 78 m due to evapoconcentration and little variation above 120 m, the upper limit of Fryxell Basin (Toner et al., 2013). Together with GPR data this indicates that paleolakes during the LGM did not likely exist in eastern Taylor Valley above 120 m, except during periods of drainage from the flooded Bonney Basin, and that Ross Sea I must have extended up valley to the Nussbaum Riegel leaving only the Bonney Basin flooded above 120 m (Toner et al., 2013).

### HOLOCENE LACUSTRINE HISTORY OF LAKE BONNEY

Holocene records of the Taylor Valley lakes indicate lake desiccation events that reduced lake level to below modern levels at ~1.2 kyr B.P. (Doran et al., 1999; Lyons et al., 1998a). In some cases, lakes may have either desiccated completely or, as Lake Bonney, into hyper-saline brine ponds. Lyons et al. (1998a) argue that ELB evaporated to near dry conditions during this period, but retained its salts. The oxygen and hydrogen isotopic compositions of WLB suggest that the dominant source of recharge following the Holocene desiccation event was Taylor Glacier meltwater, whereas the heavier isotopic concentrations in ELB suggest a dominantly atmospherically equilibrated source and more complete desiccation (Lyons et al., 1998a). These stable isotope data, along with supporting geochemical data, indicate that a desiccated ELB may have lost its ice cover during this time while WLB, supported by the freshwater input of Taylor Glacier, may have retained its ice cover throughout the Holocene (Lyons et al., 1998b).

Estimates of the duration of the present ice cover on Lake Bonney based on <sup>4</sup>He and <sup>36</sup>Cl abundances have been attempted with mixed results. The <sup>36</sup>Cl data produced bottom water model ages of 780 kya for ELB 1.62 Mya for WLB (Lyons et al., 1998b). The large variability in these two values may be due to a number of factors, including different Holocene histories (as described above), input from salt-rich Blood Falls or subglacial fluid sources linked to Blood Falls, or a combination of all of these (Lyons et al., 1998b). Helium isotope data were interpreted to indicate that WLB has been an ice-covered water body for over 1 Myr and ELB has been ice-covered for only 200±50 yr (Poreda et al., 2004). The flux of <sup>4</sup>He from WLB lake bottom sediments required to support the observed diffusion profile seemed anomalously high (Poreda et al., 2004). A radiocarbon history of Lake Bonney suggests that ELB has been ice covered for no less than 3000 years (Doran et al., 2014). The uncertainties inherent in the proxies used in these previous studies allowed a wide range of interpretation. Fortunately, noble gas radionuclides provide a tool by which previous interpretations based on other isotopic measurements can be tested and refined.

#### **METHODS**

#### SAMPLING AND ANALYTICAL

Dissolved gas samples were collected directly from WLB at 11.5, 21.5, 31.5 and 38 m depths using a field based gas-extraction system known as EDGAR (Extraction of Dissolved Gases for

the Analysis of Radiokrypton) (Probst et al., 2007). These depths yield a salinity profile including both recent freshwater and older saline and hypersaline waters. Large quantities of water (340 to 600 L per sample) were required to obtain sufficient amounts of the radionuclides intended for analysis. Lake water was pumped to the surface using a 12 VDC stainless steel Monsoon pump through 45 m of 0.95 cm ID tygon tubing lowered to sampling depths by a winch at the surface. Water was passed directly into the EDGAR apparatus to prevent gas loss or atmospheric contamination. The EDGAR system uses a hydrophobic semi-permeable membrane contactor (Liqui-Cel, Membrana Corp.) and a pressure gradient to extract dissolved gases through the membrane. Extracted gas was compressed into 5-lb. CO<sub>2</sub> cylinders. These were shipped to the University of Bern, Switzerland where bulk gas compositions were measured by quadrupole mass spectrometry and Kr and Ar were separated using cryogenic distillation, gas chromatography and Ti-gettering. Separated Kr fractions were returned to Argonne National Laboratory for analysis of noble gas radionuclides <sup>81</sup>Kr and <sup>85</sup>Kr by atom-trap trace analysis (ATTA-3) (Jiang et al., 2012). Argon-39 was measured by low-level decay counting at the University of Bern (Loosli, 1983).

### DATA MODELING

A steady-state diffusion transport model for total Ar was constructed in RStudio using total Ar concentration data and the Ar diffusion coefficient ( $D = 0.091 \text{ ccSTP m}^{-2} \text{ year}^{-1}$ ) from Poreda et al. (2004). The model operates between 10 m and 38 m depths in 1 m increments with yearly time steps and assumes that transport is purely Fickian. The total Ar model initial conditions include a steady-state upper boundary (10 m depth) concentration of 0.946 ccSTP L<sup>-1</sup> and initial subsurface concentrations equivalent to the 0°C air-saturated water (ASW) value of 0.4489 ccSTP L<sup>-1</sup>. To account for bottom flux of <sup>40</sup>Ar by radioactive decay of <sup>40</sup>K, we used an initial

approximation 25 percent of the reported He flux of  $1.4 \text{ cm}^3 \text{ m}^{-2} \text{ year}^{-1}$  from Poreda et al. (2004). Production of <sup>40</sup>Ar by decay of <sup>40</sup>K (t<sub>1/2</sub>=1.248 Ga) has been observed to be approximately 25 percent of <sup>4</sup>He production by the U- and Th-series in various crustal rock and sediment types (Andrews et al., 1989; Torgersen et al., 1989; Hiyagon and Kennedy, 1992; Lippmann et al., 2003; Yokochi et al., 2012). The model calculates 500 years of concentrations at all depths and a linear regression value for fit to the [Ar] profile reported in Poreda et al. (2004).

Depth		-		-				-
(m)	Vol. (L)	% Ar	% CH <sub>4</sub>	% N <sub>2</sub>	% CO <sub>2</sub>	% O <sub>2</sub>	N <sub>2</sub> /Ar	O <sub>2</sub> /Ar
11.55	340	1.907	0.0390	42.9	0.0711	55.0	22.5	28.8
21.5	600	0.528	0.0735	76.4	20.1	2.80	144	5.31
31.5	349	0.221	0.0583	66.9	27.6	5.13	301	23.1
38.5	371	0.228	0.0575	67.0	27.0	5.62	292	24.5

Table I. Percent bulk gas inventories (dry basis) of samples collected by EDGAR and relevant bulk gas ratios.

#### RESULTS

Bulk gas compositions of extracted dissolved gas samples are given in Table I. Trends in these samples are in accordance with the findings of Anderson et al. (1998), Poreda et al. (2004) and Warrier et al. (2015) with diminishing  $O_2$  and increasing  $CO_2$  with depth as well as ubiquitous supersaturation of  $N_2$  and Ar, decreasing generally with depth.



Figure 2 - Modeled total Ar concentrations versus Ar concentrations reported in Poreda et al. (2004) generated using a steady state bi-directional diffusion model with a fixed concentration for 10 m depth;  $D_{Ar} = 0.091 \text{ m}2/\text{year}$ , initial conditions [Ar] = ASW; bottom flux is 0.350 ccSTP m<sup>-2</sup> year<sup>-1</sup>. Time required to reach modern values is 63 years.

Measured <sup>81</sup>Kr, <sup>85</sup>Kr and <sup>39</sup>Ar abundances for WLB are reported in Table 2 along with model ages and air-saturated water (ASW) concentrations at 0°C for comparison to expected moatwater concentrations. Reported <sup>85</sup>Kr activities are given in dpm/ccSTP (decays per minute per cubic centimeter of Kr at 0 °C and 1 bar) where 100 dpm/cc corresponds to an isotopic abundance of <sup>85</sup>Kr/Kr =  $3.03 \times 10^{-11}$ . The sample from 11.5 m has a <sup>85</sup>Kr/Kr ratio of  $2.03 \times 10^{-12}$ , and deeper samples have <sup>85</sup>Kr concentrations below the detection limit of the measurement.. Reported values for <sup>39</sup>Ar indicate a range of mean water residence times between 0 and 285 years, significantly younger than any previous ice-cover time estimates reported for WLB. Logistical limitations on the volume of water sampled led to relatively small volumes of Ar being collected. As a result, measurement errors for <sup>39</sup>Ar are relatively large. The best-fit total Ar diffusion model output required 63 years to reach modern conditions from model initial conditions and can be viewed in Figure 2 in comparison with the Ar concentrations reported by Poreda et al. (2004).



Figure 3 - Measured <sup>85</sup>Kr and <sup>39</sup>Ar age depth profiles for WLB from Table 2. Dashed lines represent measurements greater than the adjacent <sup>85</sup>Kr data points.

### DISCUSSION

The <sup>81</sup>Kr/Kr ratios of the 21.5, 31.5 and 38 m samples are equal to modern atmosphere within analytical error, which precludes the aforementioned very old ice-cover formation times postulated by Lyons et al. (1998) and Poreda et al. (2004) [Table 2]. The <sup>85</sup>Kr/Kr ratios observed at all depths indicate that samples are uncontaminated with modern air, assuming that the <sup>85</sup>Kr/Kr ratio in the sample from 11.5 m is representative of dissolved Kr at that depth [Table II].

The measured <sup>39</sup>Ar and <sup>81</sup>Kr activities indicate that either: (1) efficient vertical mixing is occurring in the water column; (2) atmospheric <sup>39</sup>Ar and <sup>81</sup>Kr are being introduced to the water column from a process other than by exchange of gas with atmosphere at the lake surface; (3) the diffusion gradients for <sup>39</sup>Ar and <sup>81</sup>Kr are sufficiently large to transport <sup>39</sup>Ar and <sup>81</sup>Kr rapidly to WLB bottom waters from the lake surface; or some combination of these three possibilities.

Table II. Noble gas radionuclide concentrations for WLB. Radiokrypton concentrations measured by ATTA-3; <sup>39</sup>Ar concentrations measured by Low level counting.

Depth	<sup>81</sup> Kr	<sup>81</sup> Kr <sub>age</sub>	<sup>85</sup> Kr	<sup>85</sup> Kr <sub>age</sub>	<sup>39</sup> Ar	<sup>39</sup> Ar <sub>age</sub>
(m)	sample/air	(ka)	(dpm/cc)	(years)	(% mod.)	(years)
11.5	NA	NA	6.30±0.62	40.0±0.11	92±13	32±55
21.5	0.99±0.05	3.32±17	<0.27	>88.9	96±12	16±44
31.5	$1.08\pm0.05$	0±17	<0.71	>73.9	48±24	285±194
38	1.02±0.05	0±17	<0.70	>74.1	73±25	122±133

It is highly unlikely that significant vertical mixing is occurring across the chemocline in WLB due to the strong density stratification observed there, though this does not prevent eddy diffusion processes from occurring in the epilimnion in response to summer moat formation at the ice cover margin, which may introduce fresh water to the lake, as well as by freezing-induced density inversion as ice is added to the base of the ice cover and increases salinity of the residual water at the ice-water interface [Figure 3]. A secondary source for atmospheric <sup>81</sup>Kr would require a surface source directly supplying WLB deep waters for which no mechanism is known.

A possible subsurface source of <sup>39</sup>Ar is the subglacial brine beneath adjacent Taylor Glacier. The production rates and transport of <sup>39</sup>Ar would need to be unreasonably high, however, to support our measurements. Ar model results indicate that diffusion gradients are sufficient to support the presence of young <sup>39</sup>Ar in WLB deep waters. The diffusion model results are used to examine diffusion transport and mixing characteristics in WLB as they relate to measured <sup>39</sup>Ar and <sup>81</sup>Kr.



Figure 4 - WLB density profile generated with data from 2011 CTD casts.

#### TOTAL ARGON MODEL

Two important assumptions were necessary in the construction of the total Ar model. Subsurface input of  ${}^{40}$ Ar was estimated based on the known  ${}^{4}$ He input rate (based on Poreda et al., 2004) and the Ar model's initial conditions which assumed a total Ar concentration equivalent to that of air-saturated water at 0 °C. These assumptions, while reasonable, led to an unexpected result of only ~78 years have elapsed since WLB was actively exchanging gases with the atmosphere

(i.e., exchange ceased around calendar year 1937). Doran et al. (2014) used radiocarbon dating to infer that until 200 years ago the WLB epilimnion flowed from WLB to ELB over a shallow sill that allowed for exchange with the atmosphere. Poreda et al. (2004) agreed that by 200 years ago ELB lake level had risen sufficiently to allow for a continuous ice cover across both lobes. Our total Ar diffusion model result indicates that exchange of dissolved gases with the atmosphere, possibly across the shallow sill, may have occurred until as early as about 63 years before the date of sampling (1999-2000 austral summer field season). Disparity between the results of this model and the results of Doran et al. (2014) and Poreda et al. (2004) could be the result of historic seasonal melt over the sill. At the time of the first recorded observation of Lake Bonney (Discovery Expedition, 1903) the depth of the sill was less than 1 m below the ice surface (Spigel and Priscu, 1998). Modern summer ablation at this location is on average >0.8 m (Dugan et al., 2013). With a sill at this depth it is very reasonable that seasonal melt would have been sufficient to allow for atmosphere-lake surface exchange of dissolved Ar flowing to ELB until very recently. The ventilation process would be aided by turbulent mixing in the WLB epilimnion. Additional support for recent ventilation can be seen in the cryo-concentration of <sup>39</sup>Ar. Cryo-concentration concentrates the heavy noble gases (Ar, Kr, and Xe) in the lake water by exclusion during ice formation. The fraction of Ar exclusion during ice formation is 45 percent (Top, 1988). If a static ice thickness is considered for WLB, annual ice growth for WLB is on average 0.64 m (Dugan et al., 2013). This suggests that cryo-concentration should increase surface water concentrations of  ${}^{39}$ Ar by  $1.04 \times 10^{-16}$  ccSTP L<sup>-1</sup> year<sup>-1</sup> and that cryo-concentration of dissolved Ar is likely to be a major contributor to high surface water concentrations. The time required for cryo-concentration of <sup>39</sup>Ar to increase surface concentrations from ASW (0 °C) to

current values is ~75 years by the aforementioned factor, which agrees well with the time required for total Ar to reach modern conditions from ASW.

#### CONCLUSIONS

Noble gas radionuclides <sup>81</sup>Kr, <sup>85</sup>Kr and <sup>39</sup>Ar were measured in the perennially ice covered West Lake Bonney. The results of these radionuclide analyses indicate surprisingly young ventilation times for the lake water. The total Ar diffusion model allows the possibility that WLB had been exchanging gas with the atmosphere as little as 78 years B.P., which is consistent with the noble gas radionuclide results. While the origins of WLB remain ancient, modern WLB has been in direct communication with the atmosphere more recently than previously thought. With a more precise <sup>39</sup>Ar analysis of WLB and a complimentary analysis of ELB a more precise estimate of the timing of ice-cover formation of these two lobes would be possible.

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## APPENDIX: TOTAL ARGON MODEL R-STUDIO CODE

WLB\_Ar\_Bi<-function(){

ArSurf<-0.946/.001

ArASW<-(.4489/.001)

ArBottom<-0.5/.001

BottomFlux<-0.350

D<-.091

Depths <-c(10:38)

Concs<-integer(length=(length(Depths)))

Output<-data.frame(Depths)

Concs[1]<-ArSurf

Concs[2:length(Depths)]<-ArASW

Years<-0

R<-integer(length=(length(Depths)))

SSResSum<-0

SSTot<-integer(length=(length(Depths)))

SSRes<-integer(length=(length(Depths)))

yi<-read.csv(file="linearfit.csv")

yimean<-mean(yi[,1])</pre>

repeat{

Concs[length(Depths)]<-Concs[length(Depths)]+BottomFlux

```
for(i in 2:(length(Concs))){
```

```
if(i<length(Concs)){
```

```
Concs[i] <-Concs[i] + ((-D)^*((Concs[length(Depths)]-Concs[i])/(Depths[i]-Depths[length(Depths)])))
```

}

```
Concs[i] {<} {-} Concs[i] {+} (({-}D)^*((Concs[1] {-} Concs[i])/(Depths[1] {-} Depths[i])))
```

}

```
Years<-Years+1
```

```
for(i in 1:(length(Concs))){
    SSRes[i]<-(((Concs[i])-yi[i,])^2)
}
for(i in 1:(length(Concs))){
    SSTot[i]<-((yi[i,]-yimean)^2)
}</pre>
```

```
SSTotSum<-sum(SSTot)
SSResSum<-sum(SSRes)
```

```
R[Years+1] < -abs((1-(SSResSum/SSTotSum)))
```

```
Output[Years+1]<-Concs/1000
```

```
if(Years = 500){break}
```

}

write.csv(Output,file="WLB\_Ar\_Poreda.csv")
write.csv(R,file="WLB\_Ar\_Poreda\_Fit.csv")
}

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- Bachelor of Science, Earth and Environmental Science, University of Illinois at Chicago, Chicago, IL; May 2012
- Triton Community College, River Grove, IL; 2005-2007

# Grant Awards:

- Geological Society of America Research Grant \$2500; 2013
- Knourek Scholarship \$2000; 2013

## Teaching Experience:

• Hydrology/Hydrogeology – TA; 2013

## Software Experience:

- RStudio Developed a steady state diffusion model for noble gas stable and radioisotopes.
- Matlab Produced long-term trend analyses on 20+ years of meteorological data for the MCMLTER.
- LabVIEW Developed a solenoid valve control system for a pressure swing adsorption instrument.
- ArcGIS 10.1 Performed analysis of regional data sets for visual interpretation.