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Geochimica et Cosmochimica Acta 98 (2012) 19–30
Geochimica et Cosmochimica Acta
www.elsevier.com/locate/gca

# Perchlorate and chlorate biogeochemistry in ice-covered lakes of the McMurdo Dry Valleys, Antarctica

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Received 15 February 2012; accepted in revised form 5 September 2012; available online 19 September 2012

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## Abstract

We measured chlorate ($ClO_3^-$) and perchlorate ($ClO_4^-$) concentrations in ice covered lakes of the McMurdo Dry Valleys (MDVs) of Antarctica, to evaluate their role in the ecology and geochemical evolution of the lakes. $ClO_3^-$ and $ClO_4^-$ are present throughout the MDV Lakes, streams, and other surface water bodies. $ClO_3^-$ and $ClO_4^-$ originate in the atmosphere and are transported to the lakes by surface inflow of glacier melt that has been differentially impacted by interaction with soils and aeolian matter. Concentrations of $ClO_3^-$ and $ClO_4^-$ in the lakes and between lakes vary based on both total evaporative concentration, as well as biological activity within each lake. All of the lakes except the East lobe of Lake Bonney support biological reduction of $ClO_3^-$ and $ClO_4^-$ either in the anoxic bottom waters or sediment. The younger less saline lakes (Miers and Hoare), have surface $ClO_3^-$ and $ClO_4^-$ concentrations, and ratios of $ClO_3^-/Cl^-$ and $ClO_4^-/Cl^-$, similar to source streams, while Lake Fryxell has concentrations similar to input streams but much lower $ClO_3^-/Cl^-$ and $ClO_4^-/Cl^-$ ratios, reflecting the influence of a large $Cl^-$ source in bottom sediments. $ClO_3^-$ and $ClO_4^-$ in Lake Bonney are the highest of all the lakes reflecting the lake's greater age and higher concentration of $Cl^-$. $ClO_4^-$ appears to be stable in the East Lobe and its concentration is highly correlated with $Cl^-$ concentration suggesting that some $ClO_4^-$ at depth is a remnant of the initial seawater that formed Lake Bonney. $ClO_3^-$ and $ClO_4^-$ concentrations provide a simple and sensitive means to evaluate microbial activity in these lakes due to their relatively low concentrations and lack of biological sources, unlike $NO_3^-$, $NO_2^-$, and $SO_4^{-2}$.

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## 1. INTRODUCTION

Ice-covered lakes are the main sites for biological activity in the McMurdo Dry Valleys (MDVs) of Antarctica, and represent one of the most pristine aquatic ecosystems on Earth. These lakes have been extensively studied in relation to their physical structure, ecology, and biogeochemistry (e.g. Green and Lyons, 2009 and references therein). Most of the ice-covered lakes in the MDV contain both oxic and anoxic zones within the water column, although several lakes are oxic throughout. Lake water temperatures are always close to 0 °C, and the water columns are characterized by relatively low biological productivity. In all cases, the lakes are perennially ice-covered, which influences all physical, chemical, and biological processes. The deep waters of the east lobe of Lake Bonney rank among the most saline aqueous environments on our planet with very limited or no microbial activity, while other lakes contain essentially fresh water and support diverse and widespread

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http://dx.doi.org/10.1016/j.gca.2012.09.014

photosynthetic microbial mats, as well as chemolithotrophic and heterotrophic processes such as nitrification, sulfur oxidation, denitrification, and sulfate reduction (Voytek et al., 1999; Green and Lyons, 2009).

Many major and trace element geochemical and biogeochemical processes have been evaluated in these lakes (e.g. Lee et al., 2004), but no information is available concerning the occurrence, distribution and fate of $ClO_3^-$ and $ClO_4^-$. These two oxyhalides are produced in the atmosphere by $O_3$ and possibly UV mediated oxidation reactions (Kang et al., 2006, 2009; Rao et al., 2010a), and are ubiquitously transferred to the surface through dry and wet deposition (Rajagopalan et al., 2009), where they are available as alternate electron acceptors to support a variety of microbial metabolisms (Coates and Achenbach, 2004, 2006). As such, the biogeochemistry of chlorine oxy-anions ($ClO_x$) in the MDV may provide clues regarding microbial activity and the chemical evolution of soils and lake water. Understanding the environmental limits of $ClO_x$ metabolism is also especially important given the discovery of $ClO_4^-$ on Mars (Hecht et al., 2009).

Natural $ClO_4^-$ has been known to occur at near parts per hundred levels in the Atacama Desert for well over a hundred years (Ericksen, 1981), but up until the recent decade no information was available concerning its worldwide distribution, production, or fate in the environment. Due to the recent interest in $ClO_4^-$ as an anthropogenic contaminant, there is now a much better understanding of these issues (e.g. Jackson et al., 2010). Based on stable isotope ratios of O in $ClO_4^-$, it appears that $ClO_4^-$ has at least two atmospheric production pathways: $O_3$ mediated oxidation of Cl species and possibly photo-oxidation of oxy-chlorine compounds (Bao and Gu, 2004; Bohlke et al., 2005; Jackson et al., 2010). $ClO_4^-$ occurs ubiquitously throughout the world, and it tends to accumulate in arid areas including the MDV (Kounaves et al., 2010; Rajagopalan et al., 2009; Ericksen, 1981; Jackson et al., 2010). Preferential accumulation in arid areas is due to limited liquid water and the generally oxic conditions, which prevent the infiltration into the soil and reduction of $ClO_4^-$ by bacteria capable of using it as an electron acceptor under anoxic conditions. During microbial reduction, $ClO_4^-$ is sequentially reduced through $ClO_3^-$ to $ClO_2^-$, which is then disproportionated by chlorite dismutase to produce $O_2$ and $Cl^-$ ($ClO_4^- \rightarrow ClO_3^- \rightarrow ClO_2^- \rightarrow Cl^- + O_2$). The oxygen is consumed within the $ClO_4^-$ reducing bacterial cell. (Per)chlorate reducing organisms are facultatively anaerobic or micro-aerophilic and can utilize a broad range of electron donors including hydrogen, organic matter, ferrous iron, and hydrogen sulfide and have been isolated from a wide range of natural environments (Coates and Achenbach, 2004, 2006). $ClO_4^-$ is very soluble and in oxic environments highly conserved and is not transformed by known abiotic processes under relevant environmental conditions. In this sense it is somewhat similar to $NO_3^-$, with the important exception that $NO_3^-$ can be produced *in situ* by nitrification and is readily taken up by organisms as an N source.

Natural $ClO_3^-$ is even less studied than $ClO_4^-$ mainly due to the difficulty in the analysis of environmental samples as a result of their relatively low concentrations, and has not been previously reported in Antarctica. New techniques for the measurement of $ClO_3^-$ have shown that it has a similar distribution to $ClO_4^-$ (Rao et al., 2010b). In addition, mechanisms proposed for $ClO_4^-$ production generally include simultaneous production of $ClO_3^-$. Laboratory experiments evaluating $ClO_4^-$ production from oxidation of $Cl^-$ and less oxygenated oxychlorine compounds (HOCl, $ClO_2^-$, $ClO_2$) by $O_3$ and UV all produce $ClO_3^-$ generally in excess of $ClO_4^-$ (Rao et al., 2010a,b; Kang et al., 2006, 2009). It also can be biologically reduced under anoxic conditions as all known organisms capable of $ClO_4^-$ reduction can also reduce $ClO_3^-$. In addition, $ClO_3^-$, but not $ClO_4^-$, can be transformed by nitrate respiring organisms through nitrate reductase enzymes (de groot and Stouthamer, 1969; Roldan et al., 1994).

The purpose of this study was to measure $ClO_4^-$ and $ClO_3^-$ levels in ice-covered lakes of the MDV, and to evaluate whether these species were being reduced by bacteria capable of (per)chlorate reduction. Results are discussed with regard to the ecology, chemical evolution, and history of lakes in the MDV.

## 2. METHODS

$ClO_4^-$, $ClO_3^-$, $NO_3^-$, $SO_4^{-2}$, and $Cl^-$ concentrations were measured for samples from a number of surface water bodies (e.g. streams, creeks, ponds; see Table 1) and 4 ice-covered lakes within the MDV: Lake Bonney (East and West Lobe), Lake Hoare, and Lake Fryxell in Taylor Valley and Lake Miers in the Miers Valley. All samples were obtained from the Long Term Ecological Research group (LTER) using techniques previously outlined (http://www.lternet.edu/sites/mcm/). Samples were collected in either December of 2008 (Lake Fryxell and Miers) or 2009 (Lake Hoare and Bonney). Samples were filtered (GF/F filter) within 6–8 h of collection and stored frozen.

### 2.1. Analysis

Major anions ($Cl^-$, $NO_3^-$, and $SO_4^{2-}$) were analyzed by ion chromatography following EPA Method 300.0 (Pfaff, 1993). Anion concentration distribution within the lakes is well documented but was evaluated here to demonstrate consistency with past efforts and to evaluate $ClO_4^-$ and $ClO_3^-$ concentrations with respect to other anions on a consistent set of samples. $ClO_4^-$ and $ClO_3^-$ concentrations were separately measured by sequential ion chromatography-mass spectroscopy–mass spectroscopy (IC-MS/MS) following the method detailed in Rao et al. (2007); Rao et al. (2010b). $ClO_4^-$ and $ClO_3^-$ were quantified using a Dionex LC 20 ion chromatography system consisting of GP50 pump, CD25 conductivity detector, AS40 automated sampler and Dionex IonPac AS16 (250 × 2 mm) analytical column. The IC system was coupled with an Applied Biosystems – MDS SCIEX API 2000™ triple quadrupole mass spectrometer equipped with a Turbo-IonSpray™ source. A hydroxide (NaOH) eluent at 0.3 mL $min^{-1}$ was followed by 90% acetonitrile (0.3 mL $min^{-1}$) as a post-column solvent. To overcome matrix effects, all samples were spiked with $Cl^{18}O_3$ (produced in house) or $Cl^{18}O_4$ (Dionex) internal

Table 1
$ClO_3^-$, $ClO_4^-$, $Cl^-$ and $SO_4^{-2}$ concentrations in surface waters of the Dry Valleys.

| Valley | Basin | Water boy | Date | $ClO_4^-$ | $ClO_3^-$ | $Cl^-$ | $SO_4^{-2}$ |
|---|---|---|---|---|---|---|---|
| | | | | μg/L | | mg/L | |
| Taylor Valley | E. Bonney | Priscu | 12/2009 | 0.07 | 0.20 | 10.7 | 5.4 |
| | | Priscu | 12/2008 | 0.15 | 0.35 | 9.8 | 6.3 |
| | | Priscu | 01/2009 | 0.47 | 0.47 | 43.0 | 11.3 |
| | W. Bonney | Lawson | 01/2009 | 0.14 | 0.18 | 8.22 | 5.4 |
| | | Lawson | 12/2008 | 0.25 | 0.17 | 5.7 | 3.6 |
| | | Lawson | 12/2009 | 0.18 | 0.25 | 4.9 | 3.5 |
| | | Blood Falls | 12/2008 | <0.05 | <0.05 | | |
| | Fryxell | Aiken | 12/2009 | 0.18 | 0.21 | 12.8 | 3.6 |
| | | Aiken | 12/2009 | 0.12 | <0.1 | 7.1 | 3.2 |
| | | Canada | 01/2009 | 0.06 | 0.55 | 2.4 | 2.4 |
| | | Canada | 12/2009 | 0.09 | <0.1 | 2.2 | 3.3 |
| | | Canada | 01/2010 | 0.06 | 0.25 | 1.7 | 2.2 |
| | | Canada | 12/2008 | 0.13 | 0.11 | 4.0 | 3.9 |
| | | Common Wealth[a] | 12/2008 | 0.10 | 0.21 | 4.7 | 2.2 |
| | | Crescent | 12/2008 | 0.51 | 0.48 | 14.1 | 6.6 |
| | | Delta | 01/2009 | 0.34 | 0.25 | 9.1 | 6.0 |
| | | Delta | 01/2010 | 0.16 | 0.11 | 15.4 | 6.8 |
| | | Delta | 12/2008 | 0.19 | 0.22 | 18.9 | 6.4 |
| | | Fryxell Pond | 01/2010 | 0.13 | 0.48 | 8.4 | 3.3 |
| | | Green | 01/2009 | <0.05 | <0.05 | 4.0 | 0.6 |
| | | Green | 01/2010 | 0.09 | 0.35 | 1.4 | 0.7 |
| | | Green | 12/2008 | 0.06 | <0.1 | 2.3 | 0.9 |
| | | Green | 01/2009 | 0.05 | 0.15 | 2.7 | 0.9 |
| | | Harnish | 01/2009 | 0.7 | 0.22 | 13.7 | 7.8 |
| | | Howard Pond | 01/2010 | 0.11 | 0.20 | 8.0 | 3.9 |
| | | Huey | 01/2009 | 0.21 | 0.26 | 10.3 | 12.3 |
| | | Huey | 12/2008 | 0.43 | 0.43 | 10.3 | 12.1 |
| | | Lost Seal | 12/2008 | 0.18 | 0.07 | 12.6 | 5.4 |
| | | Lost Seal | 01/2010 | 0.07 | <0.1 | 7.9 | 3.6 |
| | | Lost Seal | 12/2008 | 0.51 | 0.24 | 12.7 | 5.9 |
| | | Von Guerard | 01/2009 | 0.16 | 0.05 | 6.1 | 3.2 |
| | | Von Guerard | 12/2008 | 0.49 | <0.1 | 6.8 | 3.8 |
| | | Von Guerard | 01/2010 | 0.01 | <0.1 | 61.7 | 13.7 |
| | Hoare | Andersen | 12/2008 | 0.1 | <0.05 | 2.8 | 3.8 |
| | | Andersen | 12/2009 | 0.09 | <0.1 | 1.9 | 2.2 |
| | | Andersen | 12/2008 | 0.07 | <0.1 | 3.1 | 5.4 |
| | | Andersen | 12/2008 | 0.18 | 0.17 | 14.2 | 11.1 |
| | | House | 12/2008 | 0.10 | <0.05 | 3.1 | 2.7 |
| | | House | 12/2008 | 0.13 | 0.11 | 3.6 | 3.5 |
| | | House | 12/2008 | 0.09 | 0.21 | 6.6 | 3.1 |
| | | House | 12/2009 | 0.08 | <0.1 | 2.4 | 2.3 |
| | | Wharton | 12/2009 | 0.11 | <0.1 | 2.0 | 1.6 |
| | | Parera Pond | 01/2010 | 8.1 | 15.5 | 1300 | 198 |
| Wright | Vanda | Onyx | 12/2009 | 0.08 | 0.39 | 5.2 | 2.5 |
| | | Onyx | 11/2009 | 0.13 | 0.16 | 6.8 | 3.4 |
| | | Onyx | 01/2009 | 0.08 | 0.43 | 4.9 | 2.6 |
| | | Onyx | 01/2009 | 0.13 | 0.28 | 8.0 | 4.8 |
| | | Onyx | 12/2008 | 0.06 | <0.1 | 8.9 | 2.7 |
| | | Onyx | 12/2008 | 0.20 | 0.34 | 7.9 | 5.1 |
| | | Onyx | 01/2010 | 0.17 | 0.18 | 5.9 | 3.9 |

[a] Common Wealth stream does not feed Lake Fryxell but Common Wealth Glacier, it source, does provide inflow to Lake Fryxell and so it was grouped in this basin.

standards. The MDL was 2 ng/L for both $ClO_3^-$ and $ClO_4^-$, while the MRL for these samples was 50 ng/L. Samples were analyzed in batches of 8 including an analytical duplicate and spike. The errors in duplicate samples were less than ±10% and the spike recoveries were between 90% and 110 %. Samples with elevated $Cl^-$ (>10,000 mg/L) or $SO_4^-$ (>1000 mg/L) were either diluted prior to analysis or in some cases pre-cleaned using On-Guard™ II Ag or Ba cartridges (Dionex).

### 2.2. Modeling

Two simple models were used to evaluate $ClO_4^-$, $ClO_3^-$, and $SO_4^{-2}$ concentrations relative to the conserved species

$Cl^-$ in order to establish if non-transport related processes (e.g. bacterial reduction and evapoconcentration) were affecting the distribution of these species with depth in the water column. For Lakes Hoare, Miers, and Fryxell, for which the source of salts in the lakes is glacier and snow melt augmented by chemical weathering and possibly input of relic seawater for the hypolimnion of Lake Fryxell (Lyons et al., 1998, 2000), we assumed that in the absence of sinks all anions should increase in concentration proportional to $Cl^-$. For each species we calculated the mass ratio with respect to $Cl^-$ (e.g. $ClO_4^-/Cl^-$) at the depth closest to the bottom of the lake ice. This ratio was then multiplied by the $Cl^-$ concentration at lower depths to determine the expected concentration of each species as shown below.

$$C_{Dx} = C_{Ds}/Cl^-_{Ds} \text{ X } Cl^-_{Dx}$$

where $C_{Dx}$ and $C_{Ds}$ are the concentration of $ClO_4^-$, $ClO_3^-$, or $SO_4^{-2}$ at depth X and the surface, respectively; and $Cl^-_{Ds}$ and $Cl^-_{Dx}$ are the concentrations of $Cl^-$ at depth X and the surface, respectively. For Lake Bonney, for which the salts are attributed to both surface inflow and relic seawater (Lyons et al., 2005), we used a simple two component mixing model. We calculated the mixing ratio of surface and water from 35 m (deepest depth) to produce the observed $Cl^-$ profile using a simple mass balance.

$$Cl^-_{Dx} = f^s_{Dx}Cl^-_{Ds} + f^{35}_{Dx}Cl^-_{35}$$

where $f^s_{Dx}$ and $f^{35}_{Dx}$ are the fraction of surface water and water at 35 m respectively at any depth $D_x$, $Cl^-_{35}$ is the concentration at 35 m and all other variables are previously defined. The values of $f^s_{Dx}$ and $f^{35}_{Dx}$ determined for each depth using $Cl^-$ were then used to calculate the concentration of $ClO_4^-$, $ClO_3^-$, or $SO_4^{-2}$ using the same mass balance but substituting the concentrations of each species for $Cl^-$ at the surface and at 35 m to predict the concentration at intermediate depths. Modeled results are only used to highlight processes impacting oxyanions relative to $Cl^-$. The modeled concentrations are plotted as dashed lines on the figures presenting the concentration distribution with depth for each Lake.

## 3. RESULTS AND DISCUSSION

### 3.1. Surface waters in Wright and Taylor Valley

The permanently ice-covered lakes in the MDV are supplied by glacial melt and include streams, creeks, and the Onyx River that feed various lakes as well as ponds (Fig. 1). $ClO_4^-$ concentrations in a subset of these water bodies ranged from 0.05–8.1 μg/L but were generally less than 0.5 (45/49 samples) with an overall average of 0.19 μg/L excluding one outlier (Parera Pond) (Table 1). Of the samples that exceeded 0.5 μg/L all but one (Parera Pond) were in streams that feed Fryxell Lake. Only two samples (Green Creek and Blood Falls) were below the detection limit (0.05 μg/L). In most cases, we report concentrations for multiple samples from the same water body, taken at either different dates and/or different locations. In these instances, concentrations are generally within a factor of 2 of each other. Most $ClO_3^-$ and $ClO_4^-$ concentrations in surface waters of the MDV are higher than those reported for wet precipitation from North America (average = 0.014 μg/L) (Rajagopalan et al., 2009) or in ice cores from Wyoming (0.0002 < to 0.009 μg/L), Yukon Territory (0.0002 < to 0.002 μg/L), and the Devon Ice Cap (0.001–0.015 μg/L) (Furdui and Tomassini, 2010; Rao et al., 2012). The higher concentrations in the MDV surface water are not surprising given that they include both dry and wet deposition from glacier melt, which may have experienced evapo-concentration due to ice sublimation as well as input from dissolution of salts from the surrounding catchment. $ClO_3^-$ concentrations in the non-lake surface water bodies were similar to $ClO_4^-$ with concentrations ranging from <0.05 to 15.5 μg/L and an overall average excluding Goldman Pond of 0.25 μg/L (Table 1). Little information is available concerning $ClO_3^-$ in the environment but ratios of $ClO_3^-/ClO_4^-$ in North American precipitation and evaporites from the Mojave, Atacama and Namibia Deserts generally plot close to a 1:1 (W/W) ratio line (Rao et al., 2010b) and ice core samples from the Devon Island Ice Cap have an average ratio (W/W) of 3.8 ± 2.9 (Furdui and Tomassini, 2010). Samples from Taylor and Wright Valleys have an average ratio (W/W) of 1.7 ± 1.1 similar to other reported samples.

### 3.2. Ice-covered lakes in Taylor and Miers Valley

#### *3.2.1. Lake Hoare*

Lake Hoare is a fresh water lake ponded by the Canada Glacier (Fig. 1). The lake water is relatively young ~1000–2500 year and the source of $Cl^-$ and other salts is attributed to snow and glacial melt, as well as weathering of minerals and dissolution of dust on melting glaciers (Lyons et al., 1998, 2005; Voytek et al., 1999). The lake is uniformly oxic (~20 mg $O_2$/l) to a depth of ~17 m at which point oxygen sharply decreases to near 0 at the sediment interface (Clocksin et al., 2007). There is a chlorophyll-a peak at 15 m and $NO_3^-$ is below detection (<0.5 μg N/l) above 15 m and increases due to nitrification below 15 m reaching a maximum of ~112 μg N/l (Voytek et al., 1999). Microbial analysis indicates that nitrifiers are present at all depths and of the eight isolates obtained all were obligate aerobes (Clocksin et al., 2007; Voytek et al., 1999). The presence (~0.7 mg/L) of $H_2S$ near the sediment–water interface clearly indicates anoxic processes are occurring near the sediment water interface (Clocksin et al., 2007).

Our results show that $ClO_4^-$ and $ClO_3^-$ in Lake Hoare are present throughout the water column at concentrations ranging from 0.1 to 0.3 and 0.15 to 0.42 μg/L, respectively (Fig. 2). Concentrations were lowest near the surface and at the sediment interface with a peak concentration near 10 m. As previously reported, $Cl^-$ concentrations decrease exponentially towards the surface. $SO_4^{-2}$ follows a similar trend increasing proportionally to $Cl^-$ with the exception of the deepest sample (30 m) consistent with the presence of $H_2S$ at the same depth. Neither $ClO_4^-$ nor $ClO_3^-$ concentrations increase proportionally to $Cl^-$, although the concentrations do initially increase.

This relationship with $Cl^-$ is further highlighted by the predicted concentrations (dashed lines Fig. 2) of these spe-

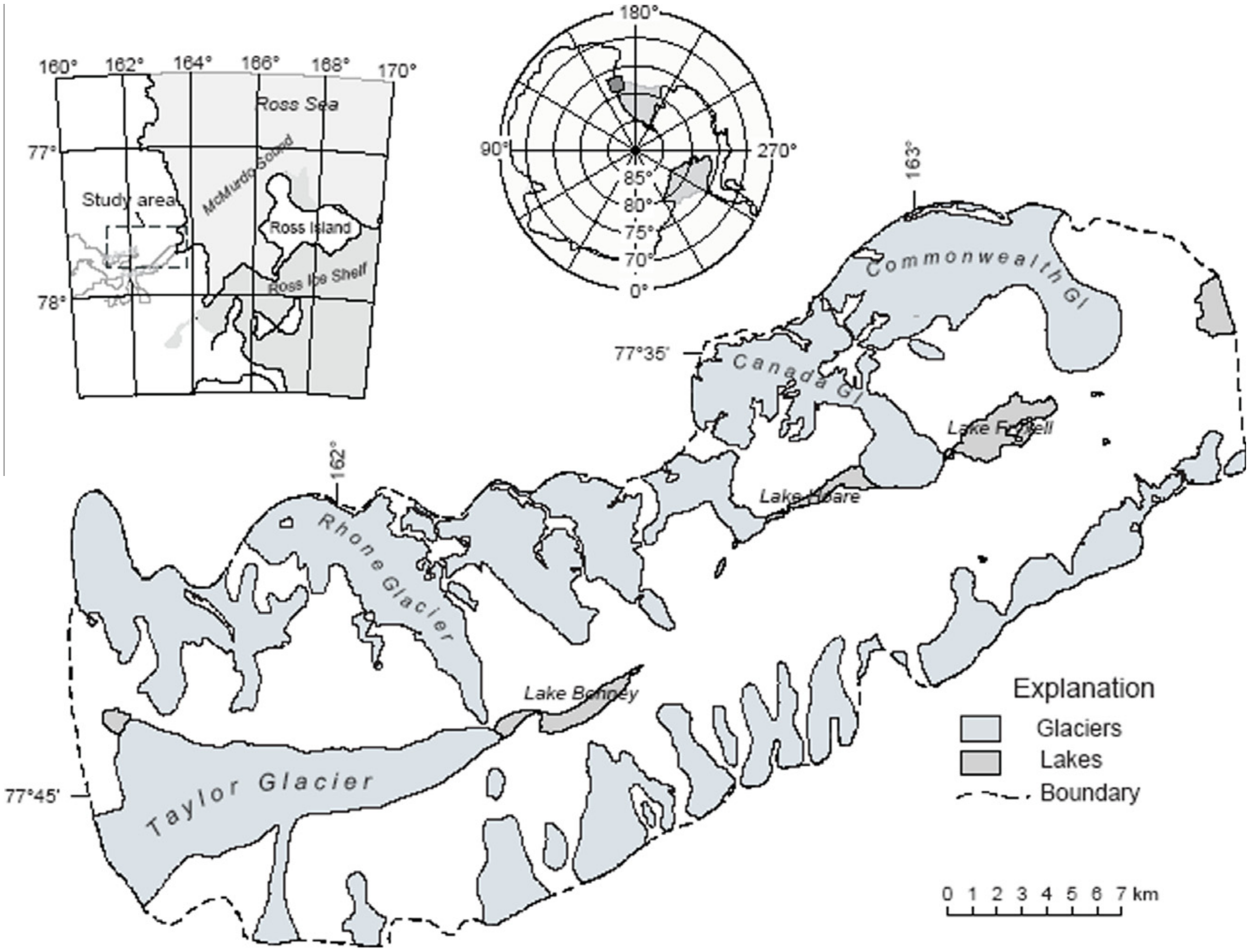

Fig. 1. Map of Taylor Valley, Antarctica showing the locations of Lake Fryxell, Lake Bonney, and Lake Hoare. Adapted from Lyons et al. (2005).

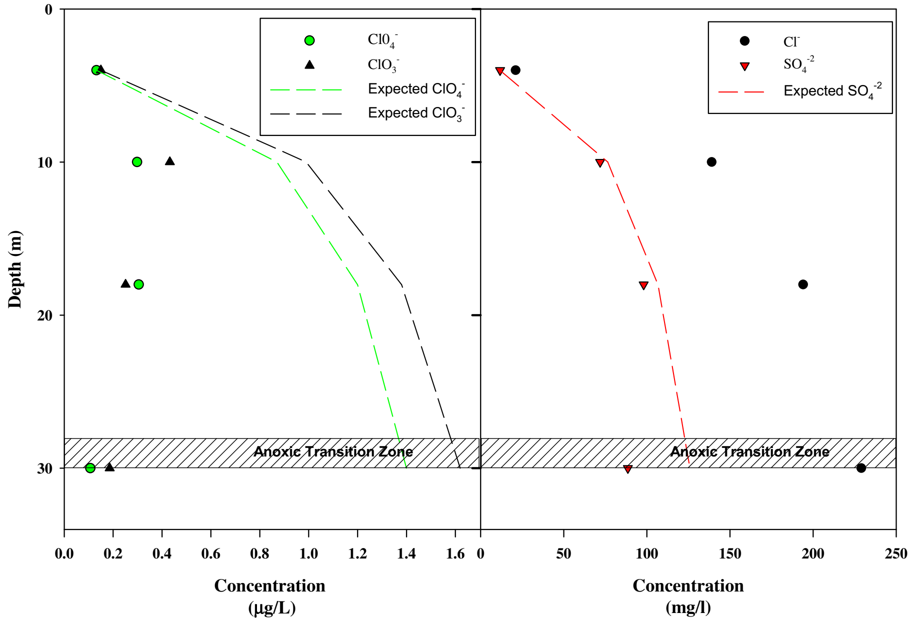

Fig. 2. Concentration profiles of $ClO_4^-$ and $ClO_3^-$, $Cl^-$ and $SO_4^{-2}$ in Lake Hoare, December 2009. Dashed lines represent modeled concentrations based on maintaining surface water ratios of $ClO_3^-$, $ClO_4^-$ and $SO_4^{-2}$ relative to $Cl^-$ throughout the lake depth.

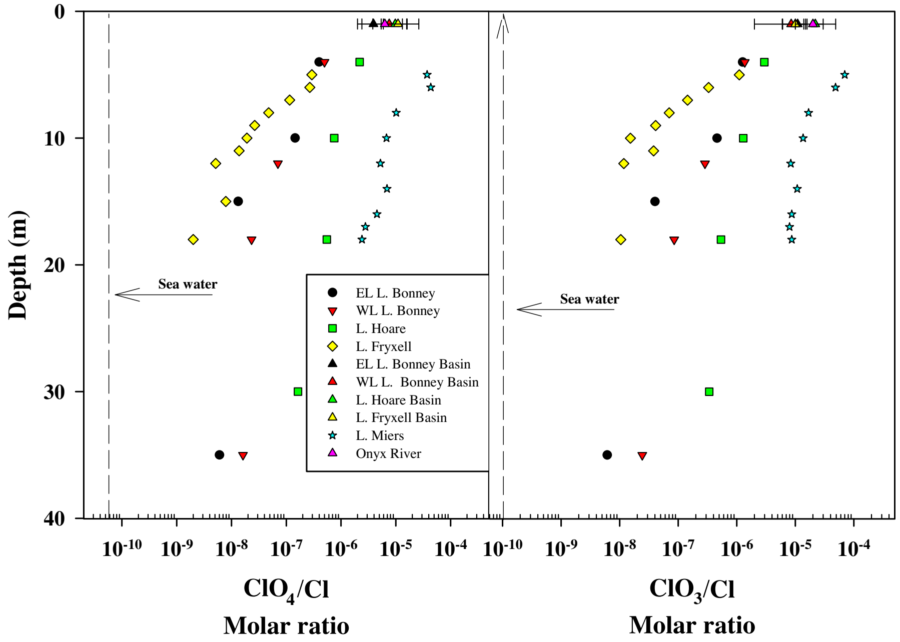

Fig. 3. Molar ratios of $ClO_4^-/Cl^-$ and $ClO_3^-/Cl^-$ with depth in MCM lakes and feed waters for lake basins in Taylor Valley and the Onyx River in Wright Valley. The black dashed line in each figure represents the ratio in seawater sampled at McMurdo Station.

cies using a simple model based on maintaining the initial ratios of each species relative to $Cl^-$ in the lake surface water with depth. The ratios of $SO_4^{-2}$ to $Cl^-$ are largely conserved with depth except as discussed near the sediment water interface. $SO_4^{-2}$ reduction has apparently not been extensive enough to impact the concentration of $SO_4^{-2}$ in the majority of the lake profile (Fig. 2). The ratio of $ClO_4^-$ and $ClO_3^-$ to $Cl^-$ in the lake surface water are close to the measured values in stream input to Lake Hoare (Fig. 3). Predicted concentrations of $ClO_3^-$ and $ClO_4^-$ based on $Cl^-$ concentration with depth are up to an order of magnitude higher than measured concentrations indicating a depletion of $ClO_x^-$ for all depths below the surface water.

The concentration of $ClO_4^-$ and $ClO_3^-$ can likely be explained by a similar process as $SO_4^{-2}$. Like $NO_3^-$ both $ClO_4^-$ and $ClO_3^-$ are only reduced at oxygen concentrations below ~1 mg/L. Therefore given the elevated $O_2$ concentrations throughout the lake depth, $ClO_4^-$ and $ClO_3^-$ are unlikely to be reduced in the bulk lake water. However, as sulfate reduction is clearly occurring in the lake sediment the conditions exist to support $ClO_x$ reduction. Both $ClO_4^-$ and $ClO_3^-$ are utilized as electron acceptors prior to $SO_4^{-2}$, and consequently the upper portions of the sediment should support $ClO_x^-$ reduction. The very large differences in concentrations of $SO_4^{-2}$ and $ClO_x^-$ ($SO_4^{-2}$/ $ClO_x^- > 10{,}000$) explain the difference in $ClO_x^-$ depth profiles compared to $SO_4^{-2}$. The relatively low organic matter input to the sediments sustains relatively low rates of electron acceptor ($O_2$, $NO_3^-$, $SO_4^{-2}$) reduction, but given the ratio of $SO_4^{-2}$ to $ClO_x^-$ this rate would lead to the rapid consumption of $ClO_x$ but a negligible decrease in $SO_4^{-2}$ concentration. This would eventually lead to a depleted $ClO_x^-$ concentration profile relative to $Cl^-$ throughout most of the depth of the lake as observed. Hence, one implication of the data presented here is that $ClO_x$ species can be used as a very sensitive marker for microbial activity in the water column of ice-covered lakes. Finally, the presence of trace amounts of $NO_3^-$ at lower depths suggests that it is being produced in excess of the consumption rate.

### *3.2.2. East Lobe Lake Bonney*

Lake Bonney is the largest lake in Taylor Valley with a maximum depth of ~40 m (Green and Lyons, 2009). It has two lobes (west and east) that have had very different evolutionary histories (Matsubaya et al., 1979; Poreda et al., 2004). In the East Lobe (EL), the surface water is fresh (~0.6 g TDS/l) to highly saline at depth (~273 g TDS/l). Both lobes are vertically stabilized by the strong salt gradients in the lake (Spigel and Priscu, 1998). The lake has existed in some form for a minimum of 300,000 years and the hypolimnion has been attributed to a Tertiary period marine fjord (Hendy, 2000; Lyons et al., 2005). The EL geochemistry has been modified due to the loss of ice cover in the mid-Holocene which reformed ~200 years ago. The loss of the ice cover led to cryo-concentration causing precipitation of various salts leading to a thick deposit of NaCl on the surface sediments. The lake geochemistry has been further modified by input from the west lobe due to overflow and input from glacier inflow including weathering products. Dissolved Organic Carbon (DOC) increases with depth reaching a maximum of 30 mg/l and is attributed to primary production in the lake, evapoconcentration (Green and Lyons, 2009) and subglacial flow from the Taylor Glacier (Mikucki et al., 2004).

The biogeochemistry of the EL is to some extent not fully understood. Oxygen is above saturation (~20 mg/l) above 20 m and rapidly declines to suboxic concentrations (<1 mg/l) across the chemocline (20–23 m). Dissolved inor-

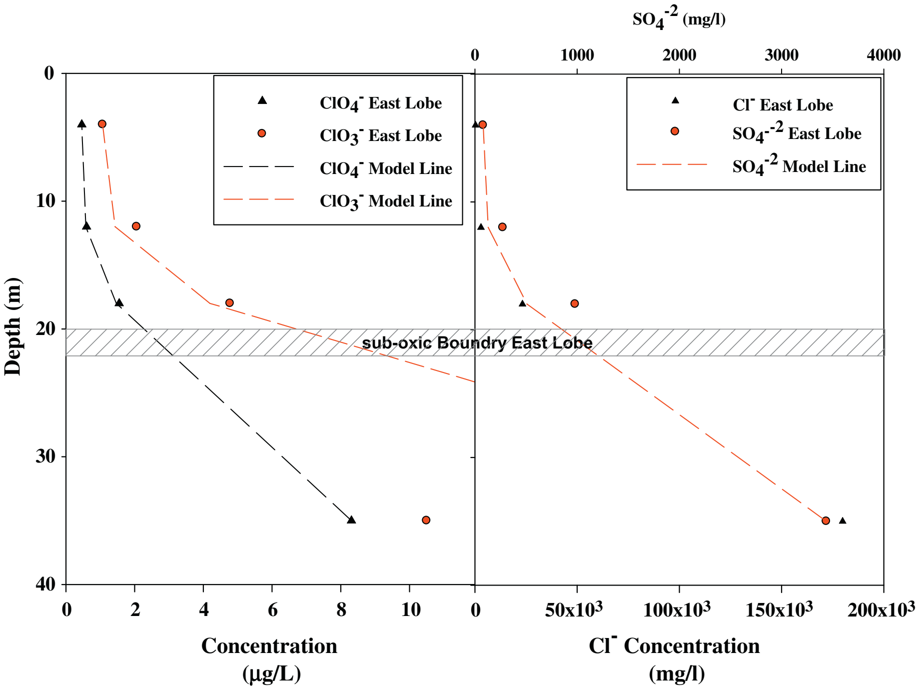

Fig. 4. Concentration profiles of $ClO_4^-$ and $ClO_3^-$, $Cl^-$ and $SO_4^{-2}$ in the EL of Lake Bonney, December 2009. Dashed lines represent modeled concentrations based on a two part mixing model of concentrations at the surface and 35 m except for $ClO_3^-$ for which the concentration at 35 m is predicted from the $ClO_4^-$ concentration using the ratio from Fig. 5. See text (Section 3.2) for more explanation.

ganic nitrogen ($NO_3^-$, $NO_2^-$, $NH_4^+$) rapidly increases below the chemocline reaching stable maximums (2.4, 0.6, and 3.7 mg-N/l, respectively) at a depth ~30 m and below (Priscu et al., 2008). Dissolved $N_2O$ in EL increases similarly below the chemocline and declines rapidly (<1 µM) below 30 m. The anomalously elevated concentrations of $NO_3^-$ and $NO_2^-$ under suboxic conditions in the deep water are not understood, but multiple studies indicate that denitrification is either not occurring or is occurring at such low rates as to have minimal impact (Priscu et al., 2006; Priscu et al., 2008; Ward and Priscu, 1997). Factors contributing to the lack of denitrification activity include the elevated TDS, low temperatures, and elevated redox potential (>400 mV) (Ward and Priscu, 1997; Ward et al., 2005). Isotopic studies of $^{15}N$ and $^{18}O$ in $N_2O$ in concert with genomic studies suggest the origin of the $N_2O$ was due to nitrification and the current profiles are attributed to a legacy of a former biogeochemical condition that have been preserved due to the extreme stability of the lake (Priscu et al., 2008). Sulfate concentrations increase with depth but the ratio of $SO_4^{-2}/Cl^-$ decreases from the surface to the top of the chemocline (~20 m) below which it remains reasonably constant. Given the elevated redox condition, the presence of $NO_3^-$, $NO_2^-$, as well as the lack of any $H_2S$, the reduction in ratio is most likely due to precipitation of a $SO_4^{-2}$ mineral phase in the hypersaline waters rather than sulfate reduction.

$ClO_4^-$ concentration increases with depth in the EL of Lake Bonney (0.46 to 8.3 µg/L at the surface and 35 m, respectively) (Fig. 4). The increase in $ClO_4^-$ concentration is proportional to the increase in $Cl^-$ concentration ($r^2 = 0.99$) over the entire water column. $ClO_4^-$ and $SO_4^{-2}$ concentrations are predicted accurately with a simple mixing model of concentrations at the surface and 35 m (Dashed lines Fig. 4). The $ClO_4^-/Cl^-$ molar ratio ($5 \times 10^{-7}$) at the shallowest depth (4 m) is less than the ratio in Taylor Valley surface streams ($4 \times 10^{-6}$) and decreases with depth to a relatively constant value of ~$6 \times 10^{-9}$ at 35 m (Fig. 3). The ratio at 35 m is still substantially enriched compared to seawater $3.0 \times 10^{-10}$ which is considered the major source of salts in the EL. It is possible that water below 18 m became enriched in $ClO_4^-$ relative to $Cl^-$ from *in situ* precipitation of NaCl which is reported to be at least 1.6 m and up to 10 m thick in EL sediments (Hendy et al., 1977). $Cl^-$ concentrations reach a maximum at 24 m and remain constant at lower depths (Lyons et al., 2005). $ClO_4^-$ would not precipitate given its low concentrations relative to other anions and its very high solubility. There is no evidence (such as a selective loss of $ClO_4^-$ at depth with respect to $Cl^-$) of biological reduction of $ClO_4^-$ which is not unexpected given the stability of $NO_3^-$ and $NO_2^-$ at depth and the noted lack of any significant nitrate reduction and (Priscu et al., 2008; Ward et al., 2005; Ward and Priscu, 1997). All of this suggests the $ClO_4^-$ concentration profiles and $ClO_4^-/Cl^-$ ratio profiles are a product of dilution of evapoconcentrated seawater by surface inflow and subsequent diffusion which is consistent with the proposed history of the EL. The origin of $ClO_4^-$ in the EL could be a mix of surface water inflow and seawater, although it is currently not possible to determine if the $ClO_4^-$ in the original seawater is still present. It is possible the east lobe could have experienced conditions that supported $ClO_4^-$ reduction in the distant past given the estimated age of isolation of the seawater 1.7–5.1 Ma. Regardless, the $ClO_4^-$ must be reasonably old as the concentration at 35 m is at least ~70X the average Taylor Valley stream concentration and 170X seawater concentrations.

In contrast to $ClO_4^-$, $ClO_3^-$ is not as conservative with respect to $Cl^-$ concentration. $ClO_3^-$ concentration does increase with depth (1.1 and 10.5 μg/l at 4 and 35 m, respectively) but the increase is proportional to $Cl^-$ only to a depth of 18 m (Fig. 4). This is highlighted by evaluating the relationship between $ClO_3^-$ and $ClO_4^-$ (Fig. 5) which is highly correlated ($R = 0.97$) up to a depth of 18 m. The predicted $ClO_3^-/ClO_4^-$ ratio (3.1) is very similar to the ratio in Taylor Valley surface streams (2.2). However, the sample point at 35 m is clearly depleted in $ClO_3^-$ relative to $ClO_4^-$. Modeled $ClO_3^-$ concentrations at 4, 12, and 18 m are well predicted based on the two parts mixing model and using the predicted $ClO_3^-$ concentration at 35 m based on the $ClO_4^-$ concentration. $ClO_3^-/Cl^-$ molar ratios in EL surface water ($1 \times 10^{-6}$) are similar to streams throughout Taylor Valley and are still well above seawater ratios ($1 \times 10^{-10}$) even with the apparent reduction of $ClO_3^-$ at 35 m. What is clear is that at least at 35 m some loss of $ClO_3^-$ relative to $ClO_4^-$ has occurred. This could be due to low level $ClO_3^-$ reduction by low level nitrate reductase activity. While $NO_3^-$ and $NO_2^-$ concentrations appear to be temporally stable at 35 m and denitrification is reported to be either absent or at most occurring at insignificant rates (Ward and Priscu, 1997; Ward et al., 2005; Priscu et al., 2008), it is still possible that $ClO_3^-$ has been reduced. $ClO_3^-$ concentrations are only 0.1% and 0.3% of the molar concentrations of $NO_3^-$ and $NO_2^-$, respectively and therefore reduction rates too small to impact bulk $NO_3^-$ and $NO_2^-$ could have an impact on $ClO_3^-$ concentrations over long periods. Whether this reduction is ongoing or simply a fossil of previous conditions in the EL is unknown.

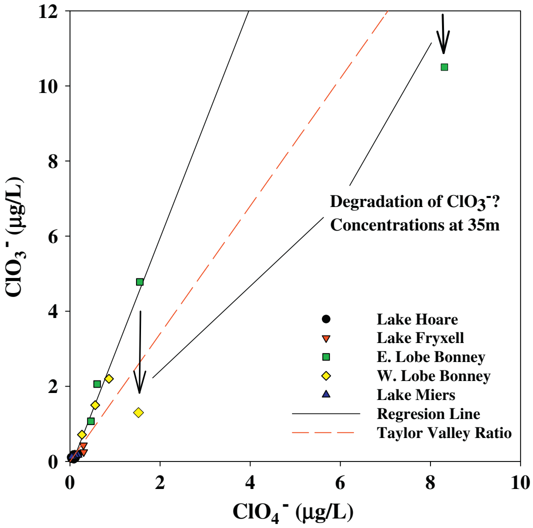

Fig. 5. Relationship of $ClO_3^-$ and $ClO_4^-$ concentration in Dry Valley Lakes. The solid black line represents the regression line ($r^2 = 0.97$and ratio = 3.1) and the red dashed line represents ratio of $ClO_3^-$ and $ClO_4^-$ in streams of Taylor Valley.

### 3.2.3. *West Lobe Lake Bonney*

The West Lobe (WL) is much smaller than the EL and exchanges water with the EL down to 13 m at which depth a sill separates the deeper waters of the east and west lobes. The water quality above the sill layer is therefore similar between the two lobes but the deeper depths are distinct presumably due to their separate evolutionary histories. The WL has apparently not ever lost its ice cover (Hendy et al., 1977; Matsubaya et al., 1979). The source of the deeper water is also attributed to seawater which has been cryo-concentrated but to a lesser extent (144 g/L) due to the presence of the ice cover (Lyons et al., 2005), and from subglacial outflow from the Taylor Glacier (Mikucki et al., 2004, 2009). A number of lines of evidence suggest that the water may be quite old. The biogeochemistry of the WL follows a more conventional redox profile (Lee et al., 2004). Oxygen concentrations are supersaturated above 13 m and decline rapidly to less than 1 mg/L at ~25 m. $NO_3^-$, $NO_2^-$, and $N_2O$ all peak in or near the chemocline (15–18 m) and then rapidly decline below the oxycline due to denitrification (Priscu et al., 1996; Ward and Priscu, 1997; Voytek et al., 1999). Ammonium and DOC concentrations steadily increase below the chemocline but hydrogen sulfide is not present (Voytek et al., 1999; Green and Lyons, 2009; Downes and Priscu, 1995).

Concentration profiles of $ClO_4^-$ and $ClO_3^-$ are similar to the EL except at the lowest sampling depth (35 m) at which concentrations are ~5 and 8X lower even though $Cl^-$ is only 2X lower (Fig. 6). $ClO_4^-/Cl^-$ and $ClO_3^-/Cl^-$ ratios are also similar for comparable depths (Fig. 3). The loss of $ClO_3^-$ relative to $ClO_4^-$ is also similar to the EL (Fig. 5). Predicted concentrations based on the two component mixing model are reasonably similar to measured values for $SO_4^{-2}$ and $ClO_4^-$, although some loss of $ClO_4^-$ has occurred at 35 m. Predicted concentrations of $ClO_3^-$ are similar for depths above 35 m if the concentration at 35 m is predicted from the $ClO_4^-$ concentration and expected ratio of $ClO_3^-/ClO_4^-$ from Fig. 5. $ClO_4^-$ concentration at 35 m and the ratio from Fig. 5 is used to predict the $ClO_3^-$ concentration at 35 m rather than the measured concentration. The differences between the EL and WL are likely due to the biological reduction of $ClO_4^-$, $ClO_3^-$and $NO_3^-$ at depth in the WL as opposed to only $ClO_3^-$ in the EL. The WL has an active denitrification zone below 18 m and $NO_3^-$, $NO_2^-$ and $N_2O$ are completely reduced by 30 m (Priscu et al., 1996; Priscu, 1997; Voytek et al., 1999). Taken together this implies that loss of $ClO_4^-$ and $ClO_3^-$ was active in the past but has now ceased or that loss commenced in the relatively near past compared to the age of the lake. Otherwise, we would expect much lower concentrations of both species at depth especially with respect to $ClO_4^-$ which is only slightly depleted with respect to $Cl^-$.

### 3.2.4. *Lake Fryxell*

The geochemistry of Lake Fryxell has recently been reviewed by Green and Lyons (2009). TDS varies from near fresh water at the surface (0.99 g/L) to brackish (7.8 g/L)

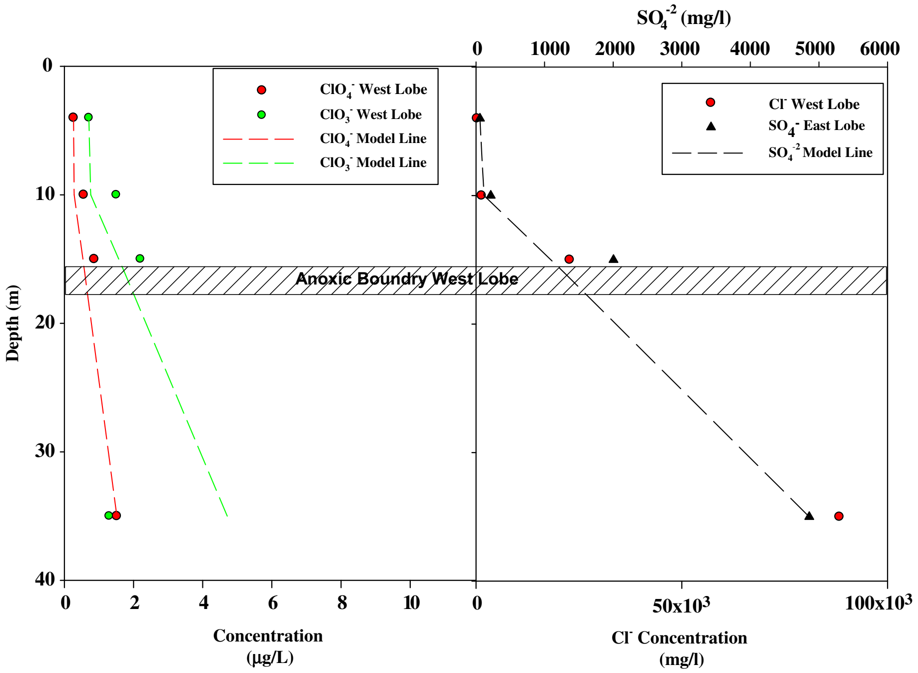

Fig. 6. Concentration profiles of $ClO_4^-$ and $ClO_3^-$, $Cl^-$ and $SO_4^{-2}$ in the WL of Lake Bonney, December 2009. Dashed lines represent modeled concentrations based on a two part mixing model of concentrations at the surface and 35 m except for $ClO_3^-$ for which the concentration at 35 m is predicted from the $ClO_4^-$ concentration using the ratio from Fig. 5. See text (Section 3.2) for more explanation.

water at depths below the oxicline (∼9.5 m) where high levels of hydrogen sulfide exist. The lake has been subject to a number of draw down and refill events (Wagner et al., 2006). The conserved $Cl^-$ profile steadily increases with depth and has previously been attributed to diffusion of $Cl^-$ from the sediment to the surface (Green and Lyons,

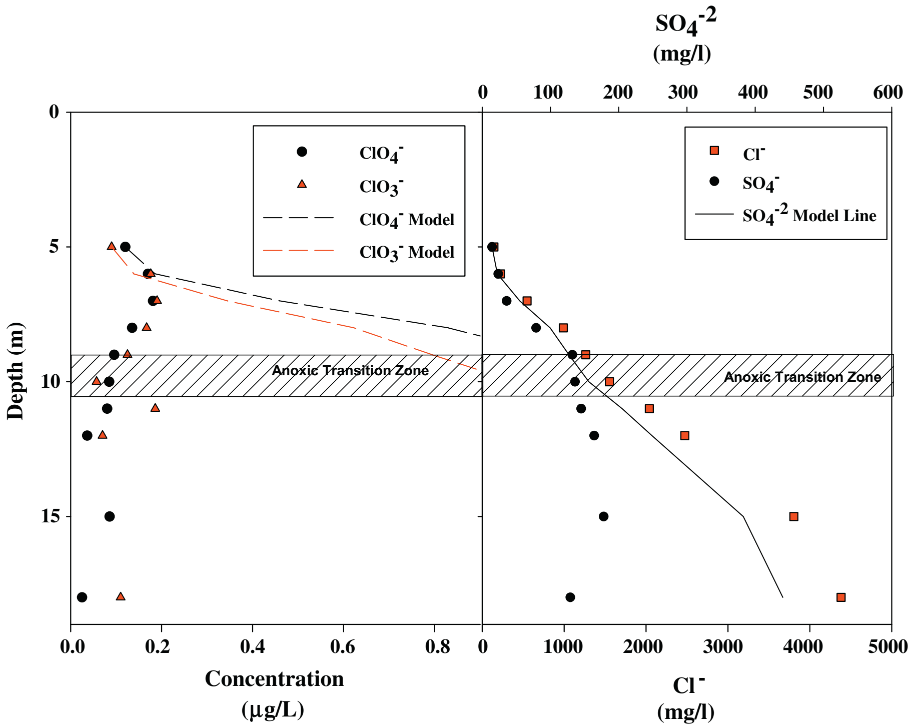

Fig. 7. Concentration profiles of $ClO_4^-$ and $ClO_3^-$, $Cl^-$ and $SO_4^{-2}$ in Lake Fryxell, December 2008. Dashed lines represent modeled concentrations based on maintaining surface water ratios of $ClO_3^-$, $ClO_4^-$ and $SO_4^{-2}$ relative to $Cl^-$ throughout the lake depth.

2009). At depths above ~9 m the water is supersaturated with $O_2$ and between ~9–11 m a chemocline exists in which $O_2$ is rapidly depleted and in which chlorophyll-a reaches a concentration maximum (Priscu, 1995). $SO_4^{-2}$ slowly increases with depth to a maximum at ~11–12 m and then rapidly decreases to below 0.1 mM at the sediment water interface. $H_2S$ reaches a maximum (1.4 mM) at the sediment water interface and declines steadily to 9 m above which it is not present (Aiken et al., 1996; Karr et al., 2005; Sattley and Madigan, 2006). An active sulfur oxidizing population is present with a population maximum within the chemocline but extending into the anoxic depths. DOC distribution is similar to $Cl^-$ with a minimum at the surface (~3.0 mg/L) and a maximum (31.2 mg/L) at the sediment water interface. Like $Cl^-$ the distribution of DOC is attributed to diffusion from the sediment of degraded and relic sediment organic matter, and new input from surface water inflow (Aiken et al., 1996). $NH_4^+$ was reported to be near the detection limit from the surface to the bottom of the chemocline, below which the concentration steadily increases to a maximum (5.6 mg-N/l) at the sediment water interface. $NO_3^-$ was below detection for all depths and $NO_2^-$ was present at trace concentrations (<0.0042 mg-N/L) at 7 m and below 15 m (Voytek et al., 1999).

Concentrations of both $ClO_4^-$ and $ClO_3^-$ increase slightly from 5 m to a maximum at 7 m and then decline steadily to just below the chemocline at 10 m below which they remain relatively constant (Fig. 7). Concentrations at depths above 9 m are generally similar to surface water concentrations in Taylor Valley (Table 1). The ratio of $ClO_4^-$/Cl and $ClO_3^-$/Cl are the lowest of all the lakes, likely due to both the addition of $Cl^-$ from the sediment and strongly reducing conditions below 11 m that facilitate $ClO_4^-$ and $ClO_3^-$ bacterial reduction. Predicted concentrations based on surface water ratios of $ClO_4^-/Cl^-$ and $ClO_3^-/Cl^-$ over estimate both $ClO_4^-$ and $ClO_3^-$concentrations at depths below 6 m. $SO_4^{-2}$ concentrations are likewise over predicted at depths below the chemocline. Collectively, these results in concert with the complete lack of $NO_3^-$ and $NO_2^-$ below the chemocline (Voytek et al., 1999; Priscu, 1997) suggests that $ClO_4^-$ and $ClO_3^-$ are actively being reduced. These data further imply that $ClO_4^-$ and $ClO_3^-$ were either not present during the last lake drawdown (~1000 Ka) or were consumed since the lake has been refilled. The $ClO_3^-$ and $ClO_4^-$ concentration profile appear to reflect a surface source, distribution by diffusion, and consumption at depth below 11 m.

### 3.2.5. Lake Miers

Lake Miers is relatively unstudied compared to other MDV lakes. It is much younger (<300 years) and is the only lake with both hydraulic inflow and outflow and, as such, its chemistry resembles glacier meltwater. The lake is oxic throughout its depth but approaches anoxic conditions at the sediment water interface. Nitrification rates while not directly measured are believed to be very low and $NO_3^-$and $NO_2^-$, are essentially constant with depth (<0.03 and 0.002 mg-N/l, respectively) (Voytek et al., 1999). $ClO_3^-$ and $ClO_4^-$ concentrations are essentially constant with depth with exception of depths below 14 m where $ClO_4^-$concentrations decrease (Fig. 8). Chloride increases with depth until 12 m below the surface beyond which it remains relatively constant. $ClO_3^-/Cl^-$ and $ClO_4^-/Cl^-$ ratios in surface water are near but above Taylor Valley surface water and consistently decrease with depth (Fig. 4). While the lake is oxic, the reduction in $SO_4^{-2}$ below 14 m strongly suggests that the sediments may support anoxic processes. This would be congruent with the reduction in $ClO_4^-/Cl^-$ and $ClO_3^-/Cl^-$ ratios.

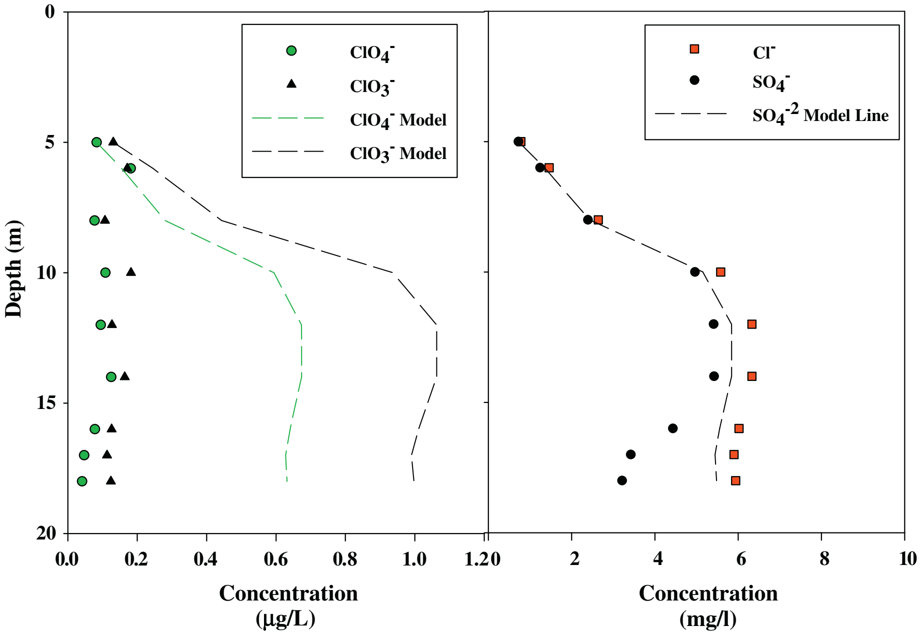

Fig. 8. Concentration profiles of $ClO_4^-$ and $ClO_3^-$, $Cl^-$ and $SO_4^{-2}$ in Lake Miers, December 2008. Dashed lines represent modeled concentrations based on maintaining surface water ratios of $ClO_3^-$, $ClO_4^-$ and $SO_4^{-2}$ relative to $Cl^-$ throughout the lake depth.

### 3.3. Summary and Conclusions

$ClO_3^-$ and $ClO_4^-$ are present throughout the water columns of the MDV lakes and other surface water bodies in the area. Concentrations among surface water bodies are generally similar reflecting a common atmospheric source. Variations in streams are likely due to site-specific processes, such as the degree of evaporative concentration and the differential input of salts due to leaching of soils and aeolian materials and subsequent inflow to streams. The concentrations of $ClO_3^-$ and $ClO_4^-$ in the ice-covered lakes are dependent on both the total evaporative concentration that has occurred as well as the biological activity within each lake. The two relatively young lakes (Miers and Hoare), have $ClO_3^-$ and $ClO_4^-$ concentrations and ratios of $ClO_3^-/Cl^-$ and $ClO_4^-/Cl^-$ in surface waters that are similar to source streams, but suggest $ClO_3^-$ and $ClO_4^-$ reduction at depth or in the sediments. Lake Fryxell has $ClO_3^-$ and $ClO_4^-$ concentrations similar to input streams but $ClO_3^-/Cl^-$ and $ClO_4^-/Cl^-$ ratios much lower due to the large $Cl^-$ source in bottom sediments due to its complete evaporation in the past. Based on the paucity of $ClO_3^-$ and $ClO_4^-$ in the deep waters, this lake appears to have supported $ClO_3^-$ and $ClO_4^-$ reduction at least back to the last draw down event. $ClO_3^-$ and $ClO_4^-$ concentrations in Lake Bonney are the highest of all the lakes reflecting the lake's greater age and concentration of $Cl^-$. Similar to $NO_3^-$, $ClO_4^-$ appears to be stable in the East Lobe and its concentration is highly correlated to $Cl^-$ concentration. It is even possible that some $ClO_4^-$ at depth is a remnant of the initial seawater that formed Lake Bonney. In the West Lobe $ClO_3^-$ and $ClO_4^-$ appear stable at depths above the chemocline but have or are experiencing reduction at the deepest depth similar to $NO_3^-$. Finally the concentrations of $ClO_3^-$ and $ClO_4^-$ are well correlated except in cases where reduction has occurred.

These lakes provide an excellent case study for $ClO_3^-$ and $ClO_4^-$ biotransformation in pristine extreme environments. Given their low concentrations, high solubility, and lack of any *in situ* generation mechanisms, they may offer a sensitive means to study ongoing biological activity in the lakes, and the addition of $ClO_4^-$ stable isotope evaluation could provide further clues as to the geochemical history of the lake water. Finally, $ClO_3^-$ and $ClO_4^-$ biogeochemistry in Antarctic ice-covered lakes may represent an excellent analog for similar processes in ice-covered lakes on Mars in the past (McKay and Davis, 1991), or even in more recent times, especially given the discovery of relatively large amounts of $ClO_4^-$ in the Martian soil (Hecht et al., 2009).

## ACKNOWLEDGEMENTS

This work was supported by the Strategic Environmental Research and Development Program (SERDP Project ER-1435) and by NSF OPP grants 0432595 and 0631494. We are grateful to the McMurdo Long Term Ecological Research Program for providing water samples from the MDV and would especially like to acknowledge Kathy Welch and Amy Chiuchiolo for their time and efforts. Work in the lab of J.D.C was supported by the Energy Biosciences Institute, UC Berkeley, CA. A.F.D is supported by the NASA Exobiology program (Grant Number NNX12AD61G).

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*Associate editor:* Karen Johannesson