

Thermodynamic Constraints on Microbially Mediated Processes in Lakes of the McMurdo Dry Valleys, Antarctica

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Recent research has shown that the distribution of biogenic nitrogen and sulfur compounds (in particular, N₂O, DMS and dissolved DMSO) observed in five perennially ice-covered lakes of the McMurdo Dry Valleys, Antarctica, appear to lack obvious biogeochemical explanations. This study examined the hypothesis that the distribution of these compounds resulted from thermodynamic constraints on microbially mediated processes. The thermodynamic favorableness of a number of ecologically important redox reactions in these lakes was assessed using a simplified Nernst equation and mathematically modified *E_h* measurements. Our qualitative analysis revealed that the relative dominance of denitrification and nitrification as formation and loss processes for N₂O was a complex pattern that was related to the redox conditions present. The results indicate that nitrification was initially the sole pathway for the formation of N₂O with denitrification being thermodynamically unfavorable. As the redox conditions became less oxic, both denitrification and nitrification were possible. Once complete anoxia occurred, the importance of nitrification decreased considerably and the loss of N₂O via denitrification became increasingly important. With respect to DMSO, the results

indicated that DMSO was thermodynamically unfavorable as an electron acceptor for the respiration of organic material by bacteria in well-oxygenated environments, giving a partial explanation for the relatively elevated levels of DMSO found in many aquatic environments. Overall, the results of this study showed that subtle variations in the redox conditions present provided a plausible explanation for the unusual distributions of biogenic sulfur and nitrogen compounds observed in the lakes of the McMurdo Dry Valleys.

Keywords Antarctica, bacteria, dimethylsulfide, dimethylsulfoxide, denitrification, nitrification, nitrous oxide, polar lakes, redox potential, suboxic

INTRODUCTION

The McMurdo Dry Valleys in southern Victoria Land, Antarctica, are home to a series of perennially ice-covered lakes (Vincent 1988). Several important biogeochemical implications arise from the presence of these permanent ice covers. Penetration of light is low, and consequently primary productivity rates are also low (Lizotte and Priscu 1992; Howard-Williams et al. 1998). The biomass is dominated by trophic levels no higher than protozoans (Priscu 1997; Priscu et al. 1999). Gas exchange between the water column and atmosphere is severely restricted, with most exchange occurring between the surface layer and the atmosphere through a small moat that develops for approximately ten weeks during the austral summer (Priscu et al. 1996). Furthermore, vertical transport is predominantly through molecular diffusion owing to the lack of wind-induced turbulence (Spigel and Priscu 1998). One of the manifestations of these biogeochemical conditions is an unusual distribution of certain chemical species in the water column of the lakes. For

Received 10 February 2003; accepted 3 November 2003.

We thank John Lisle, Barbara Vaughn, Valerie Sloane, and Scott Konley for their assistance in the field. We also thank Berry Lyons (Byrd Polar Research Center, Ohio State University), Mike Madigan (Southern Illinois University), and an anonymous reviewer for constructive criticisms of an early version of this manuscript. Logistical support provided through Raytheon Polar Services, Petroleum Helicopters Inc., the U.S. Air Force and New York Air National Guard is gratefully acknowledged. This research has been made possible through funding from the National Science Foundation to JCP (OPP-9815998; OPP-0096250; OPP-0237335; OPP-0085400) and to CMF (Post-doctoral Research Fellowship in Microbial Biology DBI-0074372).

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Table 1
Stoichiometries, values for ΔG° , E° , $G^{\circ'}$ and $E^{\circ'}$ for the nitrogen-containing reactions (as the reduction half-reaction) considered in this study

Reduction half-reaction	ΔG° (kJ mol ⁻¹)	E° (mV)	$\Delta G^{\circ'}$ (kJ mol ⁻¹)	$E^{\circ'}$ (mV)
R1 $\text{N}_2\text{O} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{N}_2 + \text{H}_2\text{O}$	-340.8	1766*	-260.9	1352
R2 $2\text{NO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$	-307.0	1591*	-227.1	1177
R3 $2\text{NO}_2^- + 6\text{H}^+ + 4\text{e}^- \rightarrow \text{N}_2\text{O} + 3\text{H}_2\text{O}$	-538.8	1396*	-299.1	775
R4 $2\text{NO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O}$	-1202.2	1246*	-722.8	749
R5 $\text{NO}_2^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{NO} + \text{H}_2\text{O}$	-116.0	1202*	-36.1	374
R6 $\text{NO}_2^- + 8\text{H}^+ + 6\text{e}^- \rightarrow \text{NH}_4^+ + 2\text{H}_2\text{O}$	-519.3	897*	-199.7	345
R7 $\text{NO}_3^- + 10\text{H}^+ + 8\text{e}^- \rightarrow \text{NH}_4^+ + 3\text{H}_2\text{O}$	-680.0**	881	-257.8	334
R8 $\text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O}$	-161.1	835*	-81.2	421
R9 $\text{N}_2\text{O} + 10\text{H}^+ + 8\text{e}^- \rightarrow 2\text{NH}_4^+ + \text{H}_2\text{O}$	-499.4	647*	-99.9	129
R10 $\text{N}_2 + 8\text{H}^+ + 6\text{e}^- \rightarrow 2\text{NH}_4^+$	-159.2	275*	160.4	-277

*Data taken from Milazzo and Carol (1978).

**Data derived from Amend and Shock (2001).

65 example, extreme supersaturation of nitrous oxide (N_2O ; >700,000% greater than air saturation) in the middle of the water-column has been reported for the east lobe of Lake Bonney (Priscu et al. 1996; Priscu 1997).

70 The lack of turbulent mixing also leads to density-driven stratification of the water columns of the lakes with the presence of stable, persistent chemoclines and distinct oxyclines. As a result, it has been suggested that these lakes represent ideal sites for the study of redox-sensitive biogeochemical processes (Downes and Priscu 1995). Although the use of redox potentials (E_h measurements) has become widespread in aquatic studies, many difficulties render the measurements unamenable to quantitative analysis (Whitfield 1969; Lindberg and Runnells 1984; Stumm and Morgan 1995). To alleviate some of these problems, we used an approach that allows an improved qualitative examination of redox potentials in the lakes of the McMurdo Dry Valleys. It should also be noted that our study deals with the redox conditions of the bulk phase (i.e. water column) of each lake and that different conditions are likely to exist in microenvironments such as sedimenting particles or inside cells. For the approach developed in this study, measured E_h values were compared to estimates of E_h at depths where the reduced forms of selected species such as H_2S , are known to be present due to microbial activity. The estimates of the reduction potentials for these reactions were made using simple thermodynamic approximations together with in-situ $p\text{H}$ and temperature. The measured E_h values were then scaled to match the estimates of the reduction potential for an oxidant species, e.g. sulfate, at the onset of the detectable presence of the reduced form, e.g. H_2S . Since the redox chemistry of aquatic environments is often determined by the presence of oxygen or sulfides (Stumm and Morgan 1995), the reduction of oxygen and sulfate were chosen as two of the reactions used to scale the E_h

measurements. In order to differentiate the scaled E_h values from the original E_h measurements, the scaled values are referred to as E_h^* values.

Reduction potentials for those redox reactions of interest to this study (Tables 1 and 2) were then determined using the same simple thermodynamic approximations. The E_h^* profile was used to indicate the thermodynamic constraints (i.e. favorableness) of those redox reactions. Since the presence of the reduced form of a species is an indication that microbial reduction is taking place, the reduction process must be thermodynamically favorable for the bacteria that are catalyzing the redox process. Thus in a general sense, if the estimated reduction potential is greater than the E_h^* value, then the reduction reaction is considered thermodynamically favorable. The E_h^* approach was applied to five lakes in the McMurdo Dry Valleys to identify regions where certain microbially mediated biogeochemical processes could occur.

This study focuses primarily on the nitrogen and sulfur cycles, and in particular on N_2O , dimethylsulfide (DMS) and dissolved dimethylsulfoxide (DMSO_d), since recent research has shown that observed gradients of these compounds lack simple biogeochemical explanations. Bacteria are implicated in the cycling of these compounds, yet little is known about what limits bacterial production in these Antarctic lakes (Takacs and Priscu 1998; Takacs et al. 2001; Ward et al. 2003). These biogenic compounds are also globally significant chemicals (Charlson et al. 1987; Bange 2000) and understanding the factors that determine the distributions of these compounds is pivotal in determining the extent of their global impact. Our study was also carried out largely using data that has either been published in the scientific literature or is available in the public domain. The combined data set generated by this approach yields a useful tool that provides interesting insights into the cycling of both DMSO_d and N_2O

Table 2

Stoichiometries, values for ΔG° , E° , $G^{\circ'}$ and $E^{\circ'}$ for the non-nitrogen reactions (as the reduction half-reaction) considered in this study

Reduction half-reaction	ΔG° (kJ mol ⁻¹)	E° (mV)	$\Delta G^{\circ'}$ (kJ mol ⁻¹)	$E^{\circ'}$ (mV)
R11 $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	-474.3	1229*	-305.3	791
R12 $\text{MnO}_{2(\text{s})} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	-236.2	1224*	-76.4	396
R13 $2\text{IO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightarrow \text{I}_{2(\text{aq})} + 6\text{H}_2\text{O}$	-1141	1183*	-661.6	686
R14 $\text{Fe}(\text{OH})_{3(\text{s})} + 3\text{H}^+ + \text{e}^- \rightarrow \text{Fe}^{2+} + 3\text{H}_2\text{O}$	-90.6	939*	29.3	-303
R15 $(\text{CH}_3)_2\text{SO}_{(\text{aq})} + 2\text{H}^+ + 2\text{e}^- \rightarrow (\text{CH}_3)_2\text{S}_{(\text{aq})} + \text{H}_2\text{O}$	-110.8**	574	-30.9	160
R16 $\text{I}_{2(\text{aq})} + 2\text{e}^- \rightarrow 2\text{I}^-$	-104.2	540*	-104.2	540
R17 $\text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}^- \rightarrow \text{H}_2\text{S}_{(\text{aq})} + 4\text{H}_2\text{O}$	-232.3***	301	167.2	-217
R18 $\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_{4(\text{aq})} + 2\text{H}_2\text{O}$	-122.8***	159	196.8	-255

*Data taken from Milazzo and Carol (1978).

**Data taken from Wood (1981).

***Data derived from Amend and Shock (2001).

130 that may, in turn, have important implications for the global biogeochemical cycles of these compounds. The overarching hypothesis for this study was that the unusual distributions of these compounds were a consequence of thermodynamic constraints placed on the microbial community that mediates the reduction and oxidation of the compounds.

135 MATERIALS AND METHODS

Study Area

140 We examined five lakes from the McMurdo Dry Valleys (Priscu 1997). Lakes Bonney and Fryxell are located in the Taylor Valley. Lake Vanda lies in the Wright Valley and Lake Joyce lies in the Pierce Valley. All of the lakes are stratified to various extents with stratification being controlled by salinity (Spigel and Priscu 1998). The west and east lobes of Lake Bonney have no deep water exchange between them and are considered as two separate entities in this study (referred to as West and East Bonney, respectively). Both lobes of Lake Bonney have suboxic lower layers. The remaining three lakes (Vanda, Fryxell, and Joyce) have bottom waters that are anoxic (Downes and Priscu 1995) and contain significant quantities of H₂S.

145 Nonthermodynamic Parameters

150 Data for temperature, salinity, and pH measurements in the five lakes were taken from data sets compiled for the McMurdo LTER program and are available on the McMurdo LTER website (<http://huey.colorado.edu/LTER/data.html>), Priscu et al. unpublished data). Data for the distributions of nitrate, nitrite, ammonium and N₂O in all five lakes were taken from Priscu (1997). Concentrations of dissolved Mn, dissolved Fe, and sulfides for Lake Fryxell were taken from Green et al. (1989). Some discrepancies were noted between profiles presented by the various studies for the dry valleys lakes. The differences result from inter-annual changes to the thickness of the surface layer of the

lakes (Spigel and Priscu 1998; Doran et al. 2002). Since the zero depth is taken as the surface of the lake, any changes to the thickness of the surface layer will result in differences in the depths reported for deeper features such as the chemocline. To overcome this problem, a previous study set the zero depth at the chemocline and normalized all datasets to this standard (Spigel and Priscu 1998). In case of the present study, using the chemocline standard was not practical, as some of the datasets cited by this study do not report chemocline data. However, they do all present profiles for dissolved oxygen. Thus, the datasets were normalized to the point at which dissolved oxygen concentrations fell to zero. For example, in Lake Fryxell, Priscu (1997) and the LTER dataset show that the concentration of dissolved oxygen drops to zero at 11 m, whereas Green et al. (1989) report a depth of 9 m. Consequently, the depths of the data presented by Green et al. (1989) were increased by 2 m. Through out this text, all mention of depth values refers to the normalized values, not the values presented in the original articles. Methane concentrations for Lake Fryxell were extracted from Smith et al. (1993). The depths of the data taken from Smith et al. (1993) were increased by 1 m. Data for dissolved Mn and sulfides in Lake Vanda were taken from Bratina et al. (1998) and from Green et al. (1986) for dissolved Fe. The depths of the data taken from Green et al. (1986) were increased by 7 m. The results for these background parameters are shown in Figure 1a for West Bonney, Figure 2a for East Bonney, Figure 3a for Lake Fryxell, Figure 4a for Lake Vanda, and Figure 5a for Lake Joyce.

Dimethylated-Sulfur Samples

190 Samples for DMS and DMSO₄ were gathered during the austral summers of 1999–2000 and 2000–2001 and were collected as part of a larger study aimed at elucidating the dimethylated-sulfur cycle in Lake Bonney. More complete details regarding the analyses of the dimethylated-sulfur species can be found

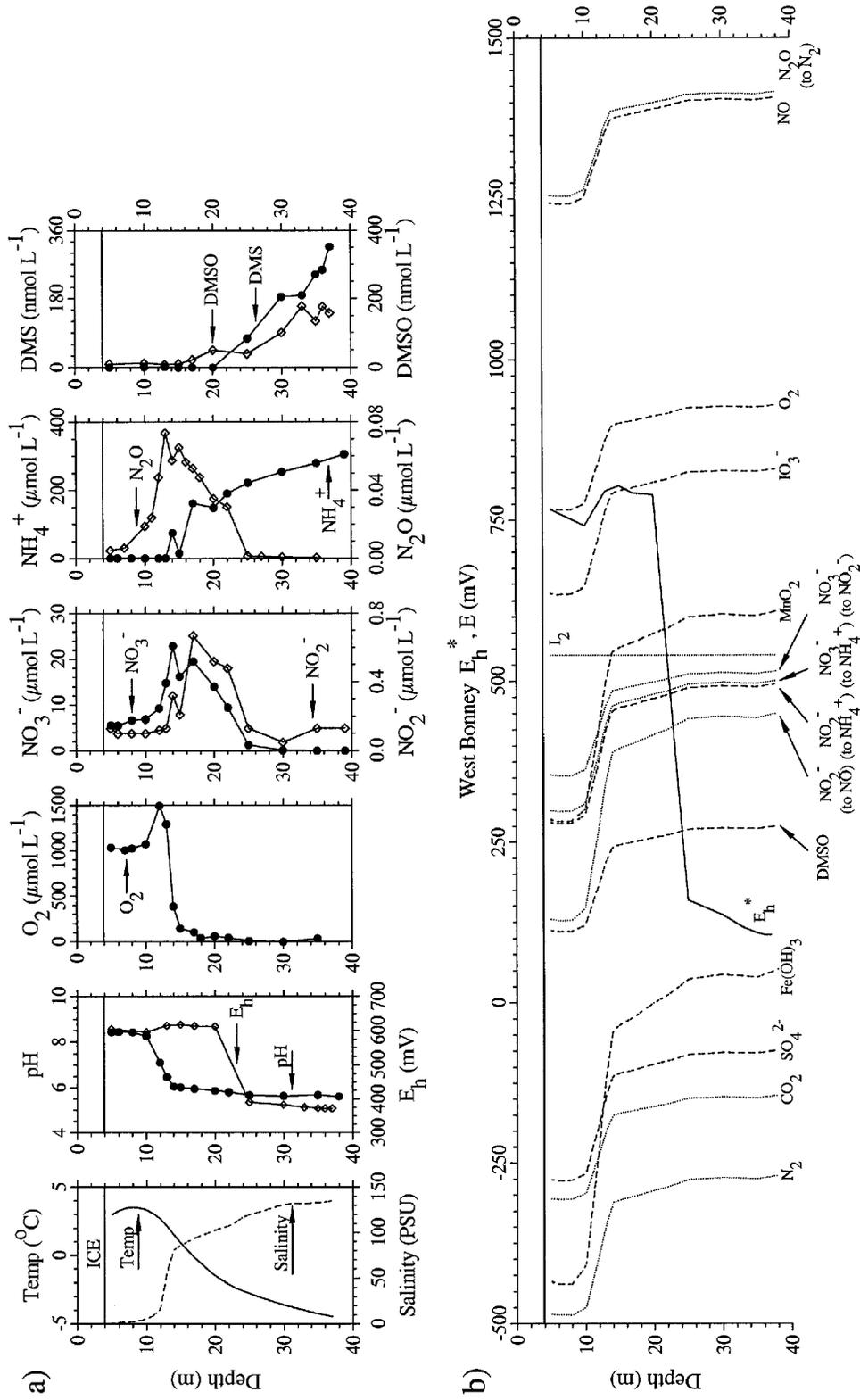


Figure 1. West Bonney. (a) Vertical profiles of temperature and salinity, pH and E_h , dissolved oxygen, nitrate and nitrite, ammonium and N_2O , and DMS and DMSO . (b) Vertical profiles of the calculated reduction potential (E) for selected reactions under consideration and derived E_h^* .

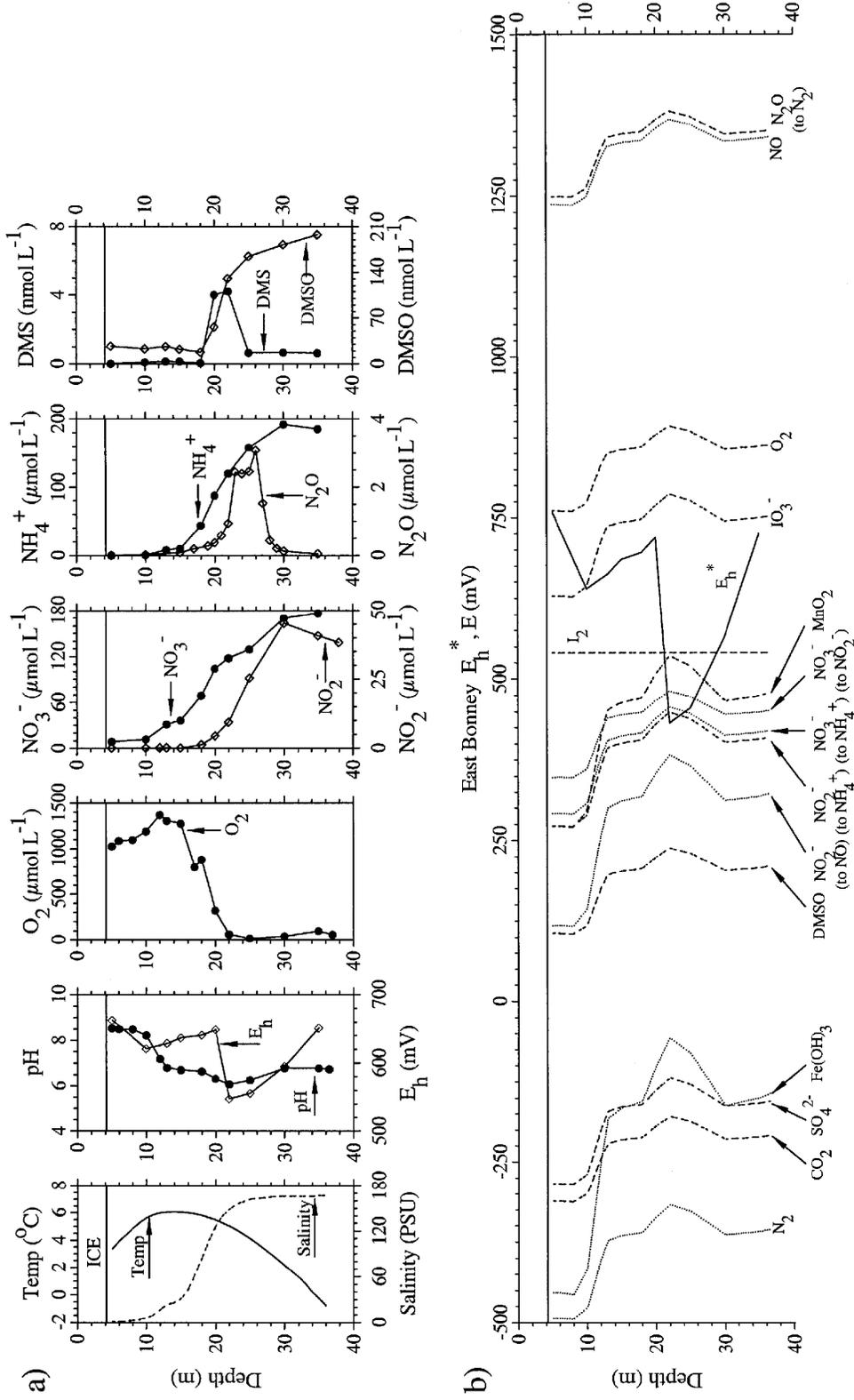


Figure 2. East Bonney. (a) Vertical profiles of temperature and salinity, pH and E_h , dissolved oxygen, nitrate and nitrite, ammonium and N_2O , and DMS and DMSO_d . (b) Vertical profiles of the calculated reduction potential (E) for selected reactions under consideration and derived E_h^* .

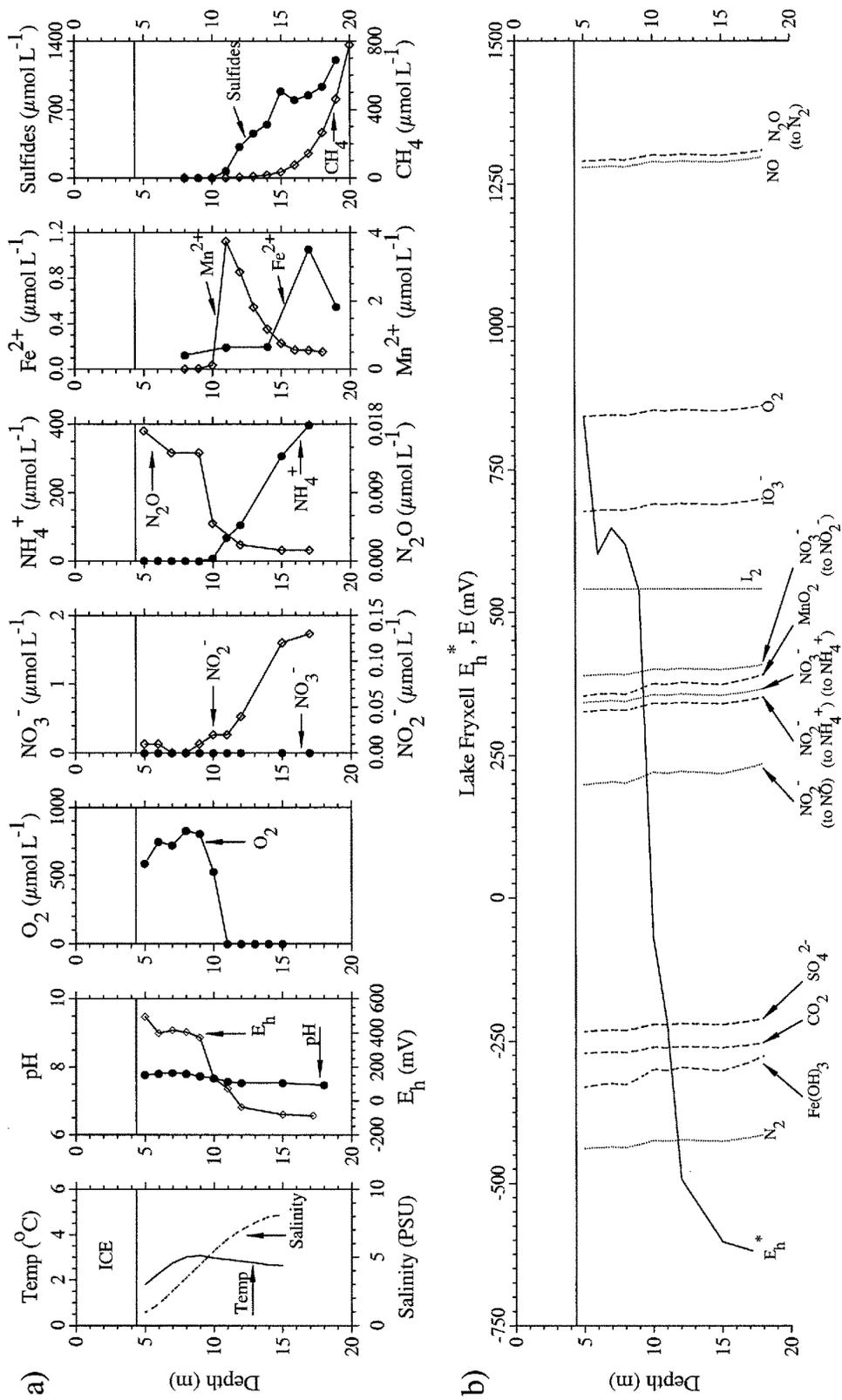


Figure 3. Lake Fryxell. (a) Vertical profiles of temperature and salinity, pH and E_h and E_h^* , dissolved oxygen, nitrate and nitrite, ammonium and N_2O , Fe (II) and Mn (II), and sulfides and methane. (b) Vertical profiles of the calculated reduction potential (E) for selected reactions under consideration and derived E_h^* .

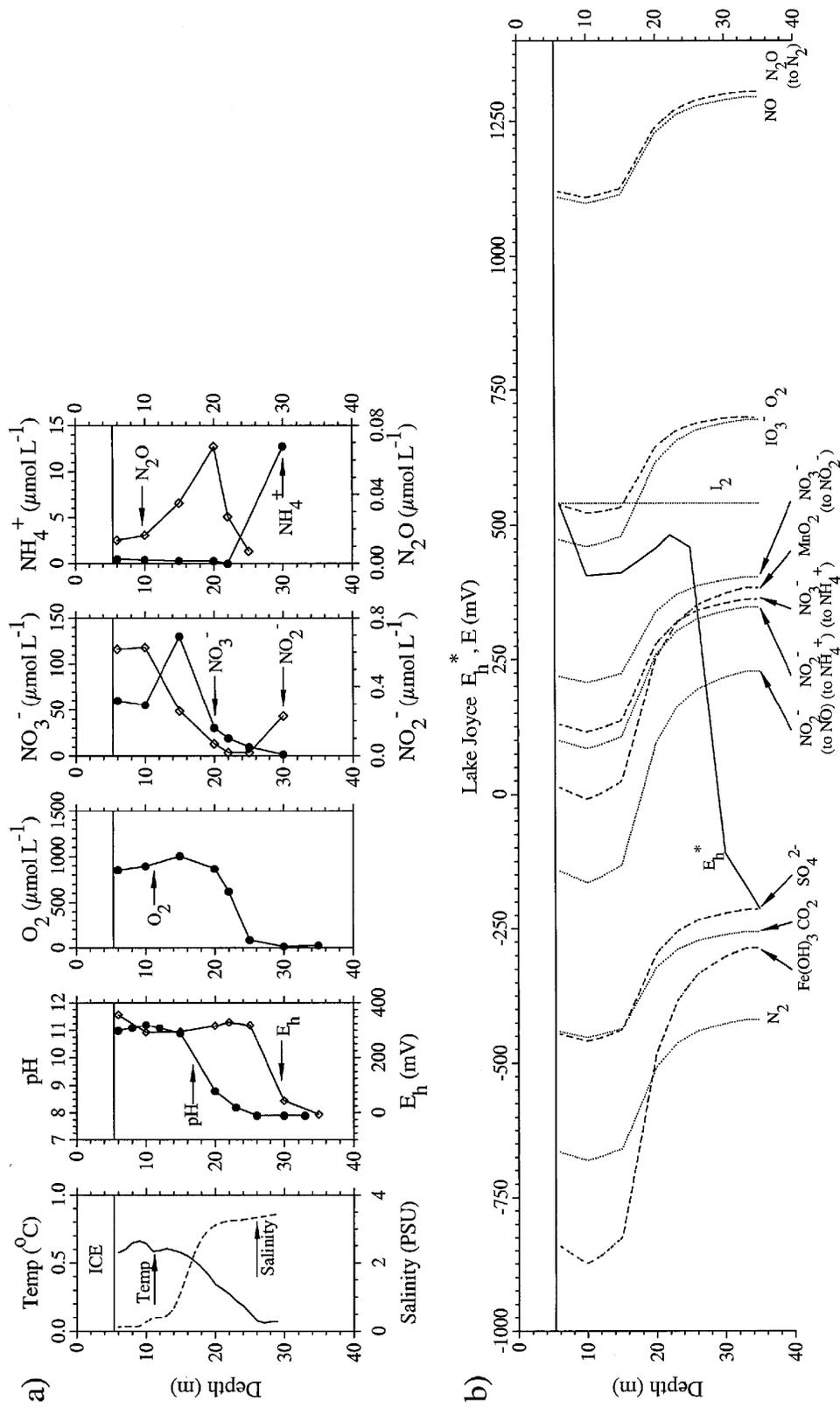


Figure 5. Lake Joyce. (a) Vertical profiles of temperature and salinity, pH and E_h , dissolved oxygen, nitrate and nitrite, and ammonium and N_2O . (b) Vertical profiles of the calculated reduction potential (E) for selected reactions under consideration and derived E_h^* .

195 elsewhere (Lee et al. in press). In brief, water samples were
 collected with a 5 L Niskin bottle and transferred to sample bot-
 200 tles with silicon rubber tubing. At all stages of sampling, care
 was taken to avoid the loss of DMS through degassing. Sub-
 samples for the analysis of DMS were transferred to 125 mL
 205 Wheaton serum bottles, which were filled to capacity, and im-
 mediately sealed with butyl rubber stoppers and aluminum crimp
 seals. DMS concentrations were determined using previously
 described cryogenic purge-and-trap techniques and instrumen-
 210 tation (DiTullio and Smith 1995; Cantin et al. 1996; de Mora
 et al. 1996). Subsamples for DMSO_d were transferred to 1 L
 HDPE Nalgene bottles for return to the field laboratory where
 they were filtered through a Whatman GF/F filter. Some sam-
 ples were analyzed in a field-based laboratory, with aliquots
 of all DMSO_d samples being stored for subsequent analysis at a
 university-based laboratory. All DMSO_d samples were analyzed
 as DMS following the reduction of DMSO to DMS using the
 sodium borohydride method (Simó et al. 1996).

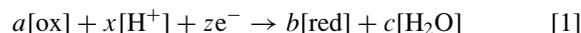
E_h Measurements

215 *E_h* measurements were carried out following the same
 methodology used by Downes and Priscu (1995; J. Priscu pers.
 comm). This procedure was undertaken to maximize the de-
 gree of compatibility between this study and that of Downes
 and Priscu (1995). Subsamples for *E_h* analyses were taken from
 220 bulk samples collected with a 5 L Niskin bottle. The aliquots of
 water for the subsamples were transferred to sample bottles with
 silicon rubber tubing to avoid contact with air, as one would for
 the analysis of dissolved gases. Measurements of *E_h* were made
 within minutes of sample collection using a Hach Oxidation-
 225 Reduction Potential (ORP) combination electrode (Hach Com-
 pany, Loveland, CO) connected to a Beckman Φ12 digital *pH*
 meter, with the appropriate corrections being made for the refer-
 ence electrode in accordance with the ORP electrode instruction
 manual. Following the recommendations of Whitfield (1969),
 230 the *E_h* readings were made after the meter's readout had been
 allowed to stabilize for several minutes but before the readout
 began to drift. The accuracy of the ORP electrode was checked
 against a Fe³⁺/Fe²⁺ standard solution described in the electrode
 instruction manual. Data for *E_h* in both lobes of Lake Bonney
 235 were collected during the 2000–2001 austral summer. *E_h* mea-
 surements in Lake Fryxell were made during the 2001–2002
 austral summer. Data for *E_h* in Lakes Vanda and Joyce were
 taken from Downes and Priscu (1995) and Priscu (1997).

Calculation of Thermodynamic Parameters and Reduction Potentials

240 The stoichiometries, chemical standard-state Gibbs free en-
 ergies (ΔG°) and reduction potentials (E°) for the reactions
 considered in this study are given in Table 1 for the nitrogen-
 containing reactions (Reactions R1–R10) and in Table 2 for the
 nonnitrogen reactions (Reactions R11–R18). Since some read-
 245 ers may be more familiar with thermodynamic parameters based

on biological standard-state conditions (*pH* 7), values for Gibbs
 free energies and reduction potentials calculated to this standard
 ($\Delta G^{\circ'}$ and $E^{\circ'}$) are also given in Tables 1 and 2. For the general
 reaction:



(where *a*, *b*, *c*, and *x* are respectively, the number of moles
 250 of the oxidized (ox) species, reduced (red) species, water, and
 hydrogen ions involved), values for in situ Gibbs free energies
 (ΔG) for the water column of the lakes were derived using insitu
 temperature and *pH* data according to the following simplified
 255 Nernst-type relationship:

$$\Delta G = \Delta G^\circ + RT \ln([10^{-\text{pH}}]^x) \quad [2]$$

where *R* is the gas constant and *T* is the absolute temperature
 (K). Conversions between Gibbs free energies and reduction
 potentials were made using the relationship:

$$E^\circ = \frac{-\Delta G^\circ}{zF} \quad [3]$$

where *z* is the number of electrons involved in the reaction and
 260 *F* is the Faraday constant.

For further details regarding thermodynamic equations and
 concepts, including the electromotive force diagrams described
 in the discussions section, readers are referred to introductory
 books such as Smith (1990) and Richet (2001), or more advanced
 265 chemistry texts such as Laidler and Meiser (1982) and Shriver
 et al. (1994).

RESULTS

E_h Measurements and E Calculations

The vertical profiles for the *E_h* measurements made during
 this study are presented in panel “a” of Figures 1 through 3
 270 for West Bonney, East Bonney, and Lake Fryxell, respectively.
 Although there were some differences between the values of
E_h measured in this study and previous studies (Downes and
 Priscu 1995; Priscu 1997), the general trends observed in the
 profiles were similar. The differences may arise for several rea-
 275 sons. Whitfield (1969) suggests that while the precision of *E_h*
 measurements can be as low as ±10 mV, it is more typically
 in the order of ±50 mV. Thus, a high degree of reproducibility
 between separate studies could be difficult to achieve. Spatial
 280 and temporal differences could also have produced this varia-
 tion, particularly given the sharp gradients and the changes that
 have been observed in lake level, ice thickness, glacial inflow
 and primary productivity (Doran et al. 2002). The vertical pro-
 files for *E_h* taken from the literature for Lakes Vanda and Joyce
 285 are shown in Figures 4a and 5a, respectively. The results for the
 calculations of the in situ reduction potential for the reactions
 under consideration in each lake are presented in panel “b” of
 Figures 1 through 5.

Derivation of E_h^* Values

290 For the comparison between the estimated values of E and
 the measured values for E_h , the onset of sulfide formation (in
 Lakes Vanda, Fryxell and Joyce at depths of 67, 11, and 36 m re-
 spectively) and Mn^{2+} formation (at 57 m in Lake Vanda and 9 m
 in Lake Fryxell) were used as known marker points. The reduction
 295 of oxygen was also used as a marker point. It was assumed
 that the onset of the reduction of oxygen occurred immediately
 at the top of the water column. Dissolved oxygen was always
 present at high levels in the upper water column and in a vertical
 sense, this is the first point where microorganisms would have
 oxygen available as a terminal electron acceptor for respiration.
 300 The estimated values of E and the measured E_h values for the
 marker points for the three lakes are plotted in Figure 6. For each
 lake, a best-fit straight line was fitted to the data:

305 For Lake Vanda, $E_h^* = 3.94E_h - 1583.51$
 For Lake Fryxell, $E_h^* = 2.41E_h - 425.02$
 For Lake Joyce, $E_h^* = 2.07E_h - 201.57$

310 These equations are referred to as E_h^* functions and were
 used to scale the E_h profiles. The resulting E_h^* profiles were
 then compared to the estimates of the reduction potentials for the
 other ecologically important equations examined in this study
 to assess their thermodynamic favorableness. Because of the
 errors typically involved in the measurement of E_h , the slopes

of the above equations were not considered to be different to
 each other. For Lake Bonney, where sulfides are not present, the
 E_h^* functions were generated by combining the average slope 315
 of the above equations with the marker points for the onset of
 oxygen reduction. The derived functions were:

For West Bonney, $E_h^* = 2.81E_h - 933.05$
 For East Bonney, $E_h^* = 2.81E_h - 1103.03$

320 The E_h^* results derived from these calculations are plotted in
 Figure 1b for West Bonney, Figure 2b for East Bonney, Figure 3b
 for Lake Fryxell, Figure 4b for Lake Vanda and Figure 5b for
 Lake Joyce. Based on the results of the E_h^* calculations, a series
 of predictions were made as to when several of the reduction 325
 reactions considered in this study should become thermodynamically
 favorable in the five lakes. Predictions are presented for the
 onset of the reduction of iodate, manganese dioxide, iodine and
 the onset of methanogenesis (Table 3). Further discussion
 on these predictions is presented next.

DISCUSSION

330 As indicated earlier, the use of E_h measurements in the quan-
 titative analysis of natural waters is problematic as a result of
 natural waters generally being non-equilibrium systems that
 are best described by dynamic models rather than equilibrium

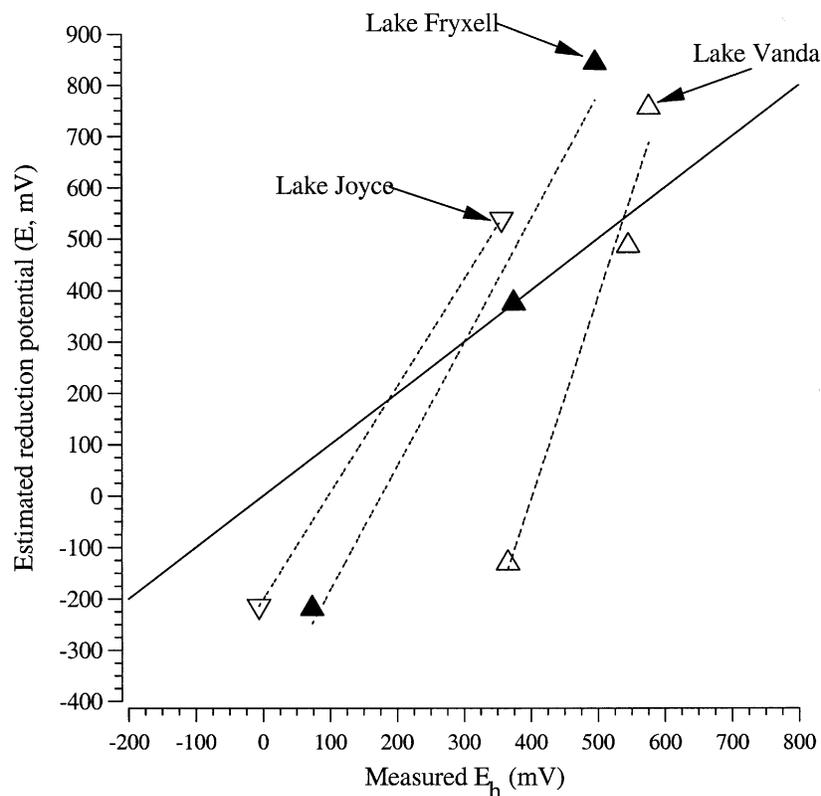


Figure 6. Relationships between the measured E_h values and estimated values of E for Lakes Vanda, Fryxell and Joyce. The solid line represents the 1:1 relationship between the x- and y-parameters.

Table 3Predictions made using the E_h^* approach for various ecologically important redox species in the lakes of the McMurdo Dry Valleys

Lake	Reduction product				
	Mn ²⁺ (Reaction 12)	I ₂ (Reaction 13)	Fe ²⁺ (Reaction 14)	I ⁻ (Reaction 16)	CH ₄ (Reaction 18)
West Bonney	>22 m	>16 m	Not present	>23 m	Not present
East Bonney	21–27 m	>10 m	Not present	21–29 m	Not present
Fryxell	—	>6 m	>11.5 m	>9 m	>11.5 m
Vanda	—	>9 m	>65 m	>55 m	>68 m
Joyce	>26 m	>6 m	Not present	>6 m	Not present

The 'greater than' symbol is used in the sense of 'deeper than'. 'Not present' indicates that the reduction will not be observed in the water column. The '—' indicates that no predictions are made for these species as they are used to derive the E_h^* functions.

335 models (Whitfield 1969; Lindberg and Runnells 1984; Stumm
and Morgan 1995). However, the objective of this study was to
use E_h measurements to identify regions where certain chemical
species, such as N₂O, might be present due to microbial activity
instead of accurately modeling the observed concentrations of
those compounds (i.e. the analysis is qualitative in nature and
340 not quantitative). Several initial assumptions or approximations
were required for the implementation of the analysis presented
in this study. Motion in the water columns of dry valleys lakes is
predominantly through molecular diffusion (Spigel and Priscu
1998) and thus the lakes can be treated as being in approximate
345 redox equilibrium (Stumm and Morgan 1995). Such equilibrium
arguments are a useful means for understanding or predicting
the redox patterns observed in aquatic environments, and for es-
tablishing boundary conditions that the system must be moving
toward (Stumm and Morgan 1995). As a consequence, the lake
350 system at any point is assumed to be controlled by a single redox
couple (and potential) even though it is likely that two or more
redox couples may be combining to produce *mixed potentials*
(Stumm and Morgan 1995).

355 While some redox pairs may not be electroactive and there-
fore do not influence E_h (Whitfield 1969; Stumm and Morgan
1995), the succession of microbially mediated redox reactions
will still follow the decrease in E_h . Yet the ecological suc-
cession of microorganisms and the chemical redox sequence are
360 linked circularly such that although a given redox pair may not
be electroactive, any decrease in E_h results from the depletion
of the oxidant species in the preceding redox pair through micro-
bial activity. The ecological succession of microorganisms that
parallels the chemical redox sequence dictates that once the pre-
ceding redox couple has become exhausted, a different group
365 of bacteria will begin to utilize the next available redox couple.
This different group of bacteria may include bacteria that might
mediate several redox pairs or it might include completely new
species of bacteria. In the case of facultative oxygen utilizing
bacteria, they will switch respiratory modes, using an alternate
370 electron acceptor. To overcome the fact that reversible electrode
potentials have not been established for the NO₃⁻-NO₂⁻-NH₄⁺-
H₂S or CH₄-CO₂ systems (Stumm and Morgan 1995), electrode

potentials for individual redox couples were taken from standard
data tables (Milazzo and Carol 1978) or evaluated indirectly us-
ing Gibbs free-energy data (Amend and Shock 2001). 375

Finally, concentration terms for the oxidant and reductant
species were not included in the Nernst equation used to esti-
mate the redox potentials since concentrations of many of the
redox species involved were not known. In some cases, such as
NO and N₂, no values were known while in other instances, such
380 as Fe, Mn, or methane, concentrations are only available for a
limited number of lakes. Although elimination of the concen-
tration terms from the Nernst equation could affect the overall
result of the calculation, the effect is likely to be small in general.
In Lake Bonney, the computed redox potentials for the reduction
385 of oxygen and sulfate, which are the two primary markers used
to scale the E_h measurements, would change by less than 65
and 20 mV, respectively, if the concentration terms are ignored.
Moreover, Lindberg and Runnells (1984) point out that a 1,000-
fold change in the ratio of sulfate to H₂S will result in a change of
390 only 20 mV in the computed E_h . Computed redox potentials for
the nitrogen-based reactions (Table 1) would change by less than
125 mV based on the concentrations present in Lake Bonney.
Overall, the presence of the concentration term for the oxidant
species would increase the computed E_h , whereas the presence
395 of the concentration term for the reductant species would de-
crease the computed E_h . Consequently, the effect of the two
terms would cancel when the concentrations of the oxidant and
reductant species were in the appropriate ratio. It is worth not-
ing that the sequence of redox reactions predicted by this study
400 for each lake are very similar to other sequences that have been
derived using traditional and more complex thermodynamic cal-
culations (Stumm and Morgan 1995; Rue et al. 1997).

The Case of Dimethylsulfoxide

405 The distributions of DMS and DMSO_d in each lobe of Lake
Bonney are highly contrasting and unusual. In the bottom waters
of the west lobe, average DMS concentrations were as high as
317 nmol L⁻¹ with average DMSO_d levels reaching 178 nmol
L⁻¹ (Figure 1a). Conversely, in the bottom waters of the east

410 lobe, average DMS concentrations were considerably lower (up
to 5 nmol L⁻¹) while higher DMSO_d concentrations (198 nmol
L⁻¹) were observed (Figure 2a). These concentrations are un-
usual in that they occur in a region of the lake that is devoid
415 of primary productivity. The DMS levels in the west lobe are
considerably higher than those typically measured in marine
environments that do not contain ice-algal diatoms, *Phaeocys-
tis* sp. or dinoflagellates (DiTullio and Smith 1995; Matrai and
Vernet 1997; Kettle et al. 1999). However, they are not unusual
for high-salinity terrestrial environments (Richards et al. 1994;
420 de Mora et al. 1996). DMSO_d concentrations in both the east
and west lobes are amongst the highest concentrations that have
been observed (Lee et al. 1999; Bouillon et al. 2002).

A previous study has pointed out that in the east lobe, ox-
idized forms of nitrogen (nitrate and nitrite) are present whereas
425 in the west lobe only reduced nitrogen (ammonium) is found
(Downes and Priscu 1995). Downes and Priscu suggested that
the difference in nitrogen species was a result of the differences
in the redox environments of the bottom waters of each lobe.
Wood (1981) stated that reduction potential for the DMSO/DMS
430 couple was similar to that of the nitrate/nitrite couple. Thus, the
implication is that the redox environments of each lobe might
also influence DMSO_d and DMS, as is the case for nitrogen.

The redox conditions of the west lobe are more reducing
than that of the east lobe with E_h levels of 325–400 mV in the
435 lower layer of the west lobe (Figure 1a) and 550–650 mV in
the bottom waters of the east lobe (Figure 2a). Estimates of E
for the reduction of DMSO to DMS (R14, Table 2) when cal-
culated for the in situ pH and temperature conditions present
in the lower layer of each lobe are marginally higher in the
440 west lobe (250–300 mV; Figure 1b) than in the east lobe (200–
230 mV; Figure 2b). This combination of electrochemical factors
would appear to make the reduction of DMSO thermodynamically
more favorable for bacteria in the west lobe than the east
445 lobe. Using the E_h^* approach yields unequivocal results for this
supposition. Results for West Bonney (Figure 1b) show that
the reduction of DMSO becomes thermodynamically favorable
below approximately 22 m, which corresponds closely to the
depth at which DMS begins to accumulate. In contrast to this,
450 the results for East Bonney (Figure 2b) show that the reduc-
tion of DMSO to DMS remains thermodynamically unfavorable
throughout the entire water column.

These results have some important ramifications for the bio-
geochemistry of DMSO. Studies have shown that DMSO can
be used as an electron acceptor or energy source by a variety
455 of aerobic and anaerobic bacteria (Zinder and Brock 1978a; De
Bont et al. 1981; Jonkers et al. 1996) and be reduced chem-
ically by sulfides (Zinder and Brock 1978b). Consequently, it
has been argued that in oceanic environments, DMSO might
be reduced to DMS thereby acting as a source for DMS in the
460 marine sulfur cycle. The findings of our study provide a con-
straint to that argument. In well-oxygenated environments, such
as the surface of the world's oceans, the microbial reduction of
DMSO to DMS is unlikely to be an important pathway for the

formation of DMS due to the fact that the use of DMSO as an
electron acceptor is not thermodynamically favorable. The ubiq-
465 uity and relatively high levels of DMSO_d that are observed in
many aquatic environments (Lee et al. 1999) could result from
this thermodynamic constraint. Furthermore, thermodynamics
alone could explain why large decreases in DMSO_d concen-
470 trations are not accompanied by relatively large increases in
DMS concentrations during incubation experiments (Lee 1999;
Simó et al. 2000). However, the accumulation of DMS may
not be observable if the production and consumption of DMS
are very tightly coupled or bacteria retain DMS for reduction to
475 sulfide (Simó et al. 2000). Clearly, additional experiments focus-
ing on the direct transformation of DMSO (e.g. involving ³⁵S-
DMSO) are required to determine which of these hypotheses is
correct.

The Case of Nitrous Oxide—Denitrification

One of the key findings of studies examining the biogeo-
480 chemistry of N₂O in Lake Bonney is that despite the presence of
denitrifying bacteria in both lobes of the lake, denitrification is
absent in the east lobe but occurs in the west lobe (Priscu 1997;
Ward and Priscu 1997). This absence is thought to allow the
build-up of N₂O through nitrification (Priscu 1997; Voytek et al.
485 1998). Analysis of the E_h^* results provides a partial explanation
for these observations. The results show that the denitrification
steps leading to N₂O are thermodynamically unfavorable in the
east lobe (Figure 2b). Although the reduction of nitrate to nit-
rite is thermodynamically favorable at depths between approx-
490 imately 22 and 27 m, the subsequent step from nitrite to NO
is unfavorable throughout the entire water column. In the west
lobe, all denitrification steps become favorable at depths below
22 m (Figure 1b).

The results also show that in all circumstances (Figures 1–
495 5b), E for the reduction of N₂O (R1) is always greater than that
of oxygen (R11) indicating that there is no thermodynamic con-
straint to the loss of N₂O. The same is true for the reduction
of NO (R2). The values of E for the reduction of N₂O and NO
500 are relatively large positive numbers which in turn means that
 ΔG values for those reactions are negative and thus the reac-
tion is exergonic. Coupling the reduction of NO or N₂O to the
oxidation of organic matter, for example, would therefore fur-
nish bacteria with a very favorable source of energy (Conrad
505 1996). This finding would suggest that there is a biochemical or
physiological explanation for the accumulation of N₂O. Bonin
et al. (2002) point out that the reductase for N₂O is the most
oxygen-sensitive enzyme involved in the sequential denitrifica-
tion process. Under low oxygen conditions, N₂O can be the fi-
510 nal product in the denitrification sequence rather than N₂. Thus,
the suboxic conditions that exist in East Bonney may have a
two-fold effect on the denitrification process. First, redox con-
ditions are poised at a level that makes the formation of N₂O
via denitrification thermodynamically unfavorable. Second, the
515 loss of N₂O via denitrification is inhibited, which provides an

explanation for the persistence of the high N_2O concentrations in the east lobe.

Priscu (1997) proposed that certain chemical gradients, including that of N_2O , in the lakes of the dry valleys might be a legacy of the processes that led to the formation of the present day geophysical setting of these lakes. Some of the lakes may have lost their ice caps and been subject to drastic volume reduction through historic dry-down processes (Lyons et al. 1998; Lyons et al. 2000). In the case of Lake Bonney, it has been suggested that the east lobe became isolated the Taylor Glacier, which is now the primary source of water to Lake Bonney. Although the east lobe subsequently refilled, the isolation created a different recent history for the bottom waters of the east lobe and presumably caused the differences in E_h values observed in the two lobes of contemporary Lake Bonney.

Comparison of the E_h^* results with the known distributions of several compounds suggests that the current redox conditions present in several of the lakes are different from historical redox conditions. Furthermore, the differences between historical and current conditions do not reflect a change to more reducing conditions as would be expected from the depletion of oxidants through microbial consumption. The E_h^* results for East Bonney show that most reduction reactions, including the reduction of nitrate, are thermodynamically unfavorable at most depths in the water column (Figure 2b). However, chemical analysis shows that both nitrite and ammonium are present, particularly outside the 21–27 m depth range where the reactions are favorable (Figure 2a). For example, the results for the west lobe indicate that the reduction of nitrate to nitrite and ammonium are only favorable below 22 m (Figure 1b) yet the onset of the accumulation of these two compounds occurs at approximately 13 m. In Lake Fryxell, the thermodynamic calculations suggest that nitrate reduction should only be favorable below 10 m (Figure 3b) whereas the actual accumulation of ammonium and nitrite starts at 8–9 m (Figure 3a).

An idea of the historical E_h conditions that might have existed in some of the lakes can be estimated in part from the observed distributions of nitrite and ammonium. The relatively high E_h conditions at mid-water-column depths create a bulge in the E_h (and E_h^*) profiles that coincides with, and most likely results from, elevated concentrations of dissolved oxygen. Craig et al. (1992) found that as new lake ice forms from stream-feed meltwater, oxygen is excluded from the ice matrix and released into the water column thereby elevating dissolved oxygen levels. About 90% of the oxygen in the upper layers results from this abiotic process with the remainder coming from primary production. With the perennial ice-cover in place, the water column cannot equilibrate with the atmosphere and oxygen can accumulate to saturation levels well in excess of 100% air saturation. Thus, the build-up of oxygen and resulting bulge in the E_h profile has occurred since the last ice-free period. Assuming that the bulge in the E_h profile is a relatively recent feature, a line can be drawn from the minimum in the near-surface E_h^* profile through the profiles of E for nitrate-ammonium and

nitrate-nitrite at the point at which the onset of nitrite and ammonium are observed (Figure 7). This line would represent potential historical conditions. For Lakes Fryxell and Joyce, the line rejoins the actual E_h^* profile. In the case of Lake Bonney, the estimate of the historical E_h^* does not rejoin the actual E_h^* profile. Given that sulfate reduction does not occur in Lake Bonney, the historical estimate of E_h^* is not likely to fall below 100–200 mV and the historical line is adjusted to take this into account.

Interestingly, in all four lakes shown in Figure 7, the observed peak for N_2O closely corresponds to the point at which the line for the historical E_h^* intersects the reduction potential profile for the reduction of nitrite to NO, which suggests that the N_2O peaks in these lakes are not contemporary features. It is also intriguing that the zone forming the E_h minimum in East Bonney corresponds to the location of the N_2O peak. Conversely, the E_h^* profile for Lake Vanda (Figure 4b) reveals that the depth at which the reduction of nitrite becomes thermodynamically favorable closely equates to the depth of the N_2O peak (Figure 4a). In Lake Vanda, there is also very little difference between the actual distributions of nitrate, nitrite and ammonium, and the distributions predicted by the reduction potentials and E_h^* profile. We interpret this observation to mean that current redox conditions and not different, historical conditions caused the observed distribution of these compounds in Lake Vanda.

The idea that the overall thermodynamic favorableness of the denitrification sequence leading to N_2O is related to the thermodynamic favorableness of the reduction of nitrite to NO does make sense. Examination of the electromotive force diagram for the denitrification sequence at chemical standard-state conditions (i.e. $p\text{H } 0$, $T = 25^\circ\text{C}$) indicates that the least favorable step is the reduction of nitrate to nitrite:



However, if the reduction potentials are recalculated for ecologically more relevant conditions for the water columns of the lakes (i.e. $p\text{H } 7$, $T = 0^\circ\text{C}$) then it is the reduction of nitrite to NO that becomes the thermodynamically least favorable step:



Thus, this provides bacteria with a thermodynamic constraint in that the reduction potential of the water column has to be low enough to allow the reduction of nitrite to NO to take place before the denitrification sequence and the formation of N_2O can occur.

The Case of Nitrous Oxide—Nitrification

The link between the thermodynamic favorableness of the nitrite reduction step and E_h of the water column only partially explains the origin of the N_2O peak. The foregoing discussion deals with denitrification whereas the formation of N_2O can

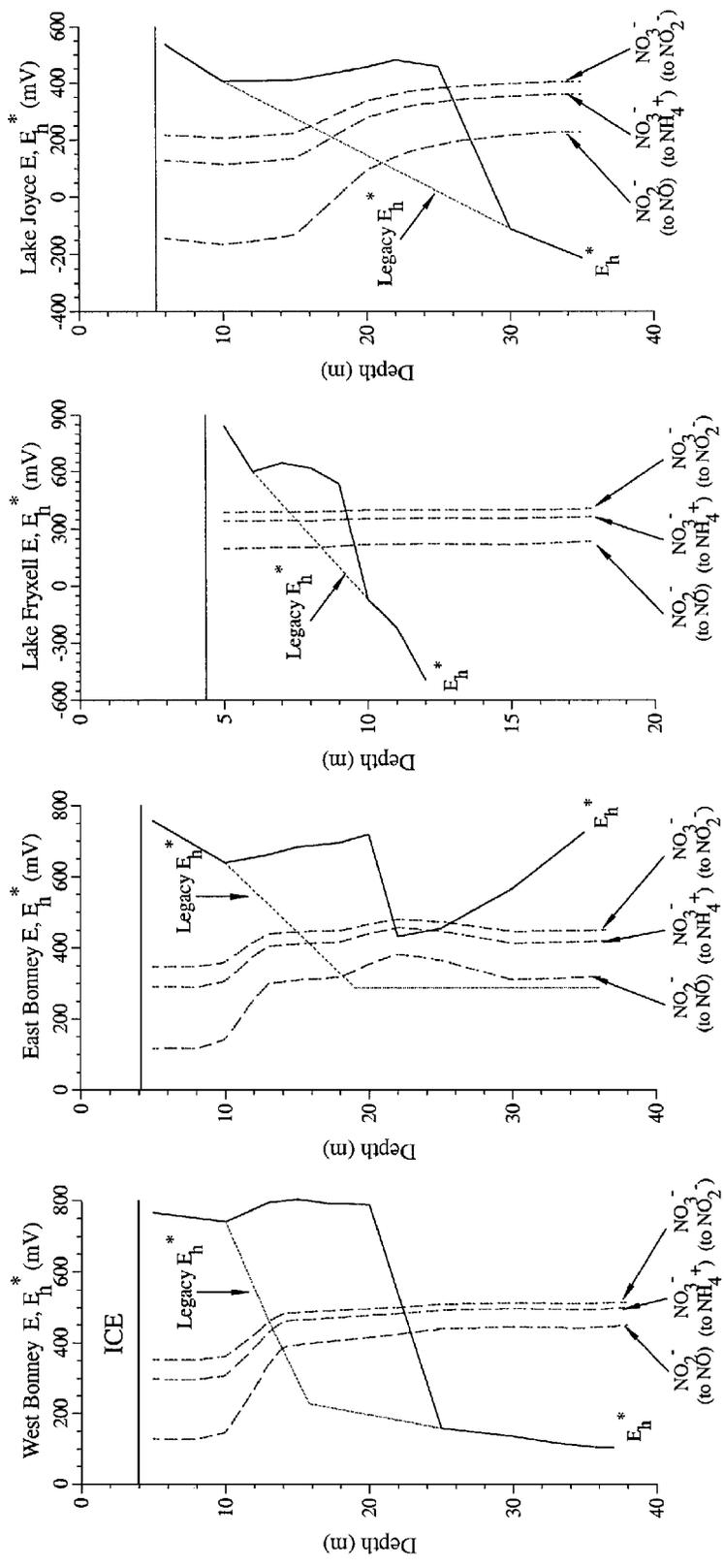


Figure 7. Estimates of historical (legacy) E_h conditions in West Bonney, East Bonney, Lake Fryxell and Lake Joyce.

605 also occur through nitrification via two pathways. First, ammonium is oxidized to N_2O (reverse of R9) instead of nitrite by ammonium-oxidizing bacteria (reverse of R6, Conrad 1996; Hapogian and Riley 1998; Bonin et al. 2002). N_2O can also be formed through incomplete nitrification. Here, nitrifying bacteria reduce nitrite to N_2O (Conrad 1996; Hapogian and Riley 1998; Bonin et al. 2002). This could potentially occur via R3 coupled to the reverse of R6 or R7. In order to assess the thermodynamic favorableness of these processes, a slightly different approach to that employed for the reduction reactions is used. Profiles of Net Gibbs free energies for the nitrification reactions described above were calculated for four lakes (West Bonney, East Bonney, Fryxell, and Vanda) to determine if these reactions were endergonic or exergonic. The results revealed that the reactions are exergonic, and therefore thermodynamically favorable, throughout the entire water column of each of the lakes.

615 Denitrification and nitrification can also occur simultaneously via a coupled, anaerobic lithotrophic pathway (Hulth et al. 1999). In this scenario, loss of nitrate results from R4 coupling to the reverse of R12 and nitrate forms from the coupling of R12 to the reverse of R7. However, a survey of the literature failed to reveal if this reaction sequence leads to the formation of N_2O through incomplete nitrification. It would certainly make additional nitrate available for sequential reduction to N_2O if there was net production of nitrate. In general, our study focuses on the use of the oxidant species as an electron acceptor for the oxidation of organic matter and does not address in detail possibilities where other reductant species, such as ammonium, Fe^{2+} and sulfides, are the electron donors. Hulth et al. (1999) contend that these processes will be of greatest importance in environments where oxidant-rich material is rapidly mixed into suboxic zones through physical mixing or bioturbation. These processes may have been important in the dry valleys lakes during periods when the dry valleys lakes had no ice cover and could be mixed through wind-induced turbulence. Since only diffusion-dominated motion is currently present in the bottom waters of the lakes and few benthic metazoans are present these lakes, these processes would not be favored. Without renewal of the oxidant species, they would become depleted and their impact would decline with time.

645 The historical redox conditions that might have existed in the lakes may also have an influence on nitrification processes. Goreau et al. (1980) and Bonin et al. (2002) point out that high concentrations of ammonium or low concentrations of oxygen, or a combination of both, enhance N_2O production via nitrification. If historical redox conditions were more reducing than current conditions, this would have allowed for the formation of ammonium as dissimilatory reduction of nitrate will be the first of the nitrogen reduction reactions to occur. Since more reducing conditions would have also meant lower oxygen levels, this may have set up the conditions described by Bonin et al. (2002) for the enhanced production of N_2O . As oxygen levels began to build up and the redox environment became less reduc-

660 ing, the formation of ammonium would have become unfavorable and the production of N_2O from ammonium would have declined.

665 It is worth noting that if the intersection of the reduction potential profile for nitrite and the E_h^* profile corresponds approximately to the N_2O maximum rather than the depth where its concentrations begin to increase as is the case for the formation of Mn^{2+} or H_2S , then the upper portion of the peak must result solely from nitrification. Above the crossover point, denitrification is thermodynamically unfavorable. Since the dissimilatory reduction of nitrate to ammonium occurs ahead of the reduction of nitrate to nitrite (i.e. the first step of denitrification; Figures 1–5b), ammonium is potentially available for nitrification before denitrification can begin. Below the crossover point, both denitrification and nitrification can take place.

675 This contention, in concert with those made in preceding paragraphs, successfully explains the findings of Vincent et al. (1981) for the cycling of N_2O in Lake Vanda. These authors found that the highest levels of N_2O occurred at depths where there was high nitrification potential and a lack of denitrification. They concluded that the source of N_2O was nitrification. This is entirely consistent with the initial stages of denitrification being thermodynamically unfavorable in the upper portion of the N_2O peak, leaving nitrification as the only pathway for the formation of N_2O . As the water column in Lake Vanda transitioned to anoxic conditions, Vincent et al. (1981) observed that N_2O concentrations declined and was coincident with measurable rates of denitrification. Once anoxia occurred, there are no thermodynamic restrictions to prevent the formation of N_2O through denitrification and more importantly, the loss of N_2O by denitrification cannot be inhibited by the presence of oxygen. With respect to nitrification, the formation of N_2O as a result of incomplete nitrification cannot take place in the anoxic layer since there is no oxygen present. Some N_2O may still be produced as a result of the oxidation of ammonium coupled to the reduction of nitrite to N_2O (the reverse of R6 or R7 coupled to R3) while nitrate and nitrite remain present. This general scenario is similar to that discussed by Naqvi et al. (2000) in continental shelf waters.

Predications and Precautions Using the E_h^* Approach

700 In a study of the geochemistry of methane in Lake Fryxell, Smith et al. (1993) found that methane was ubiquitous throughout the anoxic region of the lake. The predication made in this study using the E_h^* method is consistent with this finding (Table 3). However, Smith et al. (1993) also observed no measurable methane production in the water column of the lake and suggested that the lake sediments were the origin of the methane. Experimentally, they found that the lack of measurable methane production was not limited by substrate availability. The results of this study indicate that the lack of methane production was not due to thermodynamic constraints.

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Some caution is also required when interpreting results made using the E_h^* approach. Predicting the onset of the reduction of Fe^{3+} can be problematic. Both Fe^{3+} and Fe^{2+} can react rapidly with H_2S . The E_h^* predictions (Table 3) show that the onset of Fe^{3+} reduction should occur at a depth of 11.5 m in Lake Fryxell, whereas the presence of sulfides is observed at a depth of 11 m (Figure 3a). The chemical formation of iron sulfides will mask the microbially mediated formation of reduced Fe. The Fe data currently available in the literature for Lake Fryxell (Green et al. 1989) does not provide an unequivocal response to this observation. Green et al. (1989) have reported a maximum in 'dissolved' Fe at approximately 17 m (Figure 3a) but point out that this may be an artifact that is related to the use of a 0.45 μm filter rather than a 0.2 μm filter. These authors do, however, suggest that control of Fe by sulfide phases should occur below 11 m.

In the case of Lake Vanda, the reduction of $Fe(OH)_3$ to Fe^{2+} is predicted to occur at 65 m (Table 3), which is before the reduction of sulfate at 67 m (Figure 4a). Thus, it may be possible to detect the presence of Fe^{2+} in an approximately 1–2 m thick layer in the suboxic region above the anoxic zone. But once again, the data currently available in the literature for the distribution of Fe in Lake Vanda (Green et al. 1986) fails to resolve this question in an unambiguous manner. The dissolved Fe data presented by Green et al. (1986) shows very little dissolved Fe is present at 61 m but at 64 m, concentrations have increased almost 5-fold and at 67 m, dissolved Fe concentrations have increased a further 234-fold (Figure 4a). While the observed increase in dissolved Fe is in general agreement with the prediction that the reduction of $Fe(OH)_3$ to Fe^{2+} is the predominant process, there is a lack of data points for dissolved Fe between 64 m and 67 m. As such, there is no confirmation that the trend between these two depths is consistent and therefore no confirmation of the predication.

Clearly, additional work is required to resolve these differences. This might include measuring all of the target analytes during one field campaign rather than combining several research efforts, and incorporating measurements of redox species that are normally not examined such as those involving iodine. While the use of the iodide/iodate couple as a master E_h "indicator" is controversial (Lindberg and Runnells 1984), examination of the distribution of these compounds has been suggested as a potential indicator of suboxic conditions in oceanic environments since both forms are dissolved species and not subject to particle removal or scavenging (Rue et al. 1997). Such an examination may also prove useful in the dry valleys lakes. Moreover, measurement of all of the individual redox species may also allow improvement of the estimates of their in situ reduction potentials. Once these inconsistencies have been resolved, comparison of the predictions with the actual distribution of the species involved, as determined by chemical analysis, should confirm the utility of the E_h^* approach and allow refinement of the E_h^* functions used to scale the traditional E_h measurements. Finally, comparison of the predicted distribution of redox species with their actual distributions may provide additional insight into the

issue of the geochemical legacies of the McMurdo Dry Valleys lakes.

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