

Episodic carbonate precipitation in perennially ice-covered Lake Fryxell, Antarctica

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ABSTRACT

Benthic carbonates in perennially ice-covered Lake Fryxell (McMurdo Dry Valleys, Antarctica) precipitated from pore waters in microbial mats as calcite rhombs, acicular botryoids and interfering bundles. Carbonates span the pronounced Lake Fryxell oxycline; variations in carbonate-associated manganese and iron concentrations are consistent with local oxycline conditions and seasonal fluctuations in pore water oxygenation. Precipitation is most abundant in shallow oxic waters, but extended through the oxycline during a discrete episode lasting multiple years, as evidenced by patterns of cathodoluminescence consistent with predicted seasonal changes in redox modulating dissolved manganese and iron concentrations. Carbonates did not precipitate in isotopic equilibrium with the water column, and are enriched in ^{18}O relative to predicted equilibrium values. Carbonate layer ^{18}O values vary by $>20\%$ at the mm-scale, suggesting precipitation was driven by mixing of isotopically heterogeneous fluids in the mat pore waters. Correlation of carbonate geochemistry and mat morphology with historical observations indicates that precipitation post-dates recent lake level rise. Further investigation of the physical and geochemical carbonate proxies from Lake Fryxell and other ice-covered lakes in the Dry Valleys promises to provide a valuable framework for interpreting Antarctic carbonates as records of modern and ancient climate, Antarctic biogeochemical and hydrological systems, and the drivers of carbonate precipitation at polar climate extremes.

Keywords Antarctica, lacustrine carbonates, cathodoluminescence, carbonate stable isotopes, microbial mats

INTRODUCTION

Ice core records provide a rich record of climate change across much of Antarctica, but a similar record has not been thoroughly constructed for the ice-free regions of the continent. In ice-free areas like the McMurdo Dry Valleys (MDV) in West Antarctica, modern and ancient lacustrine carbonate deposits provide a means to develop such a record. Lacustrine carbonate deposits are useful sedimentary archives, often preserving rich multi-proxy records of changes in local climate, hydrology, and biogeochemistry. The physical and geochemical information contained in lacustrine carbonates can aid in detailed reconstruction of past local environmental conditions. The rich lacustrine carbonate record has

been most thoroughly recognized and explored in low- and mid-latitude lakes, including both open- and closed-basin lakes (e.g. DeMott et al. 2019, Hudson et al. 2017, Petryshyn et al. 2015, Talbot 1990). In Antarctic closed-basin lakes, where processes of sedimentation differ considerably from those at lower latitudes, the carbonate record has not yet been thoroughly characterized. Sedimentation in Antarctic lakes is impacted by factors such as transport of sediment through permanent ice covers on lakes, restricted liquid water input due to sub-freezing temperatures, low weathering rates, prevalence of freeze concentration over evaporative concentration, and limitation of primary productivity by the seasonal light-dark cycle and low nutrient availability (Craig et al. 1992, Green et al. 1988, Rivera-Hernandez et al. 2019, Vincent et al. 2008 and references therein). Thus, it is necessary to explore modern carbonate deposition in order to more accurately interpret drivers of carbonate precipitation in paleolake deposits (e.g. Doran et al. 1994) and their implications for terrestrial Antarctic climate records.

At present, the MDV contain a number of perennially ice-covered lakes which contain liquid water year-round. Many of these lakes contain abundant benthic carbonate deposits (e.g. Lawrence and Hendy 1985, Mackey et al. 2018); the fraction of the total sediment represented by these carbonates varies among the lakes (Lawrence and Hendy 1985, Mackey et al. 2015, Sutherland and Hawes 2008). Modern benthic carbonates in Lake Fryxell (Taylor Valley, MDV) comprise a record of modern climate, hydrology, and biogeochemistry in the lake and its surroundings. Lake Fryxell carbonates are found in close spatial association with metabolically active microbial mats on the lake floor (Wharton et al. 1982), and sediment cores indicate that carbonate precipitation occurred through changes in regional climate and hydrology over tens of thousands of years (Lawrence and Hendy 1985; 1989). This study assesses the distribution, texture, and composition of carbonates in modern microbial mats of Lake Fryxell to better interpret the roles of climate, hydrology, and biology in carbonate precipitation in this perennially ice-covered lake. Such terrestrial carbonates present a promising sedimentary archive that can enhance scientific understanding of terrestrial Antarctic environmental change.

BACKGROUND

History of Taylor Valley

Taylor Valley has been the site of extensive glaciation and deglaciation during the past 20,000 years, which has strongly affected lake water levels in the valley over time (Hall et al. 2000, Lawrence and Hendy 1989, Myers et al. 2021). Ice from the Ross Ice Shelf advanced into the valley during the Last Glacial Maximum (LGM) (28.5-12.8 years BP) when local air temperatures were 4-9 °C lower than modern (Steig et al. 2000). Ice sheet advance resulted in an ice dam at the mouth of Taylor Valley which reached elevations up to 300-350 meters above sea level (m.a.s.l.) and allowed the formation of a large paleolake, Glacial Lake Washburn (GLW), which filled all of Taylor Valley (Hall and Denton 2000, Lawrence and Hendy 1989, Myers et al. 2021). Lake levels in Taylor Valley have

undergone drastic changes since the LGM; post-LGM ice dam retreat caused drainage of GLW and lowered lake levels to approximately 81 m.a.s.l. (Levy et al. 2017, Myers et al. 2021). Lake levels fell further as drainage into the Ross Sea continued, and high rates of evaporation likely resulted in the formation of a shallow brine pond in the Fryxell basin around 1000 years BP (Lawrence and Hendy 1989, Levy et al. 2017). Lake basins subsequently refilled with glacial melt waters, and lake levels have been rising since observations began during Robert Scott's first expedition in 1903 (Doran and Gooseff 2022, Myers et al. 2021, Scott 1905).

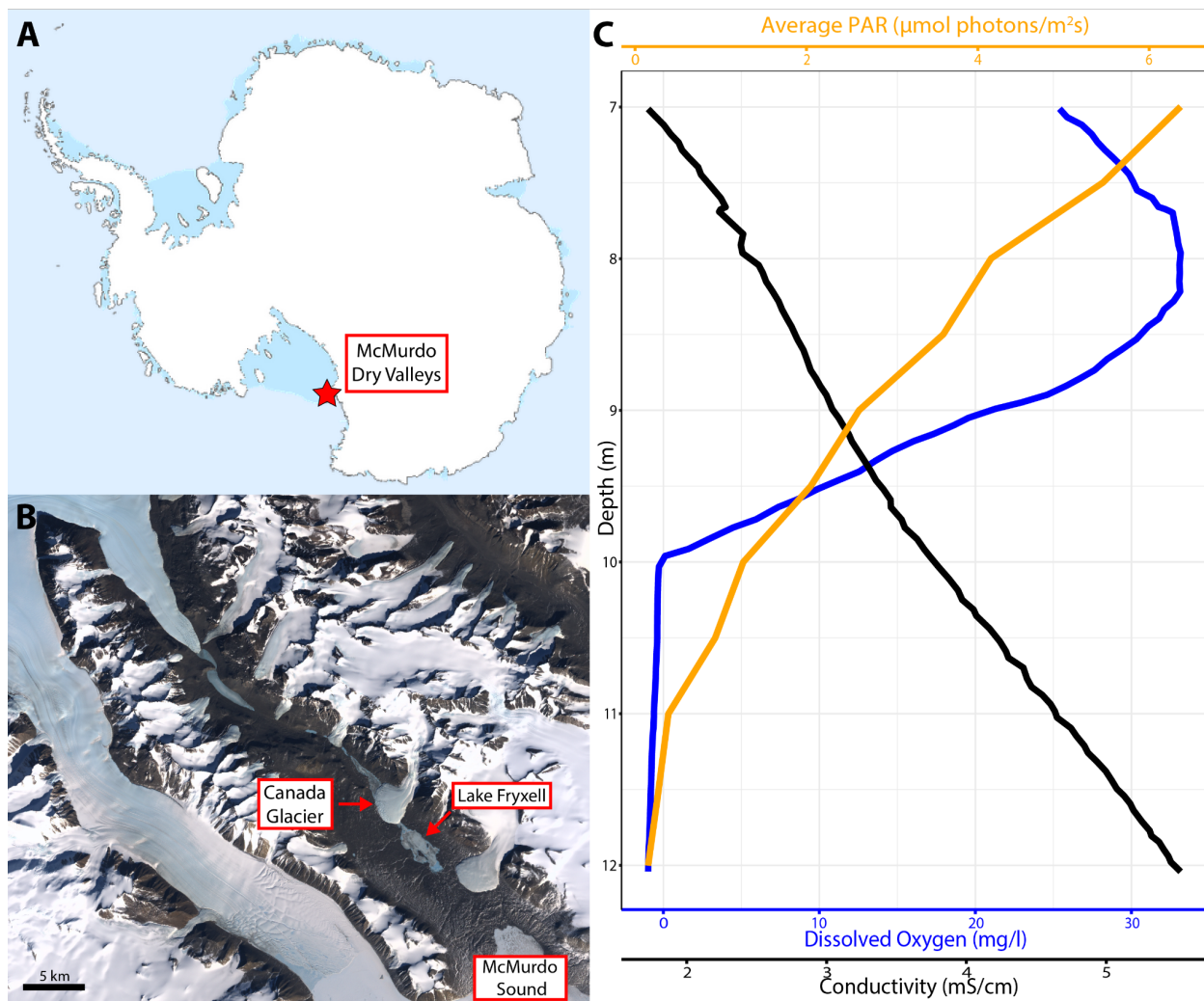


Figure 1. (A) Location of the McMurdo Dry Valleys in Antarctica. (B) USGS Landsat image of Taylor Valley, MDV. (C) Depth profile of photosynthetically active radiation (PAR), dissolved oxygen, and conductivity in the Lake Fryxell

water column (Doran 2020, Priscu 2022).

Lake Fryxell

Lake Fryxell is located near the eastern end of Taylor Valley and is the closest lake in the valley to the ocean, ~5 km from the McMurdo Sound (Figure 1B) (Chinn 1993). The lake is approximately 5 by 1.5 km at the surface (Lyons and Priscu 2014). Lake Fryxell is endorheic, with its level determined by the balance between glacial melt water influx and ablation of the ice cover (Dugan et al. 2013, Lawrence and Hendy 1985). About 1000 years BP, high evaporation rates resulted in a shallow sodium chloride-rich brine in the Fryxell basin (Lawrence and Hendy 1989), which was then refilled with glacial melt waters. The maximum lake level has increased gradually in recent decades, from 16 m.a.s.l. in 1980 to its present level of 18.3 m.a.s.l (Doran and Gooseff 2022, Wharton et al. 1982).

The water column of Lake Fryxell is chemically stratified based on density with conductivity increasing steadily with depth below a thin mixed layer immediately beneath the ice cover (Jungblut et al. 2016, Lawrence and Hendy 1985, Spigel and Priscu 1998). A steep oxycline exists between 8-10 m deep; the dissolved oxygen (DO) maximum is present around 8 m, and DO is absent from the water column below 10 m (Figure 1C) (Jungblut et al. 2016, Sumner et al. 2015). DO input to the lake is predicted to fluctuate seasonally due to the influence of the polar day-night cycle on glacial melting and microbial photosynthesis; sunlight is available 24 hours a day for about four months during summer, and no sunlight is available for about four months during winter (Doran 2020).

Lake bottom sedimentation is influenced by extensive benthic microbial mats that coat the lakebed where sufficient photosynthetically active radiation penetrates. The microbial mat community composition and metabolic potential varies across the oxycline (Dillon et al. 2020, Jungblut et al. 2016, Sumner et al. 2015). Microbial mat morphologies transition from pinnacle to ridge-pit, prostrate, and flocculent mat with increasing depth (Jungblut et al. 2016). Calcium carbonates are present in close spatial association with the microbial mats (Jungblut et al. 2016, Lawrence and Hendy 1985, Wharton et al. 1982). The depth range in which mat-associated carbonates occur spans the oxycline as well as density-stratified gradients of solutes including major ions, nutrients, and transition metals (Harnish et al. 1991, Jungblut et al. 2016, Lawrence and Hendy 1985). As a result, the mat-water-carbonate system in Lake Fryxell provides a useful “natural laboratory” in which to investigate the processes of carbonate precipitation in a polar lacustrine setting.

Geochemical proxies in Lake Fryxell

Manganese and iron are useful biogeochemical proxies in carbonates, largely due to their redox sensitivity; reduced (divalent) cations of both Mn and Fe are able to occupy Ca sites in calcite, while their more oxidized (trivalent and higher) cations cannot (e.g. Barnaby and Rimstidt 1989, Braithwaite 2016). Additionally, the ratio of Mn to Fe in carbonates allows for more detailed inves-

tigation, as Fe oxidizes more readily and is more thermodynamically stable in oxidized phases than Mn in aqueous environments (Davison 1993). Lake Fryxell contains both manganese and iron throughout the water column, with very low (<50 g/l) concentrations above the oxycline increasing to hundreds of g/l around the oxic-anoxic transition (Harnish et al. 1991).

Water column Mn and Fe concentrations may not directly correspond to carbonate concentrations in Lake Fryxell, as carbonates are present within metabolically active microbial mats. Benthic mat metabolisms modulate mat pore water oxygenation; photosynthesis further supersaturates pore water oxygen within the hyperoxic DO maximum (Sumner et al. 2015), contributing to expected perennial oxygenation of surface mats that persists through the polar winter based on extended season observations of nearby Lake Hoare (Wharton et al. 1994). The depth limit for photosynthesis extends below the oxycline in Lake Fryxell, leading to mm-scale seasonal oxygen oases within mats performing oxygenic photosynthesis (Sumner et al. 2015). Thus, seasonal changes to pore water redox vary with depth due to both the water column oxycline and local metabolic effects in the benthic microbial mats. In this study, Mn and Fe concentrations in carbonate are examined as a redox-sensitive proxy for seasonal changes to local pore water redox conditions at the time of carbonate precipitation.

Stable isotopes of carbon and oxygen in carbonates record a wealth of biogeochemical, hydrological, and climatic information, such as metabolic processes and changes in fluid sources. In the Lake Fryxell water column, $^{13}\text{C}_{\text{DIC}}$ follows a similar trend to the DO profile; $^{13}\text{C}_{\text{DIC}}$ increases from $\sim 0\text{‰}$ VPDB below the ice cover to a maximum of 3-4 ‰ around 8 m, then decreases to approximately -4 ‰ near the lake bottom (Knoepfle et al. 2009, Neumann et al. 2004). This is interpreted as a result of preferential uptake of ^{12}C by photosynthesizing microbes and a lack of water column mixing, resulting in the largest $^{13}\text{C}_{\text{DIC}}$ enrichment at the same depth where maximum primary productivity occurs (Neumann et al. 1998, Neumann et al. 2004). $^{18}\text{O}_{\text{water}}$ is nearly constant throughout the water column, varying over a narrow range of -31.9 to -31.3 ‰ VSMOW (Dowling and Lyons 2014). Existing isotopic data for the benthic carbonates are limited to bulk values of 10-20 mg samples from sediment cores (Lawrence 1982, Lawrence and Hendy 1989).

The stable stratification of the Lake Fryxell water column and the lake’s depth profiles of oxygenation, redox-sensitive metal concentrations, and stable isotope compositions offer a robust suite of geochemical proxies which can be used to construct a facies model of carbonate precipitation in this perennially ice-covered Antarctic lake. The petrography and geochemistry of Lake Fryxell carbonates presented in this study help to describe the timing of carbonate precipitation and the changes in redox and isotope geochemistry during precipitation.

METHODS

Sample collection and preparation

Benthic observations and sampling were carried out by divers in November 2012, following a transect established in 2006 (see Dillon et al. 2020, Jungblut et al. 2016). Video imagery was collected from 8.5 to 10.5 m depth in 2012 and from below the ice cover to 7.1 m depth in 2006. All water depths referenced in this study are based on the lake level in 2012. Divers measured the depth to carbonate from the mat-water interface by probing mats with an incrementally-marked metal wire until a rigid surface was encountered. Selected push cores and dredge samples were dissected in the field, dried, and shipped to the University of California, Davis. Remaining samples were frozen during the field season for shipment and subsequently stored below -20 °C.

Carbonates in sediment cores were located by halving the frozen cores. Acrylic core tubes were cut lengthwise using a hand-held rotary cutting tool with a circular diamond-edged blade, then cores were halved along the same line using a water-cooled Hi-Tech Diamond 6" trim saw (Westmont, IL, USA) to expose the interior of the core. Carbonate pieces and surrounding sediments were excised from cores using the trim saw, then lyophilized in order to separate carbonates from sediments. Dried carbonates were shipped to Spectrum Petrographics (Vancouver, WA, USA) for preparation as thin sections; carbonate pieces which appeared particularly fragile were first embedded in Epo-Tek 301-2 clear epoxy (Billerica, MA, USA) according to manufacturer instructions to prevent damage during shipping. Samples were prepared as thin sections 30 or 80 μ m thick.

Analyses

X-ray diffraction (XRD) was used to determine the mineralogy of Lake Fryxell carbonates. Four pieces of freeze-dried carbonate, two each from depths of 9.0 and 9.7 m (Table S1), were crushed into powders using a ceramic mortar and pestle, and 230-340 g of each powder was weighed out for analysis. XRD analysis was performed using a Rigaku SmartLab diffractometer (Tokyo, Japan) with Cu K radiation (wavelength = 1.54059 Å) and a DeteX Ultra detector. Spectra were collected in the 3-150° 2 θ range with a step size of 0.02° and a count time of 6°/minute.

Transmitted- and reflected-light microscopy were performed on thin sections and billets using Nikon SMZ25 stereo and Optiphot-Pol petrographic microscopes (Tokyo, Japan) to assess petrographic characteristics of these carbonates. Cathodoluminescence (CL) microscopy was conducted using a Nuclide Corporation Luminoscope ELM-2A cold-cathode microscope. Polished thin sections and billets were placed in the Luminoscope chamber under low vacuum (30-50 mtorr) and CL images were captured using a voltage of 5.5-6.0 kV to obtain a beam current of 0.7-0.8 mA.

Samples for $^{13}\text{C}/^{18}\text{O}$ analysis were extracted from billets using a hand-held Proxxon Micromot 60/E drill (Hickory, NC, USA) with Kodiak Cutting Tools carbide end mill bits (Syracuse, NY, USA) of diameters 1/64" and 1/32". Carbonate powders were washed in 30% hydrogen peroxide overnight to remove organic carbon, then dried at 50-70 °C for several hours. Carbon and oxy-

gen isotope ratios were measured at the Center for Stable Isotopes, University of New Mexico using the method described by Spotl and Vennemann (2003). Samples were loaded in 12 mL borosilicate exetainers, then the exetainers were flushed with He and the samples were reacted with H_3PO_4 for 12 hours at 50°C. The evolved CO_2 gas was measured by continuous flow isotope ratio mass spectrometry using a Thermo Fisher Scientific Gasbench coupled to a Thermo Fisher Scientific Delta V Plus Isotope Ratio Mass Spectrometer (Waltham, MA, USA). Isotope ratios are reported in delta notation on the VPDB scale.

Elemental composition data were acquired by laser ablation and inductively coupled plasma optical emission spectrometry (LA-ICP-OES). Elemental analysis focused on concentrations of Mn and Fe ([Mn] and [Fe], respectively). In-house standards were prepared by diluting BCS-CRM 393 limestone and NBS 2710 Montana soil with BCS-CRM 313 high-purity silica to create a set of references encompassing a wide range of [Mn] and [Fe]. LA-ICP-OES was performed using a New Wave Research UP-213 laser ablation system (Fremont, CA, USA) connected to a PerkinElmer Optima 4300 DV optical emission spectrometer (Waltham, MA, USA) with Ar plasma and Ar as a carrier gas at a flow rate of 600 mL/min. [Mn] and [Fe] were measured at selected locations on four billets corresponding to thin sections of Lake Fryxell carbonates (see Table S1). Ablation was conducted with the laser set to 80% power and 10 Hz firing speed. Linear transects were scanned with a spot size of 55 or 80 μm and a scanning speed of 4-8 $\mu\text{m/s}$; single-spot analyses were performed with a spot size of 55-100 μm and a dwell time of 45-75 seconds.

RESULTS

Benthic mat observations

The morphology of shallow water microbial mats at Lake Fryxell is influenced by the nucleation of gas bubbles on the mats (Wharton et al. 1982, Wharton et al. 1994). Gas bubbles build up in mats and induce buoyant delamination of mat layers, creating microbial mat liftoff structures. Liftoff mat was present to 6.4 m depth in 2006 (7.0 m depth in 2012; Figure 2A-B). Liftoff was not present below 7.0 meters in 2006 and was also absent from the deeper transect starting at ~8.5 m in 2012. Video footage throughout the 2012 oxycline shows ridge-pit and prostrate mat overlying discrete cm-scale, mineralized topographic highs or knobs (Figure 2C).

Carbonate mineralogy and petrography

Rigid carbonate layers are present within mats at all depths surveyed. Depth to carbonate (Table S2) from the mat-water interface ranges from 1-22 cm and is independent of depth and mat morphology. XRD spectra of carbonate layers at 9.0 and 9.7 m show peaks characteristic of calcite (Figure S1).

Lake Fryxell carbonates are closely associated with sediments and organic matter; mm- to cm-scale clots of sediment and microbial biomass are present surrounding and interspersed throughout carbonate cements (Figure 3). Carbon-

ates are present both as laminated layers and irregularly-distributed void-filling cements in microbial mats.

The distribution of carbonate in benthic microbial mats varies with depth. Samples from depths 9 m and shallower contain interconnected rhombic carbonate crystals 100–200 μm in length in addition to multiple layers of botryoidal cements (Figure 3A). At greater depths, carbonate primarily consisted of a single layer of botryoidal cements hundreds of μm to a few mm thick. At all depths, carbonates generally followed the cm-scale macromorphology of benthic mats, but finer superimposed pinnacles lacked this pervasive mineralization. Near the oxic-anoxic transition depth, acicular crystals form interfering bundles rather than botryoids (Figure 3B). Crystals most commonly grow outward from dark-colored areas indicative of high sediment/organic matter content (Figure 3). Crystal growth does not appear to occur preferentially in any specific direction; growth direction is commonly oriented perpendicular or downward relative to the mat-water interface.

Cathodoluminescence

Luminescence in Lake Fryxell carbonates is predominantly red and ranges from non-luminescent to very bright (Figure 4A, D, G). Red CL occurs in both “clean” (optically clear low sediment/organic matter content) and “dirty” (opaque high sediment/organic matter content) carbonates (Figure 4B, E, H). Shallower samples (9.0–9.3 m) commonly display CL “bands”: visually distinct, concentric or roughly parallel zones alternating between luminescent and non-luminescent calcite oriented approximately perpendicular to the crystal growth direction (Figure 4A, D, G). Most luminescent bands are several microns wide and bright, although band width and intensity are variable; luminescent bands can be dim to bright and occasionally over 100 μm wide (Figure 4D). Non-luminescent zones are typically longer in the crystal growth direction than luminescent zones (Figure 4A, D, G). CL bands occur rarely in deeper (9.4–9.7 m) carbonates; approaching the oxic-anoxic transition, carbonate CL is predominantly dim and diffuse or non-luminescent with rare, very narrow (<10 μm wide) bright bands (Figure 4G). Bright bands in deeper samples are flanked by much wider zones of dim red to purple luminescence or non-luminescent carbonate (Figure 4G).

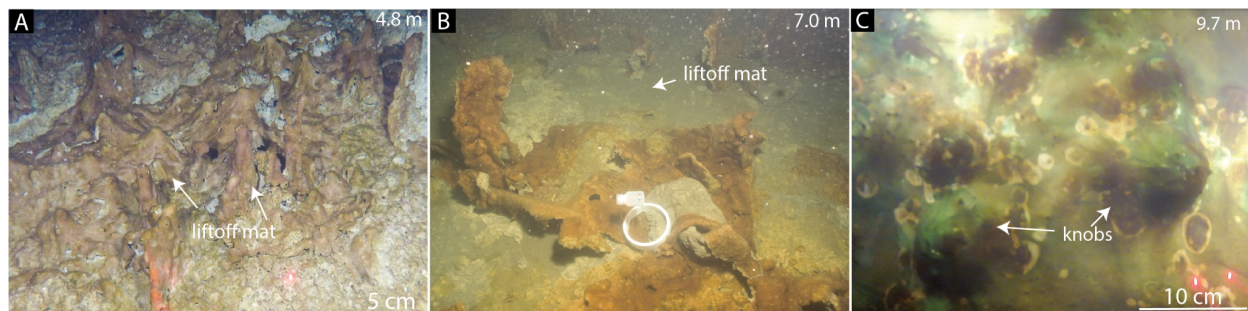


Figure 2. Comparison of Lake Fryxell microbial mat morphology at shallow

depths and the oxycline. Bubbles nucleate on microbial mats at shallow waters creating buoyant liftoff mat structures. (A) Liftoff mats below the ice-cover creating tented structures. (B) Liftoff mats at the deepest end of the liftoff zone with variable morphologies. (C) Prostrate mat in the oxycline overlying calcified liftoff structures.

Elemental analysis

Mn and Fe concentrations in Lake Fryxell carbonates range from tens to thousands of ppm; in samples from four depth points within the oxycline, [Mn] ranges from 44–8972 ppm, and [Fe] from 36–2182 ppm. The ratio of [Mn] to [Fe] also displays a broad range from 0.24–20.31. [Mn] and [Fe] display a rough covariance; the shallowest carbonates contain the lowest concentrations of both metals, while in deeper samples, the ablation sites yielding the highest [Mn] also yield the highest [Fe] (Figure 5). The minimum values of both [Mn] and [Fe] increase with depth. Carbonate [Mn] and [Fe] vary widely at 9.3 and 9.7 m, with [Mn] ranging from 52–4173 ppm and [Fe] from 178–2418 ppm at these depths. The highest values of both [Mn] and [Fe] represent dark brown to black spots in carbonates interpreted as oxide minerals (Figure 5).

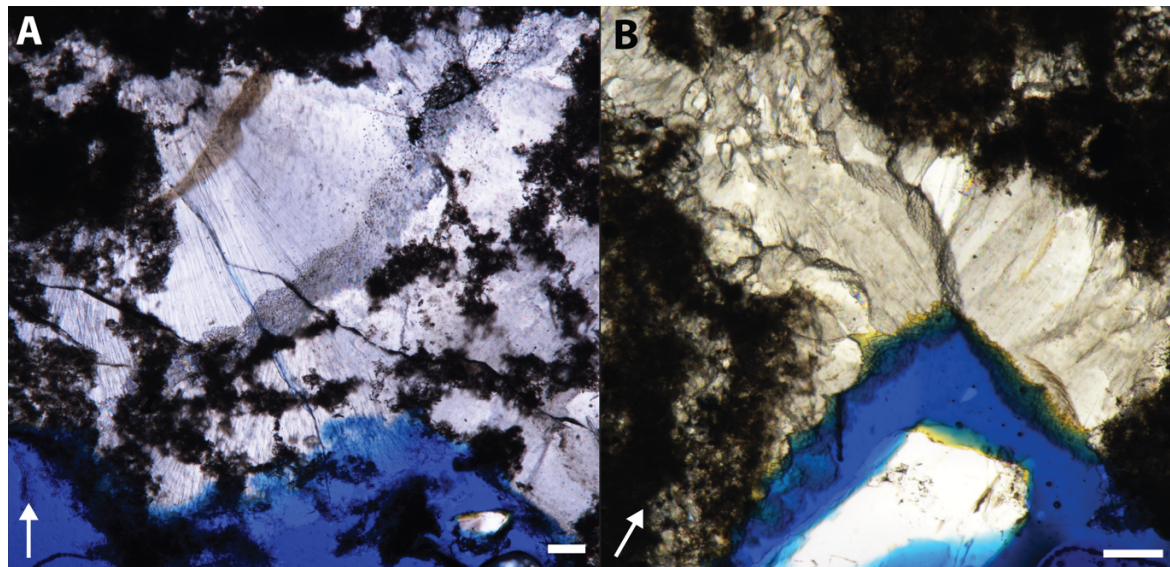


Figure 3. Transmitted-light photomicrographs of Lake Fryxell carbonates showing acicular calcite crystals forming botryoids (A) and interfering bundles (B) at depths of 9.0 and 9.7 meters, respectively. Adjacent zones of crystals often grow in different directions. Sediment and organic matter (dark-colored zones) are commonly found surrounding and interspersed throughout carbonates. Scale bars are 100 μ m. Arrows indicate direction to mat-water interface.

Stable isotopes

Carbonate ^{18}O in this depth range is highly variable and does not follow a

clear trend with depth. Carbonate ^{18}O values span $>20\text{‰}$, and carbonate ^{18}O does not match predicted values for precipitation in isotopic equilibrium with the Lake Fryxell water column (Figure 6). Carbonate ^{18}O does not covary with ^{13}C . At the shallowest depths (8.9-9.0 m), average carbonate ^{13}C values are similar to calculated values for precipitation in isotopic equilibrium with the DIC pool. From 9.3-9.7 m, carbonate ^{13}C at nearly all sampling sites is approximately 0-3‰ heavier than expected from precipitation in isotopic equilibrium with DIC (Figure 6).

DISCUSSION

Carbonate distribution and precipitation timing

Prior to this study, the presence of carbonates in Lake Fryxell’s benthic microbial mats had been attributed to microbial photosynthesis inducing precipitation of calcite in the water column and within benthic mats to form laminated stromatolitic structures (Doran et al. 1994, Lawrence and Hendy 1985, Wharton et al. 1982). This study presents an updated facies model describing in greater detail the spatial distribution, precipitation timing, and geochemistry of carbonates in this Antarctic lacustrine system in order to assess their potential to preserve evidence of local microbial activity and lake hydrology. The petrographic images presented here show that Lake Fryxell carbonates are closely associated with microbial mat biomass, typically surrounded by and/or interspersed with large amounts of sediment and biomass (Figure 3, Figure 4), indicating these carbonates precipitated from pore waters in voids distributed throughout sediments and microbial mat biomass and fill available pore spaces. Carbonates form botryoids and interfering bundles with varied growth orientations, both across the depth transect and within individual samples on the scale of tens of microns to millimeters (Figure 3). This style of precipitation contrasts that of microbial mat-associated carbonate precipitation in two other perennially ice-covered MDV lakes: Lake Joyce (Pearse Valley), where carbonates precipitate as crusts near the mat-water interface and grow outward from the surfaces of microbial mat structures, and voids are not filled in by later generations of cements (Mackey et al. 2015), and Lake Hoare (Taylor Valley), where calcite rhombs are disseminated in annual laminae and correlate to predicted changes in net photosynthetic activity (Hawes et al. 2016, Vopel and Hawes 2006).

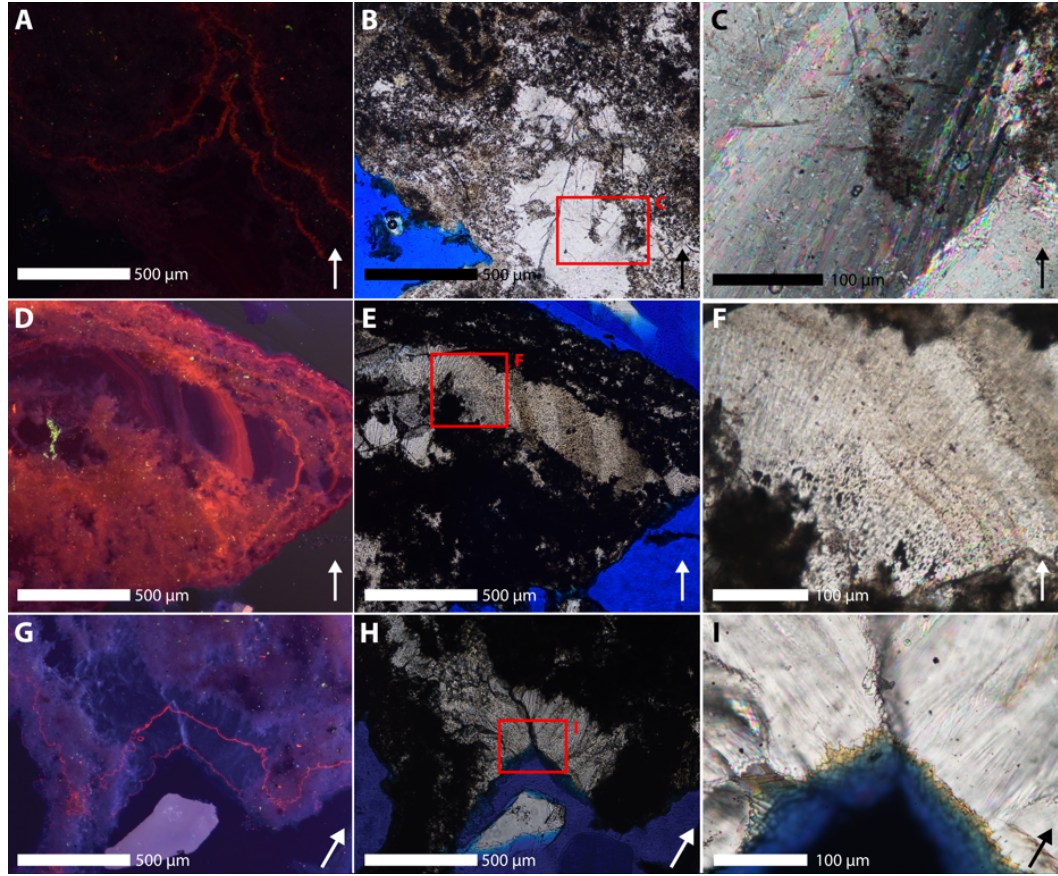


Figure 4. CL (A, D, G), plane-polarized light (B, E, H), and cross-polarized light (C, F, I) photomicrographs of Lake Fryxell carbonates from depths of 9.0 (A-C), 9.3 (D-F), and 9.7 (G-I) m. Acicular calcite crystals form botryoids and interfering bundles that fill voids in sediment- and mat biomass-rich zones. Carbonates incorporate varying amounts of reduced Mn and Fe through the oxycline, resulting in different abundances and thicknesses of CL bands. Arrows indicate direction to mat-water interface.

Where carbonates lack incorporated sediment or microbial biomass, precipitation is interpreted to have occurred in mm-scale voids within microbial mats. Voids may form due to mat growth processes, such as when microbial films overgrow open pits in ridge-pit mats (Jungblut et al. 2016), or when gas bubbles build up in mats as is the case of shallow water liftoff mats in Lake Fryxell (Wharton et al. 1982, Wharton 1994). Liftoff influence on mineralized mats is further supported by cm-scale knob macromorphologies (see Doran et al. 1994). Knob morphologies across the oxycline (Figure 2C) are more consistent with liftoff mats than with the typical prostrate or pinnacle mat morphologies observed growing at these depths (Jungblut et al. 2016, Sumner et al. 2015). Therefore, knobs are interpreted to be remnant structures formed during periods of lower

lake level.

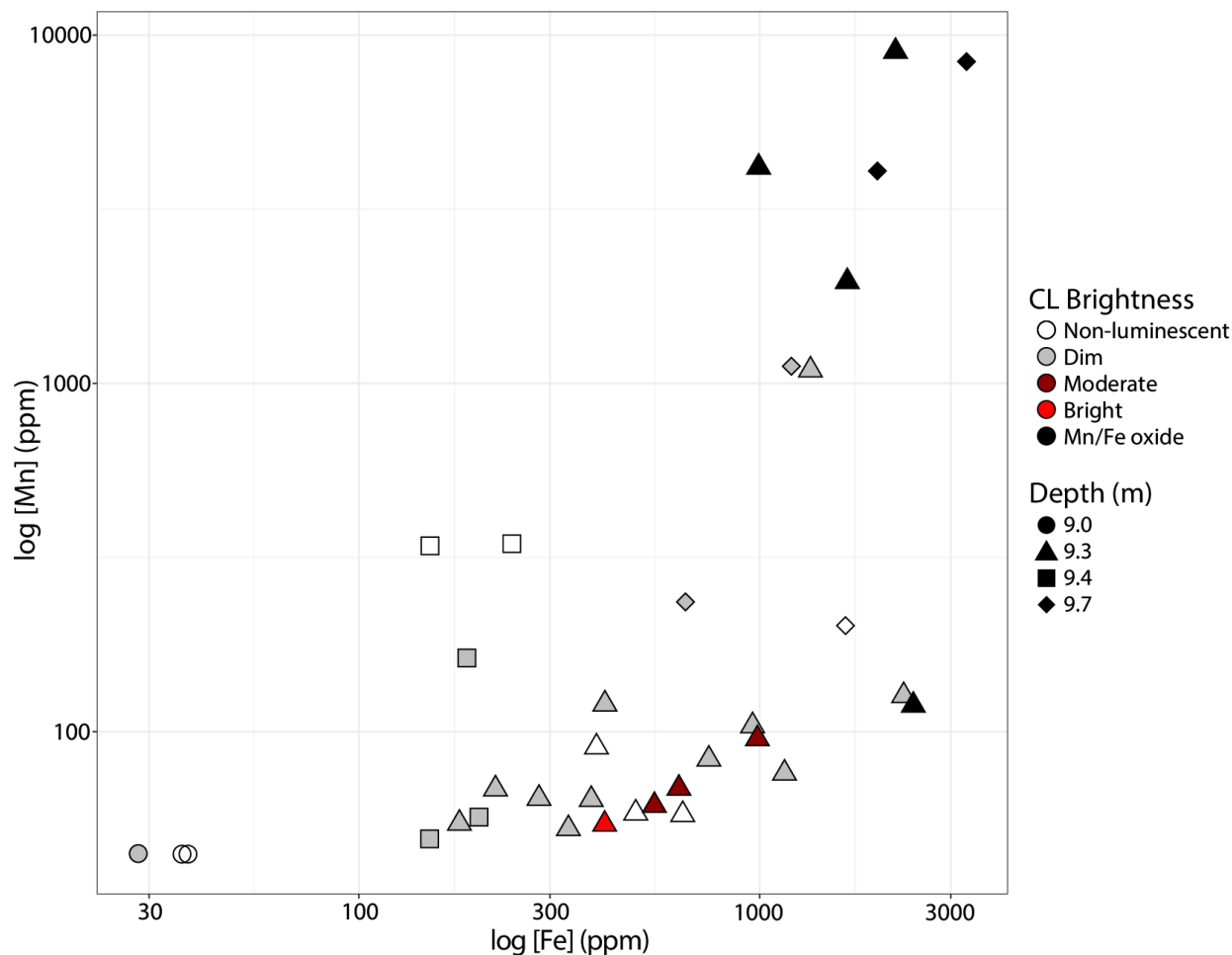


Figure 5. Log-log plot of [Mn] and [Fe] as determined by LA-ICP-OES. The lowest concentrations of both metals are found at 9.0 m, while the highest concentrations are found at 9.3 and 9.7 m. The highest concentrations of both metals are found in dark brown to black spots surrounded by calcite (black symbols), here interpreted as Mn/Fe-bearing oxides entombed in the carbonate. Neither [Mn] nor [Fe] displays covariance with CL brightness.

Both lake level and the observed depth distribution of liftoff mats at Lake Fryxell have varied through time. In 1980-1981, Wharton et al. (1983) recorded liftoff mat down to 8 m depth (10.1 m depth in 2012). Observations from 2006 show liftoff mats extended to 6.4 m depth (7.0 m depth in 2012). Liftoff depth variation is interpreted as a result of shifts in both freeze-concentration of gasses from meltwater streams entering the lake and the relative rates of net respiration versus net photosynthesis following lake level rise (Andersen et al. 1998, Craig

et al. 1992, Wharton et al. 1986, Wharton et al. 1987). The precipitation of carbonates on these shallow water mats (Wharton et al. 1982, Wharton 1994) creates a sedimentary record of liftoff mat (Parker et al. 1981) and, by extension, environmental change. Relic knob liftoff structures were overgrown with subsequent lake level rise and shoaling of the oxycline as observed in the 2006 transect. Similar juxtaposition of shallow- and deep-water microbial mat morphologies have been described at Lake Joyce (e.g. Hawes et al. 2011, Mackey et al. 2015) and are tied to changing lake levels.

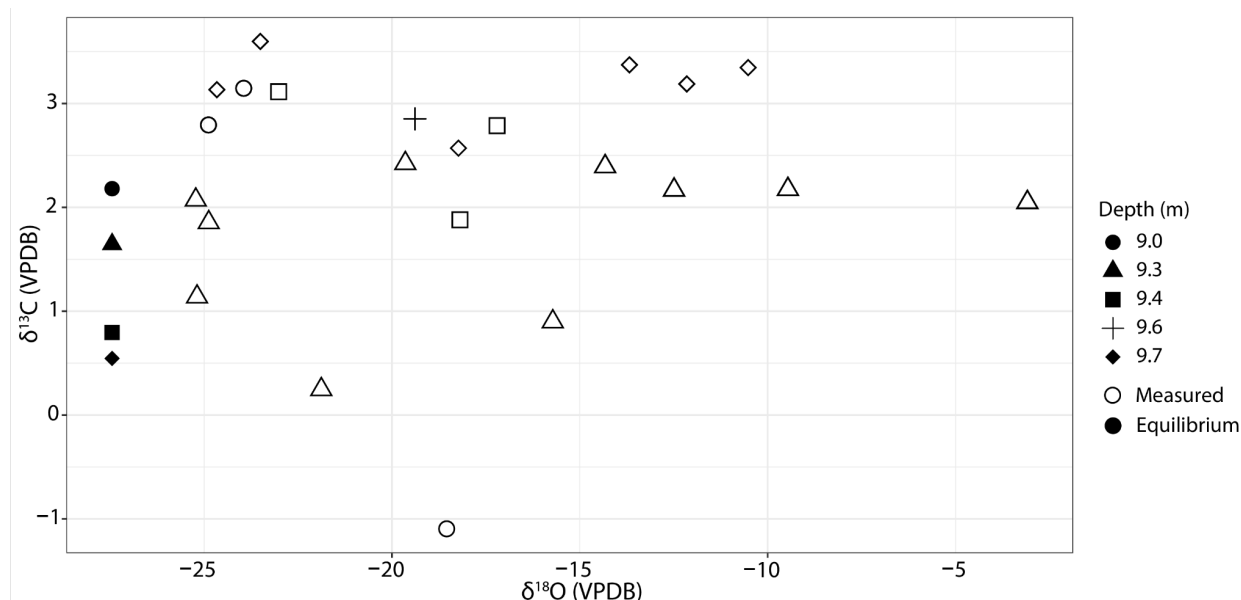


Figure 6. ^{13}C and ^{18}O of Lake Fryxell carbonates. Carbonate ^{13}C is, on average, enriched relative to expected values for precipitation in isotopic equilibrium with water column DIC (closed symbols). Carbonate ^{18}O is also enriched relative to expected equilibrium values and varies over a range of $>20\text{‰}$. ^{13}C follows an overall increasing trend with depth, while ^{18}O does not covary with depth or with ^{13}C .

Carbonate redox geochemistry

CL microscopy (Figure 4) shows that carbonate precipitation across the oxycline occurred through changes in pore water dissolved Mn and Fe concentration consistent with changes in local redox. Seasonal fluctuations in DO input and concentrations likely affect the depth of the oxic-anoxic transition within the density-stratified water column and the underlying benthic mats. During the austral summer, oxygenic photosynthesis would result in DO saturation to a greater depth. This DO increase would be greater within microbial mat pore space than in the surrounding waters due to local production within the mats, as evidenced by the emergence of seasonal oxygen oases in anoxic water below the oxycline (Sumner et al. 2015). Reciprocally, reducing conditions within mat

pore spaces are expected to extend to shallower depths than the oxic-anoxic transition in the winter with local respiration in the mats. Seasonal shifts in mat oxygenation have not been directly observed in Lake Fryxell to date, but can be reasonably hypothesized from previous observation of seasonal changes in DO at the oxycline (Lawrence and Hendy 1985) and observed summer oxygen profiles (Jungblut et al. 2016, Sumner et al. 2015).

Because carbonates precipitated in the mat subsurface and experienced significant changes in redox during precipitation, they are interpreted to have precipitated within mm to cm of the contemporary mat-water interface, within or shallower than the depth extent of benthic mat oxygen oases (Sumner et al. 2015) at the time of their precipitation. Where depth to carbonate was greater than a few cm, the difference is interpreted to be the product of sand sedimentation through the perennial ice cover. This is most dramatically evidenced by the presence of a carbonate layer in two adjacent (~1.5 m apart) sand mounds on the lake bottom; the continuous carbonate layer lies on top of one mound and at the bottom of the other (Rivera-Hernandez et al. 2019).

Because these carbonates form in pore spaces within metabolically active microbial mats, pore water redox may differ significantly from that of the local water column (e.g. Sumner et al. 2015) and leave a corresponding signal on carbonate geochemistry. The presence of Mn-bearing oxides at the oxic-anoxic transition, as interpreted from dark brown to black spots displaying high Mn concentrations (Figure 5), indicates the importance of biological activity in this redox system; oxidized Mn is thermodynamically unstable in aqueous environments unless conditions are strongly oxidizing (Davison 1993), thus necessitating the presence of an oxidizing microenvironment in which these oxides can form. These environments are most likely facilitated by microbial activity, as photosynthetic oxygen production at these depths significantly increases pore water oxygenation (Sumner et al. 2015). The presence of these oxides in carbonates which precipitated from low-oxygen waters, as evidenced by CL banding, indicates early carbonate precipitation isolating the reactive oxides from reducing waters and thereby preventing re-reduction of the metals.

CL bands correspond well to fluctuations in carbonate Mn and Fe content in instances where bands can be accurately sampled by laser ablation (Figure S3). However, this relationship is not consistent in all carbonates throughout the oxycline; CL brightness is independent of metal concentrations at the majority of LA-ICP-OES sampling sites (Figure 5). This may be due in part to methodological limitations; LA-ICP-OES cannot differentiate between oxidation states, instead capturing all Mn and Fe present in the sample regardless of oxidation state. Since only reduced Mn and Fe affect calcite CL, ablation of oxidized phases may complicate interpretation of these data. Thus, careful interpretation of combined petrographic, CL, and LA-ICP-OES data sets is necessary to accurately assess the redox record contained in these carbonates.

From the combination of CL imaging and LA-ICP-OES data, it can be inferred that carbonate redox geochemistry in Lake Fryxell preserves a record of sea-

sonal changes in pore water oxygenation and the oxic-anoxic transition depth. Both [Mn] and [Fe] show the broadest range at 9.3 m (Figure 5), providing a geochemical record of the frequent changes in redox evident from the abundant CL bands at the same depth (Figure 4). This implicates 9.3 m as a depth across which the oxic-anoxic boundary may regularly move over the course of an annual cycle. In contrast, carbonates at 9.0 m display fewer CL bands and lower [Mn] and [Fe] than at 9.3 m, indicating that pore waters at 9.0 m typically remain oxygenated perennially and are rarely reducing enough to allow Mn/Fe substitution into carbonates. Conversely, the scarcity of CL bands and high Mn/Fe content of carbonates at 9.7 m indicates that this depth is typically suboxic to anoxic, and rare episodes of oxygenation sequester Fe into insoluble oxides and prevent quenching of Mn-induced luminescence (Figure S5).

From petrographic and CL observations, it can be inferred that carbonate precipitation in the oxycline of Lake Fryxell is episodic, but that these episodes are not directly controlled by seasonal fluctuations in pore water redox. The precipitation event persisted through multiple annual light-dark cycles and associated changes in pore water redox. Although carbonate knob macromorphologies are reminiscent of liftoff features observed at these depths in Wharton et al. (1983), they are chemically consistent with precipitation under low oxygen conditions of the shallower oxycline as observed in 2006 and 2012. Thus, carbonates likely precipitated following lake level rise since 1981. Despite the lack of apparent metabolic control on carbonate precipitation, these observations highlight the potential for aspects of microbial ecosystem function to be preserved indirectly in extrinsically-driven carbonate precipitation as fluctuations in pore water geochemistry.

Carbonate stable isotopes

Enrichment of carbonates in ^{13}C provides a potential signature of net photosynthetic activity in these benthic mats. Slight (up to $\sim 3\text{‰}$) enrichment in ^{13}C relative to values expected for precipitation in isotopic equilibrium with the water column (Knoepfle et al. 2009, Romanek et al. 1992) (Figure 6) is consistent with preferential uptake of ^{12}C by photosynthesis, leaving a more enriched pool from which isotopically heavier carbonates precipitate. However, this ^{13}C signature does not covary with the changes in redox inferred from CL microscopy, which are interpreted as effects of seasonal fluctuation in microbial metabolic activity. Additionally, ^{13}C does not covary with depth. Therefore, carbonate ^{13}C may be interpreted as a general signature of microbial metabolic activity, but cannot be used to quantitatively assess seasonal or spatial changes at the resolution of this study.

The broad range of $\sim 23\text{‰}$ in ^{18}O of Lake Fryxell carbonates is unexpected. The water column of Lake Fryxell is isotopically light in oxygen (average ^{18}O -60.6‰ VPDB) and nearly uniform with respect to ^{18}O ; across 10 meters of depth, $^{18}\text{O}_{\text{water}}$ varies over a range of $<1\text{‰}$ (Dowling and Lyons 2014). Equilibrium fractionation calculations predict carbonate ^{18}O values of -27.5‰ to -25.6‰ VPDB at all depths in the lower oxycline (after Coplen 2007, Kim

and O'Neil 1997, Wostbrock et al. 2020), whereas measured ^{18}O values range from -26.4 to -3.1‰ VPDB. Carbonate ^{18}O often exhibits large differences over small (sub-mm to mm) distances; for example, two subsampling sites ~4 mm apart in carbonate from 9.3 m exhibit a difference in ^{18}O of >15‰ (Figure S2). This isotopic variability contrasts ^{18}O data from carbonates in perennially ice-covered Lake Joyce (Pearse Valley, MDV), in which ^{18}O spans a range of only 5.5‰ and does not display such broad variability on the m-to-mm scale (Mackey et al. 2018). Thus, the oxygen isotope composition of Lake Fryxell carbonates must be influenced by some process which does not occur in Lake Joyce.

Groundwater infiltration as a potential trigger for carbonate precipitation

Oxygen isotope variability may be indicative of isotopic heterogeneity in the fluid from which these carbonates precipitated, potentially caused by mixing of multiple water sources with significantly different oxygen isotope compositions. Stream waters in the Fryxell basin flow into Lake Fryxell during the summer and have slightly heavier (0.8-1.2‰) ^{18}O values than the water column (Gooseff et al. 2006, Harris et al. 2007). This relative enrichment is not of a sufficient magnitude to fully explain the oxygen isotope offset observed in Lake Fryxell carbonates, nor are other documented water sources in the basin. Lake and glacier ices, surface waters, and regional evaporatively concentrated Ca-chloride brines derived from meteoric waters cannot account for the heaviest carbonate ^{18}O values (Figure S4) (Fountain 2014, Matsubaya et al. 1979). Carbonate ^{18}O values are consistent with predicted precipitation from marine fluids at ambient temperatures (Figure S4), but despite the proximity of McMurdo Sound ~5 km down valley from Lake Fryxell, there is no evidence for surface inflow to the lake.

More diverse waters may interact with lake sediments through groundwater infiltration. Lake Fryxell is connected via a talik (an unfrozen region of ground bounded by permafrost) to a regional subsurface calcium chloride-rich brine aquifer (Foley et al. 2019, Mikucki et al. 2015, Toner and Sletten 2013). The aquifer is most likely a remnant of GLW which infiltrated the ground after extensive freezing and/or evaporation created a concentrated brine (Mikucki et al. 2015, Myers et al. 2021). Although no isotopic data exist for this brine at present, the brine would likely have higher ^{18}O values than modern meteoric-sourced waters due to incorporation of marine fluids; seawater has previously been suggested as an explanation for carbonate ^{18}O enrichment in sediments deposited from GLW (Lawrence and Hendy 1989). Any evaporative concentration with brine formation would further enrich these values as observed in other surface waters of the McMurdo Dry Valleys (Horita 2009). The isotopic data presented here indicate that this brine could have infiltrated through the lake sediments and mixed with mat pore waters, disrupting the geochemical equilibrium and inducing short-lived precipitation of isotopically heterogeneous carbonates documented in this study.

The lack of covariation between ^{18}O and ^{13}C is also consistent with precipitation from a low-DIC calcium chloride brine, such as those which have been observed in Taylor and Wright Valleys (Dickson et al. 2013, Toner and Sletten 2013). In this case, the induction of carbonate precipitation could be the product of locally increasing calcium concentrations in the pore waters of benthic mats, counteracting the otherwise low calcium levels within the pycnocline (Lawrence et al. 1985).

Geochemical constraints on Lake Fryxell carbonates suggest that an episode of enhanced connection between existing lake water and evaporatively-modified marine or marine-influenced ground water occurred in recent decades following lake level rise and shallowing of the lake oxycline. Future work on oxygen isotope composition of Antarctic carbonates and their source waters promises new insights into the hydrology and climate history of this region, as well as the processes which induce carbonate precipitation in Antarctic lakes. Additionally, the high variability of ^{18}O across m to mm in Lake Fryxell carbonates highlights the importance of high-resolution sampling in environmental reconstructions in these polar deposits; sample homogenization during bulk analysis may obscure variability important to interpret processes surrounding carbonate precipitation. Applying similar combined geochemical and petrographic characterization to Antarctic paleolake deposits is necessary to reconstruct the sources of carbonates and their significance for interpretation of terrestrial Antarctic environments.

CONCLUSIONS

Microbial mat-associated carbonates in Lake Fryxell provide a sedimentary record of episodic carbonate precipitation across biogeochemical gradients of the chemocline. CL imaging demonstrates that the episode of carbonate precipitation persisted for multiple years, with precipitation continuing through changes in pore water redox interpreted as the result of annual polar light-dark cycles. Carbonate Mn/Fe content further indicates variability of local redox in microbial mat pore spaces, both with depth as the lake transitions from oxygen supersaturation to anoxia and seasonally with varying rates of oxygenic photosynthesis.

Carbonate isotope compositions are inconsistent with predictions for precipitation in isotopic equilibrium with the Lake Fryxell water column. Carbonate ^{13}C shows overall enrichment relative to predicted equilibrium values, consistent with preferential uptake of ^{12}C by metabolic processes, but does not covary with precipitation timing or redox at this sampling resolution. Carbonate ^{18}O is offset from expected values for precipitation in equilibrium with the water column, and is highly variable on small spatial scales, likely indicating mixing of multiple water sources during carbonate precipitation. As indicated by previous water ^{18}O results from Taylor Valley, the carbonate source waters were a mix between lake and another non-meteoric source. Carbonate composition is most consistent with precipitation from a mix of lake waters and a subsurface brine in the porewaters of benthic mats. Formation of a brine aquifer via evaporative concentration of GLW waters provides a possible source for foreign waters to

Lake Fryxell.

Petrographic and geochemical observations indicate that although these carbonates precipitate in close proximity to metabolically active microbes, and that microbial metabolism influences the geochemistry of these carbonates, biological activity is not a controlling factor in precipitation timing. Rather, precipitation is interpreted as a result of short-term groundwater influx, possibly driven by changes to the local climate in recent decades, disrupting the carbonate equilibrium in pore waters and inducing this episode of carbonate precipitation. Continuing investigation of the redox and isotope geochemistry of both modern lacustrine carbonates and paleolake deposits in the MDV will facilitate more detailed reconstruction of local environmental response to past and present climate change.

REFERENCES

- Andersen, D., McKay, C., and Wharton, R.** (1998) Dissolved gases in perennially ice-covered lakes of the McMurdo Dry Valleys, Antarctica. *Antarctic Science*, **10**, 124-133.
- Barnaby, R., and Rimstidt, J.** (1989) Redox conditions of calcite cementation interpreted from Mn and Fe contents of authigenic calcites. *Geol. Soc. Am. Bull.*, **101**, 795-804.
- Braithwaite, C.** (2016) Cathodoluminescence in Quaternary carbonate deposits. *Sed. Geol.* **337**, 29-35.
- Chinn, T.J.** (1993) Physical Hydrology of the Dry Valley Lakes. In: *Physical and Biogeochemical Processes in Antarctic Lakes* (Eds W.J. Green and E.I. Friedmann) 1st edn, pp. 1-51. American Geophysical Union, Washington, DC.
- Coplen, T.** (2007) Calibration of the calcite-water oxygen-isotope geothermometer at Devils Hole, Nevada, a natural laboratory. *Geochim. Cosmochim. Acta*, **71**, 3948-3957.
- Craig, H., Wharton, R., and McKay, C.** (1992) Oxygen Supersaturation in Ice-Covered Antarctic Lakes: Biological Versus Physical Contributions. *Science*, **255**, 318-321.
- Davison, W.** (1993) Iron and manganese in lakes. *Earth-Sci. Rev.*, **34**, 119-163.
- DeMott, L., Napieralski, S., Junium, C., Teece, M., and Scholz, C.** (2019) Microbially influenced lacustrine carbonates: A comparison of Late Quaternary Lahontan tufa and modern thrombolite from Fayetteville Green Lake, NY. *Geobiology*, **18**, 93-112.
- Dickson, J., Head, J., Levy, J., and Marchant, D.** (2013) Don Juan Pond, Antarctica: Near-surface CaCl_2 -brine feeding Earth's most saline lake and implications for Mars. *Scientific Reports*, **3**, 1-7.

- Dillon, M., Hawes, I., Jungblut, A., Mackey, T., Eisen, J., Doran, P., and Sumner, D.** (2020) Energetic and Environmental Constraints on the Community Structure of Benthic Microbial Mats in Lake Fryxell, Antarctica. *FEMS Microbiol. Ecol.*, **96**, 1-10.
- Doran, P., Wharton, R., and Lyons, W.** (1994) Paleolimnology of the McMurdo Dry Valleys, Antarctica. *Journal of Paleolimnology*, **10**, 85-114.
- Doran, P.** (2020) Daily measurement summaries from lake-based "Blue Box" monitoring stations in the McMurdo Dry Valleys, Antarctica (1994-2019, ongoing). *Environmental Data Initiative*. DOI: [10.6073/pasta/3644a16962b397c127bffa0293071eace](https://doi.org/10.6073/pasta/3644a16962b397c127bffa0293071eace). Dataset accessed 1 July 2022.
- Doran, P., and Gooseff, M.** (2022) Lake level surveys in the McMurdo Dry Valleys, Antarctica (1991-2022, ongoing). *Environmental Data Initiative*. DOI: [10.6073/pasta/14d9ffabfbd50eb7d4deb7b9ca5dec56](https://doi.org/10.6073/pasta/14d9ffabfbd50eb7d4deb7b9ca5dec56). Dataset accessed 1 July 2022.
- Dowling, C., and Lyons, W.** (2014) Gas, Tritium, Stable Isotope, and Major Ion data for lake waters: 2005-2006 Antarctic Season. *Environmental Data Initiative*. DOI: [10.6073/pasta/b421fcc8837e96c5f18c3bd88872073c](https://doi.org/10.6073/pasta/b421fcc8837e96c5f18c3bd88872073c). Dataset accessed 1 July 2022.
- Dugan, H., Obryk, M., and Doran, P.** (2013) Lake ice ablation rates from permanently ice-covered Antarctic lakes. *J. Glaciol.*, **59**, 491-498.
- Foley, N., Tulaczyk, S., Grombacher, D., Doran, P., Mikucki, J., Myers, K., Foged, N., Dugan, H., Auken, E., and Virginia, R.** (2019) Evidence for Pathways of Concentrated Submarine Groundwater Discharge in East Antarctica from Helicopter-Borne Electrical Resistivity Measurements. *Hydrology*, **6**, 1-15.
- Fountain, A.G.** (2014) Isotope Ratios of Ice and Snow in Taylor Valley. *Environmental Data Initiative*. DOI: [10.6073/pasta/590165ae07d7d4dabfe2300f7473ac01](https://doi.org/10.6073/pasta/590165ae07d7d4dabfe2300f7473ac01). Dataset accessed 1 July 2022.
- Gooseff, M., Lyons, W., McKnight, D., Vaughn, B., Fountain, A., and Dowling, C.** (2006) A Stable Isotopic Investigation of a Polar Desert Hydrologic System, McMurdo Dry Valleys, Antarctica. *Arctic, Antarctic, and Alpine Research*, **38**, 60-71.
- Green, W., Angle, M., and Chave, K.** (1988) The geochemistry of Antarctic streams and their role in the evolution of four lakes of the McMurdo Dry Valleys. *Geochim. Cosmochim. Acta*, **52**, 1265-1274.
- Hall, B., and Denton, G.** (2000) Radiocarbon Chronology of Ross Sea Drift, Eastern Taylor Valley, Antarctica: Evidence for a Grounded Ice Sheet in the Ross Sea at the Last Glacial Maximum. *Geogr. Ann.*, **82**, 305-336.
- Hall, B., Denton, G., and Hendy, C.** (2000) Evidence from Taylor Valley for a grounded ice sheet in the Ross Sea, Antarctica. *Geogr. Ann.*, **82**, 275-303.

- Harnish, R., Ranville, J., McKnight, D., and Spaulding, S.** (1991) Redox-mediated cycling of iron and manganese in Lake Fryxell: Associations with particulate, colloidal, and dissolved forms. *Antarct. J. US*, **3**, 230-232.
- Harris, K., Carey, A., Lyons, W., Welch, K., and Fountain, A.** (2007) Solute and isotope geochemistry of subsurface ice melt seeps in Taylor Valley, Antarctica. *Geol. Soc. Am. Bull.*, **119**, 548-555.
- Hawes, I., Sumner, D., Andersen, D., and Mackey, T.** (2011) Legacies of recent environmental change in the benthic communities of Lake Joyce, a perennially ice-covered Antarctic lake. *Geobiology*, **9**, 394-410.
- Hawes, I., Jungblut, A., Obryk, M., and Doran, P.** (2016) Growth dynamics of a laminated microbial mat in response to variable irradiance in an Antarctic lake. *Freshwater Biology*, **61**, 396-410.
- Horita, J.** (2009) Isotopic Evolution of Saline Lakes in the Low-Latitude and Polar Regions. *Aquatic Geochemistry*, **15**, 43-69.
- Hudson, A., Quade, J., Ali, G., Boyle, D., Bassett, S., Huntington, K., De los Santos, M., Cohen, A., Lin, K., and Wang, X.** (2017) Stable C, O and clumped isotope systematics and ^{14}C geochronology of carbonates from the Quaternary Chewaucan closed-basin lake system, Great Basin, USA: Implications for paleoenvironmental reconstructions using carbonates. *Geochim. Cosmochim. Acta*, **212**, 274-302.
- Jungblut, A., Hawes, I., Mackey, T., Krusor, M., Doran, P., Sumner, D., Eisen, J., Hillman, C., and Goroncy, A.** (2016) Microbial Mat Communities along an Oxygen Gradient in a Perennially Ice-Covered Antarctic Lake. *Appl. Environ. Microbiol.*, **82**, 620-630.
- Kim, S., and O'Neil, J.** (1997) Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochim. Cosmochim. Acta*, **61**, 3461-3475.
- Knoepfle, J., Doran, P., Kenig, F., Lyons, W., and Galchenko, V.** (2009) Particulate organic and dissolved inorganic carbon isotopic compositions in Taylor Valley lakes, Antarctica: the effect of legacy. *Hydrobiologia*, **632**, 139-156.
- Lawrence, M.** (1982) Origin and occurrence of Antarctic lacustrine carbonates, with special reference to Lake Fryxell, Taylor Valley (Thesis, Master of Science (MSc)). The University of Waikato, Hamilton, New Zealand.
- Lawrence, M., and Hendy, C.** (1985) Water column and sediment characteristics of Lake Fryxell, Taylor Valley, Antarctica. *NZ J. Geol. Geophys.*, **28**, 543-552.
- Lawrence, M., and Hendy, C.** (1989) Carbonate deposition and Ross Sea ice advance, Fryxell basin, Taylor Valley, Antarctica. *NZ J. Geol. Geophys.*, **32**, 267-278.

Levy, J., Rittenour, T., Fountain, A., and O'Connor, J. (2017) Luminescence dating of paleolake deltas and glacial deposits in Garwood Valley, Antarctica: Implications for climate, Ross ice sheet dynamics, and paleolake duration. *Geol. Soc. Am. Bull.*, **129**, 1071-1084.

Lyons, W., and Priscu, J. (2014) Lake Descriptions. *Environmental Data Initiative*. DOI: [10.6073/pasta/7d9fec7af7c424ec82eae5f7e9df1c3b](https://doi.org/10.6073/pasta/7d9fec7af7c424ec82eae5f7e9df1c3b). Dataset accessed 3 October 2022.

Mackey, T., Sumner, D., Hawes, I., Jungblut, A., and Andersen, D. (2015) Growth of modern branched columnar stromatolites in Lake Joyce, Antarctica. *Geobiology*, **13**, 373-390.

Mackey, T., Sumner, D., Hawes, I., Andersen, D., and Jungblut, A. (2018) Stromatolite records of environmental change in perennially ice-covered Lake Joyce, McMurdo Dry Valleys, Antarctica. *Biogeochemistry*, **137**, 73-92.

Matsubaya, O., Sakai, H., Torii, T., Burton, H., and Kerry, K. (1979) Antarctic saline lakes – stable isotopic ratios, chemical compositions and evolution. *Geochim. Cosmochim. acta*, **43**, 7-25.

Mikucki, J., Auken, E., Tulaczyk, S., Virginia, R., Schamper, C., Sørensen, K., Doran, P., Dugan, H., and Foley, N. (2015) Deep groundwater and potential subsurface habitats beneath an Antarctic dry valley. *Nature Communications*, **6**, 1-9.

Myers, K., Doran, P., Tulaczyk, S., Foley, N., Bording, T., Auken, E., Dugan, H., Mikucki, J., Foged, N., Grombacher, D., and Virginia, R. (2021) Thermal legacy of a large paleolake in Taylor Valley, East Antarctica as evidenced by an airborne electromagnetic survey. *The Cryosphere*, **15**, 3577-3593.

Neumann, K., Lyons, W., and Des Marais, D. (1998) Inorganic carbon-isotope distribution and budget in the Lake Hoare and Lake Fryxell basins, Taylor Valley, Antarctica. *Ann. Glaciol.*, **27**, 685-690.

Neumann, K., Lyons, W., Priscu, J., Des Marais, D., and Welch, K. (2004) The carbon isotopic composition of dissolved inorganic carbon in perennially ice-covered Antarctic lakes: searching for a biogenic signature. *Ann. Glaciol.*, **39**, 518-524.

Parker, B., Simmons, G., Love, F., Wharton, R., and Seaburg, G. (1981) Modern Stromatolites in Antarctic Dry Valley Lakes. *BioScience*, **31**, 656-661.

Petryshyn, V., Lim, D., Laval, B., Brady, A., Slater, G., and Tripathi, K. (2015) Reconstruction of limnology and microbialite formation conditions from carbonate clumped isotope thermometry. *Geobiology*, **13**, 53-67.

Priscu, J. (2022) CTD profiles in lakes, McMurdo Dry Valleys, Antarctica (1993-2019, ongoing). *Environmental Data Initiative*. DOI: [10.6073/pasta/7532942ba96acc3b5c608633655f9de0](https://doi.org/10.6073/pasta/7532942ba96acc3b5c608633655f9de0)

Dataset accessed 4 October 2022.

- Rivera-Hernandez, F., Sumner, D., Mackey, T., Hawes, I., and Andersen, D.** (2019) In a PICL: The sedimentary deposits and facies of perennially ice-covered lakes. *Sedimentology*, **66**, 917-939.
- Romanek, C., Grossman, E., and Morse, J.** (1992) Carbon isotopic fractionation in synthetic aragonite and calcite: Effects of temperature and precipitation rate. *Geochim. Cosmochim. Acta*, **56**, 419-430.
- Scott, R.** (1905) The Voyage of the “Discovery”. C. Scribner’s Sons, New York.
- Spigel, R., and Priscu, J.** (1998) Physical Limnology of the McMurdo Dry Valleys Lakes. In: *Ecosystem Dynamics in a Polar Desert: the McMurdo Dry Valleys, Antarctica* (Ed J.C. Priscu), 1st edn, pp. 153-188.
- Spötl, C., and Vennemann, T.** (2003) Continuous-flow isotope ratio mass spectrometric analysis of carbonate materials. *Rapid Communications in Mass Spectrometry*, **17**, 1004-1006.
- Steig, E., Morse, D., Waddington, E., Stuiver, M., Grootes, P., Mayewski, P., Twickler, M., and Whitlow, S.** (2000) Wisconsinan and Holocene climate history from an ice core at Taylor Dome, western Ross Embayment, Antarctica. *Geogr. Ann.*, **82**, 213-235.
- Sumner, D., Hawes, I., Mackey, T., Jungblut, A., and Doran, P.** (2015) Antarctic microbial mats: A modern analog for Archean lacustrine oxygen oases. *Geology*, **43**, 887-890.
- Sutherland, D., and Hawes, I.** (2008) Annual growth layers as proxies of past growth conditions for benthic microbial mats in a perennially ice-covered Antarctic lake. *FEMS Microbiol. Ecol.*, **67**, 279-292.
- Talbot, M.** (1990) A review of the palaeohydrological interpretation of carbon and oxygen isotopic ratios in primary lacustrine carbonates. *Chem. Geol.*, **80**, 261-279.
- Toner, J., and Sletten, R.** (2013) The formation of Ca-Cl-rich groundwaters in the Dry Valleys of Antarctica: Field measurements and modeling of reactive transport. *Geochim. Cosmochim. Acta*, **110**, 84-105.
- Vincent, W., Hobbie, J., and Laybourn-Parry, J.** (2008) Introduction to the limnology of high-latitude lake and river ecosystems. In: *Polar Lakes and Rivers: Limnology of Arctic and Antarctic Aquatic Ecosystems* (Eds W.F. Vincent and J. Laybourn-Parry), 1st edn, pp. 1-23. Oxford University Press, New York.
- Vopel, K., and Hawes, I.** (2006) Photosynthetic performance of benthic microbial mats in Lake Hoare, Antarctica. *Limnol. Oceanogr.*, **51**, 1801-1812.
- Wharton, R., Parker, B., Simmons, G., Seaburg, K., and Love, F.** (1982) Biogenic calcite structures forming in Lake Fryxell, Antarctica. *Nature*,

295, 403-405.

Wharton, R., Parker, B., and Simmons, G. (1983) Distribution, species composition and morphology of algal mats in Antarctic dry valley lakes. *Phycologia*, **22**, 355-365.

Wharton, R., McKay, C., Mancinelli, R., and Simmons, G. (1987) Perennial N₂ supersaturation in an Antarctic lake. *Nature*, **325**, 343-345.

Wharton, R. (1994) Stromatolitic Mats in Antarctic Lakes. In *Phanerozoic Stromatolites II* (eds. J. Bertrand-Sarfati and C. Monty), 53-70.

Wostbrock, J., Brand, U., Coplen, T., Swart, P., Carlson, S., Brearley, A., and Sharp, Z. (2020) Calibration of carbonate-water triple oxygen isotope fractionation: Seeing through diagenesis in ancient carbonates. *Geochim. Cosmochim. Acta*, **288**, 369-388.