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Lifting the Champlain Sea: A CAS Record of the Transition to Modern Lake Champlain

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Lifting the Champlain Sea: A CAS Record of the Transition to Modern Lake Champlain

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Master of Science
in
Geological Sciences
by
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**Abstract**

Between about 9 and 13 ky bp, the isostatically depressed area of the Champlain, Ottawa and St Lawrence valleys were engulfed by the Atlantic Ocean. The resulting Champlain Sea had two distinct sources of water: fresh water sourced from large proglacial lakes fed by the collapsing Laurentide Ice Sheet and North Atlantic marine waters sourced via the contemporaneous eustatic rise. This study focuses on the most recent transition from the Champlain Sea (CS) to modern Lake Champlain when the fluxes between the two water sources were in a state of transition. Carbonate-associated sulfate (CAS) offers proxy evidence for the $\delta^{34}S$ of ancient waters, a key piece in our interpretation of both flux dynamics and primary redox conditions within the basin. Previous research into CAS has shown that sulfate can be structurally substituted into authigenic and biogenic carbonates. Following wide ranging efforts to calibrate and validate this proxy, it has been demonstrated that the isotopic composition commonly reflects the ambient waters at the time of carbonate precipitation. Because of relatively low rates of bacterial sulfate reduction, the $\delta^{34}S$ of CAS in the restricted CS can be used to approximate salinity relationships over the interval of interest. These data suggest the Champlain Sea was subject to four flood events from Lake Agassiz dropping salinity (measured in Practical Salinity Units) throughout the lifetime of the marine incursion. Splits taken from the CAS solution yield Mg, Fe, & Sr concentrations; unique to each water source, these data reflect the marine to lacustrine change in aqueous metals and identify the source of the proglacial flood source as Lake Agassiz. Due to the low concentrations of both CAS and calcium carbonate in our samples, we are in a unique position to assess the lower limits of the CAS proxy’s utility in studies of marine to lacustrine transitions. By capturing the transition from the Champlain Sea to Lake Champlain I detail the dynamics of this evolution as both unrelenting isostatic rebounding and diminishing flood sizes repeatedly lowered the salinity (PSU) of the CS. Moreover, low pyrite and iron monosulfide concentrations within the sediments reveal that aqueous sulfate must have been delivered back into the North Atlantic.

1.0 Introduction

A number of consequences accompanied the Pleistocene to Holocene transition:
warming destabilized the water cycle; previously land-locked ice melted, drained and was transported to the oceans; and coastlines were submerged on a global scale. In North America, the Eastern lobe of the Laurentide Ice Sheet (LIS) continuously affected drainage routes and carved out deep stream channels as ice dams ruptured (Franzi et al., 2007), allowing water trapped in previously land locked ice to escape to the ocean basins. The Ottawa, St. Lawrence and Champlain valleys were proximal to the LIS, acting as temporary storage for large volumes of melt-water and their associated sediments—forming ephemeral lake basins such as Glacial Lake Vermont, Lake Agassiz and Lake Algonquin. These proglacial valleys house excellent sedimentary records chronicling the nuances of this dynamic period. The importance of the Champlain Sea’s postglacial record is not only due to its proximity to a vast melting ice sheet but also its midpoint location relative to both upstream proglacial lakes and downstream marine influence.

Sedimentologically, the Champlain Sea was a large mud trap acting as an epeiric buffer zone filtering millions of cubic meters of sediments before melt waters entered the Atlantic Ocean (Cummings et al., 2011). The basin is therefore an excellent region to study, recording a period of rapid deglaciation within its borders and hosting geochemical, mineralogical and biological clues of the basin’s dynamic evolution.

During the Champlain Sea interval spanning 13-9.6 thousand years before present (ky bp), North Atlantic waters are thought to have delivered near-fully marine concentrations (28mM) of aqueous sulfate into the basin. Calcareous tests of extant Arctic species of foraminifera provided the biogenic carbonate source needed to record the $\delta^{34}S_{\text{seawater}}$ as well as capture related acid extractable metals delivered into the basin by
marine and terrestrial fluxes. This combination of factors allows the use of the carbonate associated sulfate (CAS) proxy. CAS is a widely used and well-calibrated proxy that reveals the contemporaneous $\delta^{34}S_{\text{seawater}}$ value in which the carbonates are precipitating, shedding light on the redox conditions as well as the extent of the bacterial sulfate reduction (BSR) metabolic pathway within the anoxic porewaters of the basin. Sulfate became a major marine anion during the early oxidation of the atmosphere, pO2 levels were high enough to oxidize widespread detrital sulfide minerals, leading ultimately to sulfate now being the third most abundant ion in the global ocean, lagging only sodium and chloride. BSR is the dominant process for sulfate reduction throughout the world’s oceans, as the resulting hydrogen sulfide is first removed via metastable iron monosulfides and subsequent burial as pyrite (Berner, 1984). This bacterial metabolism whereby sulfate is used to oxidize organic matter is immensely important not only in today’s anoxic sediments but throughout the Phanerozoic. Whether captured in biogenic or authigenic carbonates, sulfate is structurally substituted into the carbonate lattice, thus recording a temporally complete archive of the global sulfur cycle driven by abiotic sulfur inputs (weathering and hydrothermal) and mostly biotic sulfur sinks (BSR). In this light, the CAS proxy becomes an extremely powerful tool in accessing global redox conditions, marine contributions and dominant sulfur mineralization pathways across diverse marine settings throughout much of Earth history. The Champlain Sea, hypothesized to be comprised of marine and freshwater inputs provides a unique setting to find the lower reliable limits of the CAS proxy.

The current marine $\delta^{34}S$ value of 21‰ represents a balance of sulfur sources
(hydrothermal & weathering) and sulfur sinks (pyrite mineralization) into the global oceans. BSR communities, responsible for the initial steps of pyrite mineralization rely on labile organic carbon and aqueous sulfate to manage a chemosynthetic metabolism. As with many biological processes, the more thermodynamically efficient or lighter $\delta^{32}$S isotope is chosen over $\delta^{34}$S ultimately producing both a $\delta^{32}$S enriched sulfide reservoir and a $\delta^{34}$S enriched marine water column. High sedimentation rates of 0.8-1.2 cm yr$^{-1}$ (Freeman-Lynde et al., 1980) diluted the already minimal contents of total organic carbon (TOC) (Table 1) within the Champlain Sea; thus inhibiting the sulfur cycle and prohibiting the relatively isolated basin from outpacing average marine rates of sulfate reduction. Many studies have shown that sulfate reduction rates are directly proportional to the amount and reactivity of the organic matter (e.g., Lyons and Gaudette, 1978). This provides assurance that the $\delta^{34}$S values for CAS ($\delta^{34}$S$_{\text{CAS}}$) reflect the mixing of the two distinct water sources entering the CS: an upstream proglacial flux and a North Atlantic connection. With this in mind, $\delta^{34}$S$_{\text{CAS}}$ values reported in this study can be used to fingerprint temporal variations in marine inputs and specifically, to calculate evolving salinity levels within the water column of the CS.

Previous studies in the basin have relied on $\delta^{18}$O of CaCO$_3$ (benthic tests) as a proxy for marine and freshwater fluxes, but this approach is challenged by uncertainties about the $\delta^{18}$O of the nonmarine waters and the degree to which temperature effects and diagenetic overprints can be removed (Hillaire & Marcel, 1988; Cronin et al., 2008). The CAS approach gives an independent and potentially more robust perspective on the water sources within the Champlain Sea, helping to further illuminate the collapsing LIS and its
impact on the Champlain Sea system.

Because of the very low salinities captured in this study, I will also comment on the lower limits of the proxy’s utility, which may prove beneficial when choosing future depositional systems to analyze. Furthermore, I will show that the sulfate within the Champlain Sea must have been flushed into the Atlantic Ocean instead of mineralizing within anoxic pore fluids as the basin transitioned from a system dominated by the saline waters of the North Atlantic to the oligotrophic waters of modern Lake Champlain. What follows is in-depth discussion of the study area and its dynamic history; the methods used to obtain these data, which are broadly relevant; comments on the proxy’s integrity and breadth of its utility and a detailed discussion of the data obtained and their implications for the evolving Champlain system as reflecting the dynamic balance between glacioeustacy and isostatic rebound.

2.0 Geologic Setting and Previous Research

2.1 Geologic Setting

The Champlain, Ottawa and St. Lawrence valleys have experienced a variety of depositional systems since the retreat of the Laurentide Ice Sheet. Strongly influenced by eustacy and isostacy, and proximal to the collapsing LIS and associated flooding by melt waters as well as the North Atlantic, the basin has existed in three primary forms over the last ~14 thousand years (Cronin et al, 2008). Glacial Lake Vermont (~14-13 ky bp) was a proglacial lake and the first body of water to fill the glacially scoured basin. The lake grew proximal to the ice front fed by LIS melt waters and was dammed to the east by still lingering ice residing in the eastern St. Lawrence valley. Upon its eventual failure,
freshwater drained from the basin and marine waters of the North Atlantic flooded the valley during the concomitant post-glacial rise in sea level. This new body of water, known as the Champlain Sea, existed between ~13-9.6 ky bp (Cronin et al., 2008, 2011) and was a brackish/estuarine body reflecting both marine and fresh water sources. The continued melting of the LIS provided ample melt water, forming a number of proglacial lakes along the retreating ice margin. Lake Agassiz, the largest of the group, provided the majority of the fresh water flux to the basin during the Champlain Sea episode (Katz et al., 2011). The nutrient-rich Atlantic waters turned what would be an otherwise oligotrophic body of water, as recorded in the sediments of Glacial Lake Vermont and modern Lake Champlain, into an ecosystem with a diverse assemblage of benthic fauna (Cronin, 1977). Continued isostatic rebound provided the mechanism for the eventual end of the Champlain Sea episode leading to modern Lake Champlain following the complete cessation of marine inputs ~9 ky bp.

2.2 Sampling Locations

The transition from the CS to LC was sampled with two piston cores, MUCR-1 & MUCR-2 (at roughly 1 km apart), collected from the south end of Lake Champlain. Coring locations were chosen based on the continuous nature of deposition within the basin from ~14 ky bp to present (Fig. 1) and Cronin’s 2008 study where the end of the CS interval was identified at the CS-LC sedimentary boundary. The sedimentary evidence for the three bodies to fill the basin—Glacial Lake Vermont, the Champlain Sea and Lake Champlain—is clear in the CHIRP sonar imagines of the coring locations (Figures 2-interpreted by Pat Manley). The southern end of the basin has an advantage of
being more distal to the northern higher energy margin where a persistent proglacial flux and occasional flood events led to disturbed intervals less amenable for geochemical analysis. The mineralogy of the sediments in the CS creates areas prone to slope failure. Specifically, ‘Leda’ or ‘quick clays’ allow for the many slumps throughout the basin (Berry & Torrance, 1998). Care was taken to place the core in the center of slumps to maximize record capture (Figure 2: Core MUCR-1).

2.3 Previous Research

The changing drainage routes, flux rates, isostatic rebound and eustatic rise surrounding the Champlain Sea make paleoenvironmental interpretations difficult. There have been many stable isotope studies using benthic carbonates, terrestrial bone material and plant matter as proxies for these environmental shifts, including δ18O of benthic carbonates (Hillaire & Marcel, 1988; Moore et al., 2000; Brand & McCarthy 2004; Carlson et al., 2007; Cronin et al., 2008, 2011), δ13C of benthic carbonates (Hillaire & Marcel, 1988; Dyke & McNealy, 2000; Brand & McCarthy 2004; Carlson et al., 2007; Cronin et al., 2008) and 14C of terrestrial and CS biota (Hillaire & Marcel, 1988; Richard & Occhietti 2005; Rayburn et al., 2006). Precise radiocarbon dating of biogenic carbonates deposited within the Champlain Sea has proven difficult due to the heterogeneous composition of the basin through time and space and associated, varying effects of old carbon (Hillaire & Marcel, 1988; Cronin et al., 2008). However, varve counting, which captures annual deposition controlled by seasonal freezing and melting, and even greater reliance on δ14C dating of terrestrial carbon (Richard & Occhietti 2005) help to constrain the timing and duration of the CS.
The initiation of the CS 13.1-12.9 kybp has been well studied in relation to contemporaneous events such as the Younger Dryas thought to have been caused by proglacial floods routed through the Champlain and St. Lawrence Seaway into the Northern Atlantic, thereby shutting off North Atlantic Deep Water formation (Lasalle & Shilts 1993; Rodrigues & Vilks 1994; Leverington et al., 2000; Moore et al., 2000; Denniston et al., 2001; Teller et al., 2001; Brand & McCarthy 2005; Rayburn et al., 2006; Carlson et al., 2007; Franzi et al., 2007; Cronin et al., 2008, 2011; Rayburn et al., 2011). Carlson et al., (2007) classified Canadian Shield bedrocks based on strontium isotopes and magnesium concentrations thereby providing a measure of freshwater discharges during the Younger Dryas. Physical properties such as saturated bulk density, magnetic susceptibility and grain size have also been used to independently constrain basin transitions (Manley et al., 1999; Cronin et al., 2008).

Cronin et al., (2008) identified the variety of biogenic carbonates deposited in the CS. Both ostracodes (Cytheromorpha fuscata, Cytherura gibba, Cytherissa lacustris, Cyther-opteron, Cytheromorpha macchesneyi) and foraminifera (Miliammina fusca, Elphidium cf. albumbilicatum, Elphidium cf. albi umbilicatum, excavatum f. clavata, Elphidium hallandense) have been identified in CS sediments, with Elphidium excavatum forma clavata as the dominant species (Cronin et al., 2008; Cummings et al., 2011).

Mineralogical assessments by Berry and Torrance (1998) found that tectosilicate minerals (quartz, K-feldspar and plagioclase) comprise the bulk of CS sediments. Ramesh and Anglejan (1995) described illite, chlorite, amorphous oxides and carbonates as accessory sedimentary components predominantly sourced from ice-ground
Precambrian material derived from the Canadian Shield. Diffractograms from the same study reveal a relationship between increasing Fe concentrations and decreasing grain size thought to reflect increased Fe bound at octahedral positions, creating an Fe-rich chlorite. Chemical composition of the clay fraction reveals enrichment in Al, Fe and Mg, reflecting an increased abundance of clay minerals and Fe hydroxides. Torrance and Kirkpatrick (2004) identified detrital ooids that formed in the turbulent northern boundary of the CS. They showed an identical mineralogical makeup to the normal CS sediments and revealed no cementation or diagenetic formation of the minerals. Their “hail-stone” model for formation relies on wind-wave action to keep the particles suspended during which flocculation from brackish to marine waters induced particle accretion onto their surfaces. Dissolved metals within the CS waters therefore were associated with the dominant mineral suite throughout the Sea. This makes acid extractable assessment via the CAS method possible for measuring the relative contributions of marine and riverine inputs into the evolving CS basin.

3.0 Carbonate Associated Sulfate (CAS)

Carbonate associated sulfate is a widely used proxy for the sulfur isotope composition of modern & ancient seawater sulfate. Strauss (1997) reviewed the sulfur cycle throughout the Phanerozoic based in part on CAS, which reflects the extent to which BSR fractionates the marine reservoir of sulfate. This approach continued with the study of Kampschulte and Strauss (2004), who used a variety of biogenic calcites and whole rock carbonates to reconstruct the evolving $\delta^{34}$S of Phanerozoic seawater. Hurtgen et al., (2002) used Neoproterozoic seawater sulfate records captured in CAS to model
hypothesized Snowball Earth events. Staudt and Schoonen (1995) detailed the variety of carbonates: authigenic, biogenic, planktonic, benthic etc., able to capture and preserve seawater sulfate. Kah et al., 2004) used CAS to estimate the low sulfate contents of Proterozoic seawater, Gellatly & Lyons 2005 discussed the sulfur isotope record of Proterozoic carbonates relating to biospheric evolution and Fike et al., 2006 used CAS to track the redox evolution and progressive oxidation of the late Proterozoic ocean.

Authigenic and biogenic carbonates are both susceptible to substitution of $\text{CO}_3^{2-}$ by $\text{SO}_2^-$ in the $\text{CaCO}_3$ lattice structure, because the anions have similar charge and size. This fortuitous relationship has greatly increased our understanding of the sulfur cycle through time due to the wide spatial and temporal distribution of carbonate rocks. Evaporites, by contrast, which were previously emphasized to track the sulfur properties of the ocean, are not as ubiquitous as carbonates in time or space, are less easily dated, and are intrinsically vulnerable to signatures of local restriction (Burdett et al., 1989). Further concerns arise because long-term preservation of soluble evaporites is often poor, and evaporites by definition form in restricted basins that may shift the waters from the contemporaneous global marine $\delta^{34}\text{S}$ through local river inputs and isotopically fractionated pyrite sinks (Longinelli, 1980). Sulfate sourced from the ambient water column is bound in the calcium carbonate lattice at the time of precipitation. The sulfate, now protected within the carbonate framework is thought to faithfully record the sulfur isotope composition of the overlying water column. Gill et al. (2008) showed that diagenetic alteration of $\delta^{34}\text{S}_{\text{CAS}}$ once bound in the lattice is very limited even under heavy meteoric influence, affecting CAS concentrations but not the isotopic values. Because the
benthic foraminifera, comprising the bulk of the carbonate within the sampled sediments are relatively young groundwater exchange could have dispelled some of the captured sulfate but would have left the primary isotopic value preserved.

The success of the $\delta^{34}S_{\text{CAS}}$ proxy began with the important study of Burdett et al., (1989) who studied Neogene-age calcareous pelagic microfossils. Beforehand, knowledge of the marine sulfur cycle was limited to evaporite deposits of gypsum (Claypool et al., 1979), which, as outlined above, challenge the generation of continuous, well dated records of primary ancient seawater. Accurately dating these deposits is difficult due to the lack of diverse marine communities and paleomagnetic indicators used for biostratigraphic and magnetostratigraphic age determinations, respectively (Burdett et al., 1989).

4.0 The Sulfur Cycle: Marine and Lacustrine

Sulfur exists in various redox states and organic forms. The sources of sulfur include continental weathering and volcanism, while the sinks can be both abiotic in the form of evaporites and biotically mediated in the form of mineralized reduced iron sulfide species such pyrite. In modern marine and lacustrine systems the dominant form present in the oxic water column is $\text{SO}^{2-}_{4\text{aq}}$, while the reduced forms are most commonly found in the underlying anoxic sediments as iron monosulfides (FeS) and pyrite (FeS2). Intermediate sulfur oxidations states are typically transient and do not accumulate in sediments unless further reduced or oxidized (Urban et al., 1994). Abiotic reduction of sulfate is thermodynamically unlikely at low temperatures (<100 C) (Berner, 1970), and therefore the mechanism for the transformation of sulfate to hydrogen sulfide is
dependent on BSR (Jorgesen, 1977). The efficiency of this process depends strongly on sedimentation rates, the degree of bioturbation and the reactivity of the OM that the BSR community is consuming (Edenborn et al., 1987). The microbially mediated reduction of sulfate to sulfide produces fractionations of up to and exceeding 40-50‰ due to the preferential reduction of $^{32}$S relative to $^{34}$S by the BSR community (Canfield and Teske, 1996). Fractionation can increase via disproportionation, whereby sulfur intermediates ($S^0$, $S_2O_3$) produced by partial oxidation of sulfide are both reduced to $H_2S$ and oxidized to $SO_4^{2-}$. In these settings fractionation between the marine sulfate pool and the mineralized sulfide pool can increase up to 70‰ (Canfield & Thamdrup, 1994). Recent papers, however, have suggested that natural populations of sulfate reducing bacteria can produce fractionations between sulfate and sulfide as large as 68-72‰, confirming that both processes are important in explaining the large fractionations seen in nature (e.g., Sim et al., 2011).

BSR is the dominant pathway of anaerobic oxidation of organic matter in marginal marine sediments (Howarth, 1984; Urban et al., 1994) where rapid burial of the organic compounds escapes complete aerobic consumption within the oxygenated zone above. Conversely, in lake sediments where sulfur may be limiting, BSR may only account for 10-30% of anoxic OM consumption (Ingvorsen and Brock, 1982; Urban et al., 1994).

Organic carbon delivery to CS sediments was limited by two factors: seasonal freezing of the sea surface would have limited photosynthesis and organic carbon sequestered into the sediments would have been further diluted by the high average
sedimentation rate of 1 cm yr\(^{-1}\). Consequently, rates of BSR and the impacts of associated isotopic fractionations are low relative to the rates of sulfate resupply from the surrounding ocean, and the isotopic composition of sulfate in the local seaway therefore remained close to that of the open oceanic supply. Low rates of BSR are further indicated by the minimal amounts of iron monosulfides and pyrite sequestered within the sediments. Iron needed for mineralized sulfide phases is thought to have come from iron hydroxides and goethite, which originally coated sedimentary particle within the marine environment (Donovan & Lajoie, 1978).

5.0 Methods

5.1 Sample Collection and Preparation

Suitable piston core locations were chosen based on CHIRP sonar-imaging data provided by Pat Manley (Figure 2). Sites were chosen based seismic reflectors and Cronin et al.’s previous success in the area. Age constraints are obtained from previous studies dating the end of the CS at ~9.6 ky bp and \(^{14}\)C dating of terrestrial and marine flora and fauna giving rough time constraints for both cores (Cronin et al., 2008). Two cores were analyzed in the present study: MUCR-1 and MUCR-2 (locations provided in Fig. 1). The marine section captured in these cores are ice-distal, muddy red-gray rythmites and extremely fine grained due to larger particles dropping out of suspension near the higher energy northern end of the basin (Cummings et al., 2011). Due to the limits imposed by having only a 3-meter long piston corer, sites where chosen with the CS/LC sediment boundary comparatively close to the sediment-water interface. Coring was performed using a quick release piston corer fitted with a one-way tip allowing
sediment entry without escape. The main coring tube was lined with plexiglass tubes, which acted to hold the sediment during transport and storage. The plexiglass tubes were then cut length wise, allowing a hand-drawn piano wire to slice each core section in half lengthwise. One half of each stratigraphic column was saved as the archive, while the other half was used as the working core for obtaining sediment splits for CAS analysis. Samples were taken every 10 cm at approximately 4 cm sample thickness. Higher-resolution sampling was not possible due to the low concentrations of carbonate and CAS within the sediments. Dry sediment mass varied from ~2 to 20 g due to varying porosity, mineralogy and water content across the 3 m of core length.

5.2 CAS and Metal Extraction

All samples were centrifuged and dried before the CAS extraction. The CAS extraction was modified from Burdett et al., (1989). Each sample was first washed with a 10% NaCl solution for 24 hrs to liberate precipitated salts. The solution was then decanted off. Next, 1 L of 18.2 MΩ distilled water was added to ensure removal of soluble sulfur species prior to the addition of acid. These solutions were also decanted off before 150 ml of NaOCl was added and allowed to sit for 48 hrs to attack organically bound sulfur. After decanting the NaOCl, 1 L of 18.2 MΩ distilled water per day for two days was added then decanted. If suspended particles were slow in settling, the samples were centrifuged or allowed to stand until the suspended material settled. 4N HCl was then added to fully dissolve calcium carbonate, thus liberating the CAS and metals associated with the carbonates and other soluble mineral phases, such as oxides. The sample was allowed to sit until dissolution was complete and then was immediately
filtered over a 0.45 μm nitrocellulose filter. The remaining solution was then brought up to a known volume in volumetric glassware. A 2 ml aliquot of each solution was then taken for determinations of sulfate and metal concentrations: Mg, Fe and Sr as measured in house via inductively coupled plasma mass spectrometry (ICP-MS). 100 ml of 250 g/L barium chloride solution was then added to each solution and allowed to sit for 5-10 days at room temperature to ensure full precipitation of barite (BaSO₄). The solution was again filtered through a 0.45 μm nitrocellulose filter, oven dried and then scraped and homogenized. This barite powder was then weighed into a tin capsule to ~0.400 mg with vanadium pentoxide (V₂O₅) added as a catalyst for complete combustion.

5.3 Isotope and Concentration Measurements

Sulfur isotope measurements were performed at the Lyons Biogeochemistry Stable Isotope lab at the University of California-Riverside using a ThermoScientific Delta V+ Isotope Ratio Mass Spectrometer coupled to a Costech 4010 Elemental Combustion System via a ThermoScientific ConFlo III interface. Sample data were corrected with a regression of three international reference materials: IAEA SO₅, IAEA SO₆ and NBS127, which were run multiple times with each sample set and referenced to V-CDT (Vienna-Canyon Diablo Triolite).

Sulfate and metals concentrations were also measured in the Lyons Biogeochemistry Lab at University of California-Riverside. The aliquots, taken from the CAS dissolutions prior to addition of BaCl₂, were split further and diluted with 2% nitric acid 50-fold. These solutions were then run on an Agilent 7400 Quadrapole ICP-MS; xenon and helium were used as carrier gases when measuring sulfur and metals (Mg, Fe,
and Sr), respectively. Data are corrected to internal sulfur and metal standards run frequently during each batch to monitor for drift throughout the run. Metal concentrations were normalized to sample mass and reported on a whole-rock basis, while sulfate concentrations were normalized to total inorganic carbon (TIC) content.

5.4 TIC Measurements

Dried, roughly 100 mg sediment splits were analyzed for TIC on an Eltra CS 500 Carbon Sulfur Determinator coupled to an Eltra TIC acid module. These measurements were also performed in the Lyons lab at the University of California-Riverside. Samples were compared against carbon standard AR 1034 obtained from Alpha Resources, Inc., and analyzed in duplicate.

5.5 Salinity Estimates

Due to the muted sulfur cycle in the Champlain Sea—i.e., low amounts of BSR and iron sulfide burial relative to sulfate inputs—$\delta^{34}\text{S}_{\text{CAS}}$ values are taken to represent the mixing of the two dominant water sources to the basin. With this in mind, a simple mass balance approach can be used to calculate the relative fractions of the competing water sources:

Equation 1: $\delta^{34}\text{S}=x(21‰) + (1-x)(0 \text{ or } 10‰)$

In Equation 1, $x$ is the fraction of marine sulfate, and $(1-x)$ is the fraction of riverine sulfate. $\delta^{34}\text{S}$ are the reported CAS values from this study. Modern marine CAS value is assumed for the marine end member (21‰), and riverine sulfate was assumed to range from 0-10‰ representing average world rivers. Once relative marine and riverine contributions were assessed, it becomes possible to estimate salinity measured in
practical salinity units (PSU) via:

Equation 2: \[ \text{PSU}_{CS} = \text{PSU}_{sw}(f_{sw}) + \text{PSU}_{rw}(f_{rw}), \]

where \( \text{Sw}_{\text{salinity}} \) equals the salinity of seawater estimated at 30 PSU based on current annual mean salinities measured at the Gulf of St. Lawrence (Katz et al., 2011). The riverine salinity (PSU) was assumed to range from 0.1 and 0.5 PSU. Salinity of the basin can then be estimated by multiplying the salinity of seawater by the \( f_{sw} \) within the basin plus the salinity of riverine input multiplied by the \( f_{rw} \) into the basin. The high and low assumptions made for riverine salinity levels in Equation 2 and the riverine isotopic range enable a maximum and minimum salinity to be estimated for CS throughout the study period.

6.0 Results

6.1 \( \delta^{34}S_{\text{CAS}} \)

6.1.1 MUCR-1

Core MUCR-1 captures both lacustrine and marine sediments, illustrated by TIC concentrations (Figure 5) and saturated bulk density measurements (Figure 3), changing dramatically at 100 cm down from the sediment-water interface. As shown in Figure 4, \( \delta^{34}S_{\text{CAS}} \) for the marine section varies from values as low as 9.4‰ up to the nearly full marine value of 20.4‰ (modern marine value averages 21‰). Below 150cm depth \( \delta^{34}S_{\text{CAS}} \) values track a primarily marine input of sulfate at ~19-20‰. Several excursions to lower \( \delta^{34}S \) were observed within the marine section, dropping to as low as 15.2‰. At the bottom of the core, deposited ~11,000 ky bp, \( \delta^{34}S_{\text{CAS}} \) values are nearly fully marine at 18.6‰ then increase up core to 19.2‰, then dropping suddenly to 15.2‰. A rapid
recovery follows to near fully marine values again as we move up core from 270 cm to 200 cm. A maximum $\delta^{34}\text{S}_{\text{CAS}}$ value of 20.4‰ was obtained at 230 cm depth and slowly decreased to 16.6‰ at 190 cm depth. The variability of CAS values increases further up core, with values oscillating from near-marine values of 19.9‰ and 19.6‰ to 16.1‰ and back to 17.8‰ then finally dropping to 9.4‰ by 130 cm below the sediment-water interface. Moving up core, at a depth of 120 cm, values return to 15.4‰. There is a return to 20.9‰ at 100 cm depth, which drops to 16.3‰ at 90 cm. Above this depth, the reliability of the CAS proxy, which requires adequate levels of both carbonate minerals and sulfate concentrations within those minerals, drops below measurable levels.

6.2 TIC

TIC concentrations in both cores (Figures 6 & 10) show a dramatic first order change across the marine to lacustrine transition. The two cores, however, do not show the same consistency within their respective marine intervals. MUCR-1 shows on average 0.4 wt% higher TIC levels at 1.4 wt% within the marine section relative to MUCR-2 values, which oscillate around 1.0 wt%. Moreover, MUCR-1 records much less variation through the section, with down-core variability decreasing further in the deepest section of the core, most likely representing a relatively stable marine community. TIC levels in MUCR-2 show significantly less TIC and greater variability relative to MUCR-1 within the marine section. MUCR-2 records a period shortly after the Younger-Dryas where freshwater routed through the Champlain basin lowered the salinity, an event reported in Cronin et al. (2008), where salinities fell from 25 PSU to 7-8 PSU; such a dramatic ecological shift may have slowed biotic recovery.
6.3 Metals Contents of MUCR-1 and MUCR-2

Related metal concentrations, obtained through acid extraction, point towards terrestrial riverine inputs responsible for a negative $\delta^{34}$S excursions (Fig. 4) relative to open seawater and therefore lower salinity events punctuated throughout the marine stage of the Champlain Sea—consistent with its restricted setting and a high proglacial flux.

The Mg and Sr show a strong first-order relationship in phase with marine versus non-marine depositional conditions (Figure: 7 and 9 for MUCR-1 and Fig. 11 and 13 for MUCR-2). This pattern can be gleamed from the relatively high concentrations within the entire marine section compared to the lacustrine interval. Each of these elements also shows a second order rise and fall in concentration throughout the core. The mechanism behind this variability is discovered when comparing these metals with the concentrations of iron within the core. Iron concentrations for MUCR-1 and MUCR-2 (Figures 8 & 12), unlike the other metals, do not show the strong first-order marine to lacustrine relationship. Instead, iron concentrations show only the second order rise and fall indicating that iron was dominantly sourced from riverine inputs, most likely in the form of iron oxides delivered to the basin then bound in the clay fractions. These trends are discussed further below within a framework of Lake Agassiz flood events, which periodically freshened the basin due to continued LIS melting and isostatic rebound.

6.4 Salinity Estimates

The sluggish sulfur cycle within the Champlain Sea was driven by relatively high sedimentation rates (~1 cm yr$^{-1}$). Indeed, relatively high sedimentation would contribute to the low organic carbon contents by diluting the relative small amounts of labile OM.
thereby minimizing the available substrate for the BSR community responsible for fractionating the aqueous pool of sulfate; furthermore the freshly scoured and ice free land surface would have provided minimal terrestrial organic carbon. Consequently, $\delta^{34}\text{S}_{\text{CAS}}$ is believed to reflect the combination of two sulfate sources: a riverine source with low concentration and relatively depleted $\delta^{34}\text{S}$ of 0 -10‰ at 0.1-0.5 PSU and a marine source at a modern $\delta^{34}\text{S}$ value of 21‰ and 30 PSU, the modern value of the Gulf of St. Lawrence (Katz et al., 2011). With these parameters we have the ability to reconstruct upper and lower estimates for the change in salinity within the basin. By definition, maximum PSU estimates within the CS are reached at points where $\delta^{34}\text{SCAS}$ values are close to fully marine. At this point, not only were the waters within the Sea near fully marine but the difference in PSU estimates is minimal due to the dominant source of sulfur in the CS being derived from marine waters and the model assuming no variation for this isotopic end member. Minimum and maximum estimates diverge by a greater amount as $\delta^{34}\text{S}_{\text{CAS}}$ values become more depleted; with estimates varying up to 13 PSU. Cronin’s 2008 study, which captured a freshening event within the CS at the onset of the Younger-Dryas, is estimated to have dropped salinity levels by a similar order of magnitude potentially more so.

6.4.1 MUCR-1

MUCR-1 captures roughly 1500 years of deposition within the Champlain Sea. In this interval, (Figure 5) PSU estimates range from near fully marine for the CS at 28-29 PSU down to minimum values of 0-13 PSU. Unlike the continual drop expected if driven solely by isostatic change (a linear rate of change was measured by Rayburn et al., 2005),
the core reveals a fully marine sections punctuated by rapid freshening events. These flood events detailed in Table 3 as modified from Teller et al. (2001) show varying fluxes, volumes and timings of Lake Agassiz outbursts. Using the Cronin et al. (2008) $^{14}$C data to define a general marine time boundary of ~9.5 ky bp for MUCR-1 and knowing the core captured the final stages of the marine incursion dated at ~9.6 ky bp (Cronin et al., 2011), the floods reported in table 3 are the only documented events routed through the CS during this time interval. The flood event and associated freshening ranging from 0.5-13 PSU for 130 cm depth then becomes the 10 ky bp event with a size of 1600 km$^3$ and an estimated flux of 0.05 Sv described by Teller et al. (2001) and (Leverington et al. (2002). The 10.3 ky bp flood event (17-23 PSU) at depth 160 cm was estimated to be larger at 2100 km$^3$ overestimate based on the lack of increased metal concentrations at this depth. Sr/Mg (Figure 14) does show an increase at this depth. Carlson et al. (2007) described the Sr and Mg-rich Paleozoic bedrock that many of the Lake Agassiz floods must have passed over. This Sr/Mg ratio increase with a lack of absolute concentration increase may represent a riverine drainage route taken through another proglacial lake system where the opportunity to lose many of the Sr & Mg containing “rock flower detritus” is present or as stated above a smaller than expected flux rate which would be less efficient at scouring fresh materials. The 10.4 kybp flood event (18-24 PSU) corresponding to 190 cm depth was 3700 km$^3$ in volume, with a flux size of 0.12 Sv. The 10.6 ky bp flood event (14-22 PSU) had the largest volume at 7000 km$^3$ and a flux of 0.22 Sv.
7.0 Discussion:

7.1 Isostacy and Eustacy

The loss of the Laurentide Ice Sheet in North America had two major consequences. First, the rapid loss of weight on the continent allowed it to isostatically rebound. Secondly, the phase change from solid to liquid water forced vast amounts of water to drain into the world's oceans, raising eustatic sea level. These contemporaneous events are the mechanisms that extended the CS lifetime to ~3.2-3.4 ky (Rayburn et al., 2006; Cronin et al., 2011), longer than a purely isostatically affected system would have allowed. However, isostatic rebounding affected large swaths of high latitude areas, continuously affecting drainage routes of a variety of proglacial lakes, the largest and most violent of which was Lake Agassiz (Leverington et al., 2000; Teller et al., 2001; Leverington et al., 2002; Rayburn et al., 2006; Clark et al., 2010).

7.2 Salinity and Flux Sources

In the CS we are presented with a system that transitioned from near fully marine conditions to the modern lake we find today. The low concentrations of both sulfate and OM within the lacustrine system allow for a novel use of the proxy in contrast to classical CAS approaches, which typically focus on global sulfur cycles and redox conditions. Here, CAS provides a way to estimate salinity levels and thus the controlling factors behind the freshening of the basin. The estimates made by previous studies using both oxygen isotopes and paleontological evaluations of marine communities (Hillaire & Marcel, 1988; Moore et al., 2000; Brand & McCarthy 2004; Carlson et al., 2007; Cronin et al., 2008, 2011) are strengthened by the CAS approach as the salinity estimates within
this study estimate similar levels within the CS. An assessment of the marine community comes with the understanding that many of species are euryhaline, meaning they can survive over a wide range of salinities and therefore can only give a range for the salinity estimates for the CS. The CAS approach allows for a relatively sensitive, independent salinity estimate limited only by the concentration of TIC and sulfate within the system. One assumption of this argument is, sulfate concentration scales readily with salinity, particularly when the basin is neither strongly reducing nor severely isolated. Sulfate comes with diagnostic, source-dependent isotopic properties and, perhaps most importantly, is readily traced by the isotopic composition of sulfate trapped within carbonate minerals.

The concentration of detritally sourced and acid-soluble metals that readily bond with native clays point towards terrestrially sourced flood events. Lake Agassiz was the only source of these flood events. The concentrations of metals within both cores display two distinct patterns. Whole-rock concentrations of Mg, Fe and Sr reflect both a first-order pattern recording marine versus lacustrine deposition, with marine concentrations being much higher than in the lacustrine sections of the cores, and a second-order pattern that looks periodic or episodic and is likely diagnostic of flood events routed through the basin. The key to this interpretation is twofold. First, iron concentrations within both cores do not record the first-order marine to lacustrine transition which would represent a largely marine source but do capture the oscillating second-order changes in concentration sourced from detrital oxides they are readily bonded with chlorite and related clays ubiquitous throughout the basin. Iron therefore is not diagnostic of
fundamental differences in the depositional system but rather detrital inputs from upstream terrestrial sources. Secondly, as Carlson et al. (2007, their Fig. 1) showed, Precambrian and Paleozoic bedrocks rich in Mg and Sr are directly below the melting LIS and its associated proglacial lakes. Once glacially scoured, this bedrock provides the sediment with the metals in question that eventually make their way into the CS. Depths 130, 160, 190 and 280 cm within MUCR-1 show depleted δ34SCAS values as well as concurrent increases in metals concentrations, providing strong evidence that these freshening events were due to proglacial floods entering the CS before emptying into the North Atlantic. The most likely culprit is Lake Agassiz, the largest proglacial lake associated with the LIS. Lake Agassiz was most likely the only source for these large outbursts of proglacial waters during the last deglaciation (Teller et al, 2001). A suite of literature exists on Lake Agassiz (Leverington at al., 2000; Teller et al., 2001; Leverington et al., 2002), which includes reference to four floods that are thought to have exited through the CS interval spanning the MUCR-1 records. Though the magnitude and duration of these events are still up for interpretation, clearly some were much more effective than others at freshening the CS throughout its range, including the southerly sample locations of this study.

7.3 Isostacy, Floods and Isotopic Interpretations

The sediments within MUCR-1 reflect a system transitioning out of a near fully marine depositional system into a lacustrine basin. Marine conditions reflect the post-glacial rise in sea level. However, isostatic rebound drove the system back to nonmarine by cutting off the North Atlantic connection. This slowly freshening system was also
punctuated by Lake Agassiz flood events, which decreased in magnitude over time. The sulfur isotope values reflect the interplay between decreasing flood size and a diminishing marine contribution. The largest flood recorded within this core at 280 cm depth reveals one of the smallest negative excursions—implying the marine system was still well connected at ~10.6 ky bp, and the sulfate pool was corresponding large and dominated by seawater $\delta^{34}$S. The Champlain Sea at this point had a nearly full marine connection.

Moving toward the top of the marine section at 130 cm depth in MUCR-1, we find a system with a much weaker marine connection. The flood event at 10.0 ky bp routed through the CS was the smallest of the four floods, yet it yielded the largest negative sulfur excursion because a decreasing marine sulfate pool was losing its buffering capacity to minimize the impact of flood-sourced sulfate. Cronin et al., 2008 dated the sediment package at the MUCR-1 study site, which, even with the uncertainty of the $^{14}$C dating of marine tests, clearly brackets four Lake Agassiz flood events. These floods now identified, further constrain the timing of sedimentary deposition within the CS and the events that shaped its chemistry and mineralogy.

7.4 Lower Limits of the CAS proxy

Because of the low organic contents of these sediments, authigenic carbonate inputs tied to BSR and concomitant alkalinity production, for example, are corresponding low. Cummings et al. (2011) described the youngest Champlain Sea sediments, captured by MUCR-1, as being carbonate-poor muddy red and gray rhythmites, in contrast to the oldest 2-meter thick, carbonate-rich Champlain Sea sediments. The most likely source of
carbonate is the biogenic tests of the benthic foraminifera and ostracod community (Cronin 1977, 2008; Hillaire-Marcel, 1988) as detrital inputs during this time were minimal and authigenic carbonate production is limited by OM availability, reactivity, and the BSR community outcompeting methanic communities for resources. Staudt and Schoonen (1995) described in detail the potential for sulfate substitution into a variety of carbonate phases, including benthic and planktonic foraminifera. Perhaps for the first time, this study shows that robust $\delta^{34}S_{\text{CAS}}$ values can be derived from sediments with TIC levels never higher than 1.5 wt% and an average marine CAS concentration of 64 ppm when normalized to TIC.

The integrity of the proxy was further strengthened by the apparent inefficiency of BSR within the basin and lack of benthic anoxia. The methods used for CAS extraction are designed to reduce any chance of isotopic contamination by unwanted oxidation of pyrite and iron monosulfides, but even a small amount could be a problem given the relatively low concentrations of carbonate and primary sulfate as the basin freshened. Fortunately, iron sulfide phases were present in very low amounts of only 0.08 wt% on average for core MUCR-1 (W. Gilhooly, personal communication).

8.0 Conclusions:

The Champlain Sea had both a proglacial fresh water source relatively rich in detrital metals, fine muds and silts due to enhanced mechanical weathering and a marine source that inundated the basin and provided nutrients but supported still low overall production. Low overall organic contents supported low rates of sulfur cycling compared to the broader oceanic rates, prohibiting the restricted basin from taking on its own
isotopic properties through local redox processes. Therefore, the CAS isotopic values measured can be used to gauge the relative contributions of the two end-member water sources into the Champlain Sea; this allows for a novel use of the CAS proxy as a measure of salinity. Detrital metals, that readily bonded with native minerals, help constrain the sources of the salinity variation. The combination of negative $\delta^{34}S_{\text{CAS}}$ excursions against the otherwise stable marine-like values of $\sim$20‰, positive [Fe] excursions-representing higher volumes of terrestrially sourced proglacial floods into the basin and [Sr] and [Mg] excursions pointing to the mechanically scoured bedrock of the Canadian Shield all point to a Sea within the North American continent that was in a tenuous balance of opposing forces: eustatic sea level rise and proglacial floods partly driven by isostatic rebound. During the collapse of the Laurentide Ice Sheet, the Champlain Sea throughout its roughly four thousand-year history went through phases of both marine and freshwater dominance. Even during in the later marine-dominated stages of the CS, continued Lake Agassiz flood events could rapidly lower the salinity of the basin. Ecologically speaking, these rapid and numerous salinity events would have prohibited many macro-scaled organisms from successfully exploiting available niche spaces, which would otherwise have increased the available organic matter throughout the extent of the Champlain Sea. Instead, a prolonged organic-limited but sea-like basin existed until the regional isostatic rebound outpaced eustatic sea level, ending of the Champlain Sea and leading to the irreversible shift to modern Lake Champlain.
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Table 2: Core MUCR-2. TIC measured in wt%. CAS normalized to TIC. Mg, Fe & Sr concentrations normalized to “whole rock”.

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<th>Lake Stage</th>
<th>Outburst Vol (km³)</th>
<th>Flood Flux (Sv)</th>
<th>Route of burst</th>
<th>Time of burst (ka cal yr)</th>
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Table 3: Modified from Teller et al., 2001. Lake Agassiz stages, outburst volumes, flood flux, route of bursts and time of bursts are given. Timing of flood events falls within sediments captured in MUCR-1. Negative CAS isotope excursions at 130, 160, 190 & 280cm depths match respectively and correspond to drops in CS salinity estimates reported in PSU.
Figure 1: Lake Champlain is pictured with general coring locations represented by a star. Inset shows the more precise coring locations for MUCR-1 and MUCR-2. Light in color the majority of Champlain Sea sediments are subarially exposed filling the Champlain, Ottawa and St. Lawrence valleys. Insert credited to Dr. Pat Manley, Middlebury College.
Sea sediments lie above the blue boundary, and Glacial Lake Vermont sediments lie below the blue boundary. The vertical red line represents the approximate coring location for each site. Dr. Pat Manley, Middlebury College credited for CHIRP images.

Figure 2: Saturated bulk density for MUCR-1 and MUCR-2; clear boundaries are evident at 100cm and 170 cm depths respectively. Credited to Dr. Pat Manley, Middlebury College.
Fig 4, 5, 6 for core MUCR-1. Y-axis is core depth in cm. Fig 4: CAS $\delta^{34}$S values measured in $\%e$. CAS $\delta^{34}$S reflect the combination of marine +21$\%e$ at 30PSU and lacustrine waters estimated at +0-10$\%e$ and 0.1-0.5 PSU mixing within the Champlain Sea. Negative excursions at depths 120, 160, 190 & 280cm reflect Lake Agassiz flood events. Fig 5: PSU estimates for CS are derived from CAS $\delta^{34}$S values. Flood events from Lake Agassiz decreased salinity to varying degrees based on marine connectedness and size of event. Fig 6: Total Inorganic Carbon (TIC) measured in weight %. TIC concentrations show steady concentration throughout the marine section of the core dropping dramatically across the lacustrine boundary. As the primary source of this carbonate is tests of benthic foraminifera and ostracods this reflects an ecological shift in the basin.
Fig 7, 8, 9 for core MUCR-1. Y-axis is core depth in cm. X-axis is ppm. Circles normalized to “whole rock”. Fig 7: Magnesium concentrations show relatively high values in the marine section and low concentrations in the lacustrine section. Fig 8: Iron concentrations. Unlike other metals, Fe concentrations do not vary suddenly between marine and lacustrine deposition. Due to the limited delivery of iron via marine waters, Fe in the CS reflects detrital inputs from erosional proglacial input. Fig 9: Strontium concentrations of are particular interest due to the high strontium concentrations in the Canadian bedrocks that Lake Agassiz. Depths 130, 200 & 280cm shows a correspondingly large increase in Strontium concentrations alluding to rapid events. While depth 160 cm may not have had enough energy to create a correspondingly large pulse.
Figures 10, 11 & 12: For core MUCR-2. Y-Axis records core depth. Figures 10 & 11 show relative high marine levels and relatively low lacustrine levels. Fig 10: records TIC concentrations recorded in wt%. Shifts in TIC representing differing levels of tests of foraminifera and ostracods reflect an ecological shift in the basin associated with flooding events. Fig 11: [Mg]. Magnesium concentrations & Fig 12: [Fe] Iron concentrations reveal a strong second order relationship representing enhanced proglacial input from the collapsing LIS.
Fig 13, 14 & 15: Figure 13 records strontium concentrations for core MUCR-2. A clear lacustrine to marine transition is present at 170cm core depth. Variability increases towards the bottom of the marine section, most likely associated with increased proglacial flux. Figures 14 & 15 record Sr/Mg ratios for cores MUCR-1 & MUCR-2 respectively. The bedrock scoured by the retreating LIS and below Lake Agassiz houses increased concentrations of Sr. Excursions within respective marine sections therefore represent proglacial flood events.
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