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GEOSCIENCES

Biogeochemical and oceanographic conditions provide insights about current status of an Antarctic fjord affected by relatively slow glacial retreat

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Abstract: Understand the origin, transport, and character of organic matter entering Antarctic fjords is essential as they are major components of the global carbon cycle and budget. Macromolecular pools of particulate organic matter, bulk organic geochemistry, major and trace elements in surface sediments from Collins Bay were analysed as source indicators. Oceanographic conditions, bathymetry (multibeam) and grain size were considered as environmental controlling factors. Sediment samples were taken with a van Veen grab, during the ANTAR XXV Peruvian expedition (February 2018), onboard the R/V "*BAP Carrasco*" from the Peruvian Navy. Biopolymeric composition revealed the predominance of fresh marine protein-rich organic matter in the seafloor of Collins Bay, denoting high quality food resource for marine benthic heterotrophs. Based on Igeo values (between 0 and 1) Collins Bay can be considered unpolluted with natural levels of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn. Distribution of most of these elements with a gradient of decrease from the shallow inner fjord towards the outer deepest fjord, suggest their association with the deposition of detrital material and lithogenic particles supplied by Collins Glacier frontal ablation and runoff. This first comprehensive baseline information would assist in interpreting downcore sedimentary reconstructions and future climate-induce changes.

Key words: organic and inorganic elements, biopolymeric carbon, glacio-marine sedimentation, terrestrial inputs, unpolluted sediments.

INTRODUCTION

The rapid atmospheric and surface ocean warming undergone by the West Antarctic Peninsula (WAP) during the second half of the last century, have been associated with documented reductions in the thickness and extent ice cover (Meredith & King 2005, Turner et al. 2016). Maritime Antarctica, including the South Shetland Islands is particularly affected by these climatic changes, leading to increase precipitation, the shortening of the sea ice season, and also, the acceleration of ice melting and retreat rates of marine-terminating glaciers (Rückamp et al. 2011, Boy et al. 2016, Meredith et al. 2018). Glacier retreat impacts the adjacent marine environment in many ways, contributing to sea level rise by increased freshwater budgets, exposing newly available ice-free areas to colonization and weathering processes, and increasing the transport of organic and inorganic material from land and glaciers to the ocean (Kim et al. 2015, Boy et al. 2016). In addition, enhanced

meltwater discharge and permafrost melting lead to increased water column stratification and turbidity, promote high sedimentation rates and may supplement an extra quantity of micronutrients to nearshore areas (Dierssen et al. 2002, Rückamp et al. 2011, Meredith et al. 2018). Then, larger inputs of glacial meltwater loaded with lithogenic particles eroded from glaciers and ice-free areas, are significantly changing seawater and seabed properties, impacting the productivity of pelagic and benthic marine ecosystems and their food webs (e.g., Ingels et al. 2012, Schloss et al. 2012, Pasotti et al. 2014).

The magnitude, composition and distribution of particulate material contribution to the water column and sediments are controlled by several environmental and biological factors, all of them acting at local and regional scales (Zaborska et al. 2016). Among environmental controlling factors we can mention the oceanographic settings, ice coverage, season, depth, sedimentation rate and terrestrial input. Whereas, the pool of primary producers and productivity, the grazing efficiency, the rate of microbial degradation and heterotrophic consumption are some key biological factors (Misic et al. 2017, Zaborska et al. 2016 and references therein). Every spring-summer season, fresh and detrital marine particulate organic matter (POM) is released from sea-ice during calving and melting, is originated from phytoplankton blooms and macroalgae detritus, and is introduced from land through meltwater runoff. As a result, considerable amounts of POM accumulate in Antarctic coastal waters and sediments, since great portion is exported to the seafloor (Fabiano & Pusceddu 1998, Isla et al. 2006, Mincks et al. 2005, Passotti et al. 2014). Marine POM derived from phytoplankton provides protein-rich food to higher trophic consumers (Kim et al. 2016). On the other hand, terrestrial POM is a low-quality food resource for marine organisms, because most of them appear to be unable to digest and assimilate refractory compounds (cellulose and lignin), without earlier microbial breakdown (Danovaro et al. 1999, Antonio et al. 2010). These pulses of particle supply play a relevant role in regulating the carbon cycling, supporting benthic communities the entire year, and influencing the coupling between pelagic and benthic biogeochemical processes (Fabiano & Pusceddu 1998, Isla et al. 2006, Mincks et al. 2005, Zenteno et al. 2019).

The labile fraction of the POM deposited in marine bottom sediments, comprises simple and/or combined molecules as the biopolymers (lipids, carbohydrates and proteins) that are indeed available for benthic organisms and are quickly mineralized (Baldi et al. 2010, Danovaro et al. 1999, Pusceddu et al. 2003). Worldwide, numerous works have demonstrated that biochemical components of the POM are sensitive tools to assess, spatial and temporal, changes in the input of organic matter to the sediments associated to both natural and human-induced environmental changes (Danovaro et al. 1999, Pusceddu et al. 2003, 2009, Venturini et al. 2012, among others). In Antarctica, organic biopolymers have been used to evaluate qualitative features of POM and its role as food resource, both in the water column and sediments (Fabiano & Pusceddu 1998, Isla et al. 2006, Baldi et al. 2010, Misic et al. 2017).

Weathering of coastal rocks and soils, atmospheric circulation and deposition, together with guano contributions from seabirds and penguins, are the main natural sources of trace and major elements to the marine environment in Antarctica (Vodopivez et al. 2015, Webb et al. 2020 and reference therein). On the other hand, anthropogenic sources include operation and maintenance of scientific research stations, waste and sewage disposal, energy generation, fuel handling, ship and aircraft traffic, and

also, tourism (Bueno et al. 2018, Ribeiro et al. 2011, Vodopivez et al. 2015, Webb et al. 2020). Due to their physiochemical properties, once released into the environment elements are usually enriched in organic-rich deposits, influencing the composition of coastal marine sediments (Sweere et al. 2016, Vodopivez et al. 2019). Chemical composition and elemental ratios have been recognized as suitable proxies for contemporary assessments of sediments sources, depositional redox conditions and diagenesis, as well as, for paleoenvironmental reconstructions of driving mechanisms linked to climate variability (Bertrand et al. 2012, Sun et al. 2013, Tribovillard et al. 2006, Wagner et al. 2015).

Collins Bay is a fjord located to the north of Maxwell Bay, next to the Artigas Base (BCAA), the Uruguayan Research Station. This area covers the south side of the Collins Glacier or Bellingshausen Dome, which is placed in the southwest of King George Island (KGI) (Fig. 1). The Collins Glacier has a small area of 15 km^2 and a highest altitude of 270 m, and it has been responded slowly than other glaciers of KGI to regional climate changes (Rückamp et al. 2011, Simões et al. 2015). According to Petsch et al.

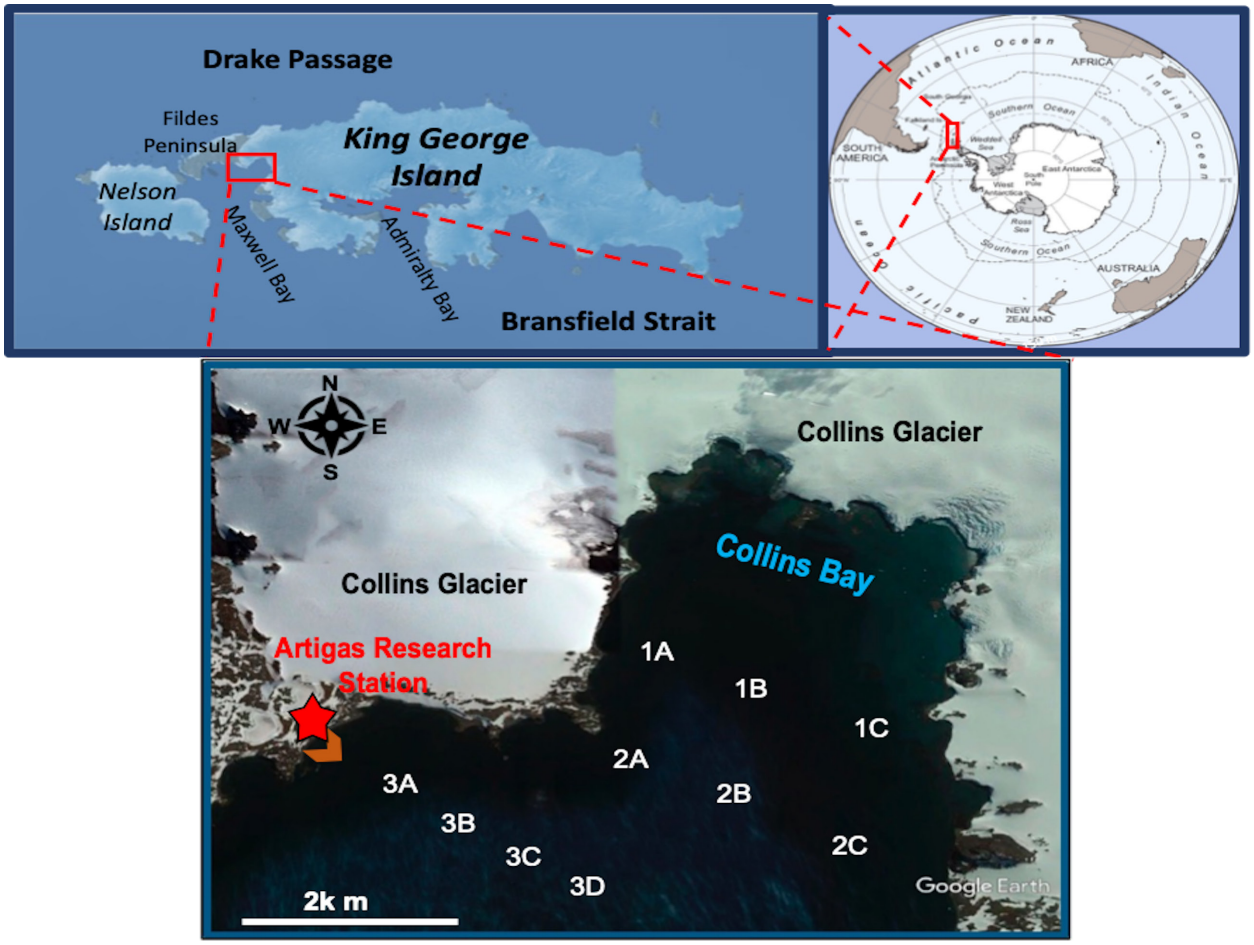

Figure 1. Map of Collins Bay showing the three sampling transects. Sampling sites in transects 1 and 2 are located at 2000 and 3000 meters from the NE coastline and tidewater terminating portions of Collins Glacier, respectively. Sampling sites in transect 3 are located 500 meters apart of each other from the mouth of the meltwater creek offshore.

(2020), Collins Glacier lost 1.4 km^2 between the Little Ice Age and 2018, and will lose further 0,90 km^2 corresponding to near 5% of its total area until 2030. Modelling scenarios predicted that it would disappear in less than 300 years, if the last decade regional climate conditions in the area persist (Rückamp et al. 2011). The increment of terrestrial suspended POM inputs to the sea, linked to warm weather conditions and thus increased meltwater runoff, have been recently shown to this area (Venturini et al. 2020). Active iceberg calving from tidewater glacier terminus has also been reported (Yoon et al. 1998).

Under a scenario of continued glacial melting and calving in the WAP, the fluxes of organic and inorganic particles from land to coastal Antarctic waters, and then, from the water column to the seafloor could change in terms of quantity and composition (Ingels et al. 2012). In consequence, pelagic and benthic communities of WAP fjords would be under increased stress in becoming decades (Eidam et al. 2019, Pan et al. 2019). With this in mind, this study aims to analyse the composition of macromolecular pools of POM (total proteins, lipids, and carbohydrates), bulk organic geochemistry, major and trace elements in surface sediments from Collins Bay, as source indicators of solid particle supply to the seafloor. Environmental controlling factors, such as oceanographic variables, bathymetry and grain size are also considered. We aim to provide first characterisation of modern Collins Bay sedimentary biogeochemistry, and insights about its primarily controls, as baseline information for interpreting downcore sedimentary reconstructions and future climate-induce changes. In addition, thoughts about the potential quality of the sedimentary biopolymeric POM as food resource to marine benthic heterotrophic organisms are given. We expected the decline of glacial and terrestrial inputs offshore across the adjacent marine environment by increasing the relative input of *in situ* produced marine POM. The potential value of the sedimentary POM as food for marine benthic heterotrophic consumers is expected to increase from near shore to offshore areas due to changes in POM composition, reflecting in the decline of terrestrial refractory *vs*. fresh marine protein-rich POM inputs.

MATERIALS AND METHODS

Study area

KGI between 61° 54 – 62° 16´S and 57° 35 – 59° 02´ W, is the largest island of the South Shetland Archipelago. It is bounded by the Drake Passage on the north, and by the Bransfield Strait on the south (Fig. 1). Maxwell Bay (62° 13.7´S and 58° 50.9´W) located in the western end of KGI has an extension of near 140 km^2, is about 15 km long, and between 6 and 15 km wide (Fig. 1). Maxwell Bay has several tributary inlets and its maximum water depth is near 500 m in the outer bay (Munoz & Wellner 2018). The glacier catchment area around Maxwell Bay is about 92 km^2 (Boldt et al. 2013). The development of overflow plumes with low salinity, temperature and high turbidity have been reported during the peak of meltwater (Yoon et al. 1998). A dominant two-layered estuarine circulation has been recently outlined during the austral summer in Maxwell Bay (Llanillo et al. 2019). Meltwater accumulation toward its head is promoting by flood tide, freshening and warming the upper 80 m. Below this depth, the flood tide enhances the intrusion and mixing of relatively warm modified Upper Circumpolar Deep Water (m-UCDW), with important implications on primary production and on the mass balance of the tidewater glaciers bordering Maxwell Bay (Llanillo et al. 2019). Collins Bay is a tributary inlet of Maxwell Bay located to the north, where high sediment accumulation rates have been

reported 5.5 mm yr^{-1} (Boldt et al. 2013). Meltwater channels, together with crag and tails parallel to ice flow direction, are the main seabed geomorphological features of this bay (Munoz & Wellner 2018). Collins Bay is a strong stratified fjord with a dominant two-layered estuarine circulation during the austral summer, which is partially countered by tidal straining (Llanillo et al. 2019). Similar to Maxwell Bay, an enhanced retention of meltwater was also observed at the head of Collins Bay during flood tide. Nevertheless, close to the ice-cliffs the water column is fresh and cold independently of the tidal phase (Llanillo et al. 2019). The presence of waters with high salinity close to the bottom may be related to episodic intrusions of the m-UCDW, as found for Maxwell Bay (Llanillo et al. 2019). The glacier catchment area around Collins Bay is about 50 km^2 and the adjacent coastal area is directly influenced by the presence of Collins Glacier (Munoz & Wellner 2018), which is characterized by a land front and tidewater-terminating portions (Simões et al. 2015). It has several limbs that melt before reaching the sea, and generates nine creeks that flow into both sides of the coast (Chinarro 2014). Five creeks compose the drainage system into the Bransfield Strait. After following separate proglacial routes, the whole flow converges at a pond. The pond output is a unique meltwater creek that flows under the bridge leading to the BCAA and finally reaches the sea (Chinarro 2014) (Fig. 1). A wet basal thermal regime revealed by flutings, push and dump moraines, was recently identified to Collins Glacier (Petsch et al. 2020). The BCAA is operating permanently since 1985. It is constituted by 11 buildings and has a maximum capacity of 65 people that is reached only in summer, as only 9 people of the permanent crew remain during winter (Bueno et al. 2018). High metal levels have been reported in soils near the BCAA, but limited to a restricted area without affecting surrounding freshwater and marine environments. They have been related to fuel storage and handling, sewage release and old leaded paint residues (Bueno et al. 2018). This area is included in an Antarctic Specially Protected Area (ASPA 125).

Field sampling and sample handling

Sampling was performed in January 2018 during the ORCA Cruise, onboard the R/V "*BAP Carrasco*" from the Peruvian Navy in the ANTAR XXV expedition. Sampling sites were distributed in three transects: transects 1 and 2 located around 2000 and 3000 meters from the NE coastline and tidewater portions of Collins Glacier, respectively, and transect 3 located from the mouth of the meltwater creek offshore (Fig. 1). Vertical profiles of temperature, salinity, dissolved oxygen concentration, turbidity and fluorescence were acquired with sensors coupled to a CTD SBE 19 PLUS, with a sampling frequency of 6 Hz and a mean descending rate of 1 m s^{-1}. Bathymetric survey was performed with a Kongsberg EM-122 multibeam echosounder at a frequency of 12 kHz. Surface sediment samples were taken with a stainless steel van Veen grab (0.1 m^2). The upper 1 cm layer and the middle of the grab were considered for metallic elements and biochemical analyses. These considerations were made to study only surface sediment composition, but also, to avoid contamination and any disturbance of the sediment by excluding smear from the grabbing processes. Sub-samples for biochemical analyses were immediately placed in pre-combusted aluminium containers and kept frozen (–20 °C) in the dark until arrived to the laboratory. Sub-samples for the analysis of metallic elements were placed in polyethylene containers. These sediment sub-samples were freeze-dried and homogenized previous to be analyzed. An additional surface sediment sub-sample was taken at each station for granulometric analysis.

Analytical procedures

About 100 g of surface sediments were submitted to the standard dry-sieve method (Suguio 1973). The GRADISTAT package was used to calculate percentages of the different grain size fractions, grain size statistics and the Folk & Ward descriptive terms (Folk & Word 1957).

Nitrogen, carbon and carbon isotope ratios were measured by Elemental Analyzer Continuous Flow Isotope Ratio Mass Spectrometry in the Center for Stable Isotopes, University of New Mexico using a Costech ECS 4010 Elemental Analyzer coupled to a ThermoFisher Scientific Delta V Advantage mass spectrometer via a CONFLO IV interface. Carbon isotope ratios are reported using the standard delta (δ) notation relative to Vienna Pee Dee Belemnite (V-PDB) as: $\delta^{13}C$ (‰) = $[(R_{sample}/R_{standard})— 1)]$ x 1000, where R is the ratio $^{13}C/^{12}C$. Three internal, laboratory standards were run at the beginning, at intervals between samples, and at the end of analytical sessions. Analytical precision calculated from the standards is ± 0.1 ‰. Analyses were normalized to the laboratory standards which were calibrated against NBS 21, NBS 22 and USGS 24 for $\delta^{13}C$. Sediments for $\delta^{13}C$ and TOC analyses were acidified with 1N HCl to remove carbonate-hosted carbon. After 24 h samples were adjusted to neutral pH with ultra-pure water, dried at 50 °C to constant weight, ground to a fine powder and loaded into tin capsules. Total inorganic carbon (TIC) content was determined using the difference between TC and TOC contents, from which $CaCO_3$ was calculated as weight percentage multiplying TIC content by 8.33, the stoichiometric calculation factor for $CaCO_3$. The $\delta^{13}C$ and the C/N ratios of the sediment samples were used to estimate the relative contributions of terrestrial and aquatic organic carbon (Meyers 1997, Perdue & Koprivnjak 2007).

Total proteins (PRT), carbohydrates (CHO) and lipids (LIP) were analyzed spectrophotometrically following Hartree (1972), Gerchacov & Hatcher (1972), Bligh & Dyer (1959) and Marsh & Weinstein (1966). Blanks for each analysis were performed with pre-combusted sediments at 450 °C for 4 h. PRT, CHO and LIP concentrations were correspondingly expressed as albumin, glucose and tripalmitine equivalents. All analyses were carried out in triplicate. Detailed information regarding these methods is provided in Danovaro (2010). PRT, CHO and LIP concentrations were converted to carbon equivalents assuming conversion factors of 0.49, 0.40 and 0.75 mg, respectively. Their sum was reported as the biopolymeric carbon (BPC), which was used as a reliable estimate of the labile fraction of organic matter easily assimilated by benthic communities (Dell'Anno et al. 2002, Pusceddu et al. 2003, 2009, Venturini et al. 2012, among others).

Inductively Coupled Plasma – Optical Emission Spectrometry (ICP OES) was the analytical technique used for As, major and trace elements. The methodology for determining these elements was based on the digestion method 3050B (USEPA, 1996). Certified Reference Materials (CRMs) SS-1 and SS-2 (EnviroMat.) and Soil-7 (IAEA) were analyzed in parallel with determination of elements. Reagent blanks were run with all sample analyses. Blank signals were lower than 0.2% of sample signals. The expressed concentrations of each element in the samples represent the mean of eight independent determinations and their values were not corrected for recoveries observed for the CRMs.

As an approach to assess anthropogenic pollution in sediment samples from Collins Bay, the geo-accumulation index (Igeo) suggested by Müller (1969) was calculated for elements of anthropogenic concern i.e. As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn using the equation:

$$Igeo = Log\ 2\ (Cn / 1.5 + Cb)$$

where Cn is the element concentration in the sediment sample and Cb is the background or baseline value. Background values were taken from Vodopivez et al. (2019) as they referred to surface marine sediments of KGI. The classes proposed by Müller (1969) were employed to assign pollution status. In addition, elements were classified in productivity proxies i.e., Ba, Ca (Tribovillard et al. 2006), terrestrial and fluvial input proxies i.e., Al, Fe, Ti, K, Mn and Mg (Martínez-Ruiz et al. 2015, Wang et al. 2016) and redox sensitive proxies i.e., Ag, Cd, Cr, Mo and V (Wagner et al. 2015). Moreover, elemental ratios were used to figure out sources and sedimentation processes of particles in Collins Bay.

Statistical analyses

Pearson correlation coefficients ($p < 0.05$) were used for testing significant dependency between two variables, through the construction of a correlation matrix with depth, oceanographic variables, grain size, bulk geochemical, biochemical and elemental data. A principal component analysis (PCA) was done to assess spatial heterogeneity among transects/stations with respect to depth and biogeochemical variables analysed in sediments of Collins Bay, after transforming the data to log x + 1 and centralizing (substracting the mean). Statistical analyses were performed using PAST software package (Hammer et al. 2001).

RESULTS

Water column oceanographic characteristics

Water temperature in Collins Bay ranged from 1.6 °C at the surface to 0.3 °C in bottom waters (Table I). Profiles showed that the thermocline extended until 20 and 40 m depth depending on the sampling station, exhibiting a progressive temperature decrease with increasing depth (Fig. 2a). Salinity ranged between 34.0 at surface waters and 34.4 in bottom waters, with slightly higher values at greater depths (Table I) and the halocline extended until 20 and 40 m depth depending on the station (Fig. 2b). Dissolved oxygen concentrations varied from 7.8 ml L^{-1} at the surface to 6.4 ml L^{-1} in bottom waters with a progressive decrease with depth (Table I). Turbidity ranged between 1.2 and 0.5 NTU (Table I). Stations of transect 1 showed higher turbidity at surface waters than the other stations (Fig. 2c). Fluorescence maximum values ranged between 0.30 and 1.35 mg m^{-3} (Table I). Profiles showed fluorescence peaks around 20-25 m depth, indicating high phytoplankton biomass in the upper water column (Fig. 2d).

Table I. Geographic coordinates, depth and seawater physico-chemical variables in the sampling stations of Collins Bay.

Stations	Latitude (S)	Longitude (W)	Depth (m)	Temperature (°C)		Salinity		Oxygen (ml L-1)		Turbidity (NTU)		Fluorescence (mg m-3)
				S (5m)	B	S (5m)	B	S (5m)	B	S (5m)	B	max
1A	62° 10' 47.4"	58° 50' 51.9"	66	1.14	0.56	34.06	34.210	7.3	7.11	0.99	0.53	0.55
1B	62° 11' 0.07"	58° 49' 51.6"	57	1.31	0.63	34	34.2	7.47	7.15	1.06	0.54	0.93
1C	62° 11' 17.0"	58° 48' 36.4"	57	1.33	0.46	34.01	34.24	7.47	6.99	1.23	0.56	1.12
2A	62° 11' 26.0"	58° 51' 34.0"	106	1.19	0.41	34.05	34.26	7.48	6.91	0.89	0.5	0.81
2B	62° 11' 43.7"	58° 50' 35.6"	186	1.27	0.32	34.05	34.300	7.5	6.7	0.86	0.57	1.05
2C	62° 12' 3.82"	58° 49' 4.34"	97	1.23	0.46	34.08	34.26	7.51	6.9	0.84	0.47	0.95
3A	62° 11' 28.8"	58° 53' 9.64"	136	1.59	0.39	34.1	34.25	7.82	6.98	0.8	0.48	1.35
3B	62° 11' 36.0"	58° 52' 40.2"	166	0.81	0.35	34.16	34.28	7.28	6.78	0.66	0.61	0.3
3C	62° 11' 47.9"	58° 52' 4.32"	206	1.03	0.27	34.14	34.35	7.49	6.41	0.74	0.61	0.61
3D	62° 11' 53.8"	58° 51' 44.0"	216	1.15	0.27	34.08	34.34	7.52	6.46	0.84	0.63	0.89

S = surface waters; B = Bottom waters

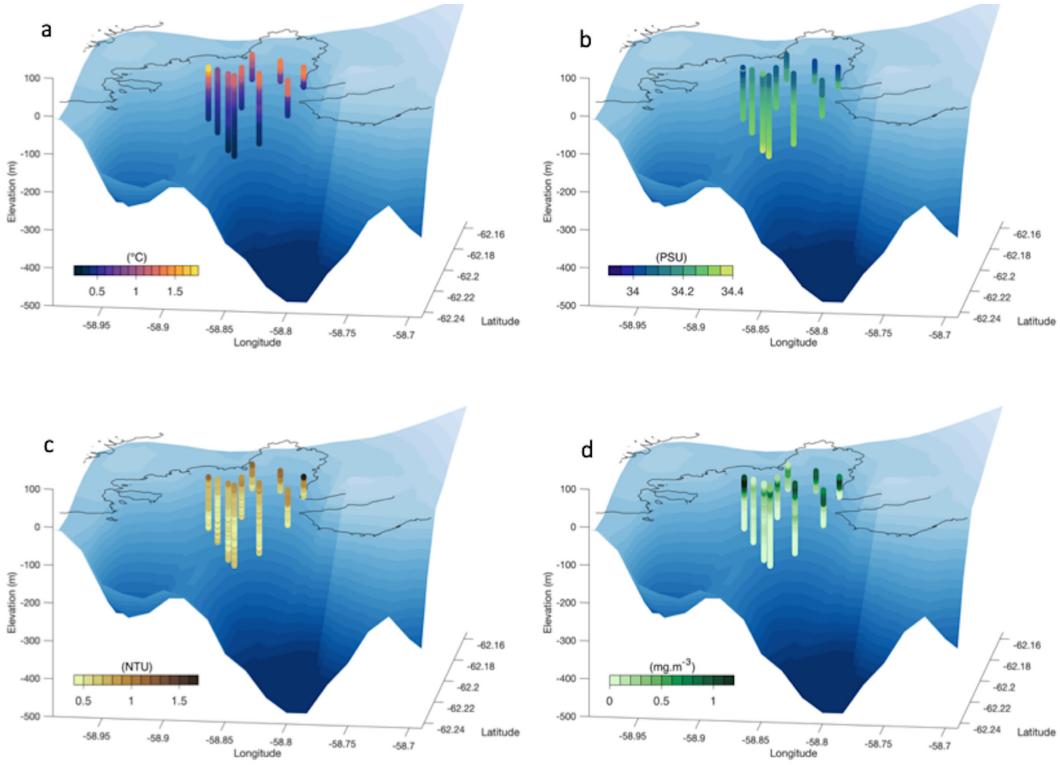

Figure 2. CTD profiles during sampling survey in the three transects of Collins Bay. a) Temperature, b) Salinity, c) Turbidity, d) Fluorescence. Bathymetry from ETOPO1.

Bathymetry, bulk sediment composition and organic geochemistry

Depth of the sampling stations ranged between 57 to 216 m (Fig. 3a). The bathymetric map showed a maximum depth of near -300 m below sea level for the submarine environment of Collins Bay. Shallow depths about 50 m occurred in the northern inner fjord (transect 1), which has gentle bathymetric gradients (Fig. 3a). A steep gradient is observed in the west coast (transect 3) with variations from 140 to more than 200 m in water depth. The transition from the middle to the outer sector of the fjord has the sharpest bathymetric slope (Figure 3a). The most common sediment type was mud with contributions > 68 % excepting in station 3A, where mud represented 44 % (Fig. 3b). An increment in mud content occurred from the northern inner fjord (transect 1) and from station 3A towards the deepest outer sector of the fjord. Stations 1B and 3A showed great gravel and sand contents and the largest mean grain size (Fig. 3b and Table II). Based on Falk & Ward descriptive terms, sediment composition in Collins Bay ranged from poorly sorted medium silt to very poorly sorted very fine sand (Table II). $CaCO_3$ contents varied between n.d. to 2.41%. TOC showed values between 0.49 – 1.55 %, while values between 0.10 – 0.21 % were recorded for TN (Table II). C/N ratios ranged from 5.4 to 9.0, while stable carbon isotopic signatures ($\delta^{13}C$) showed values between – 24.5 to – 26.6 ‰ (Table II). A smooth decreasing gradient to depleted $\delta^{13}C$ values from the inner shallow fjord (transect 1) towards the outer deepest fjord (transect 3) was recorded (Table II). The $\delta^{13}C$ versus C/N ratios showed that terrigenous organic carbon contribution is very small even in the innermost part of the fjord

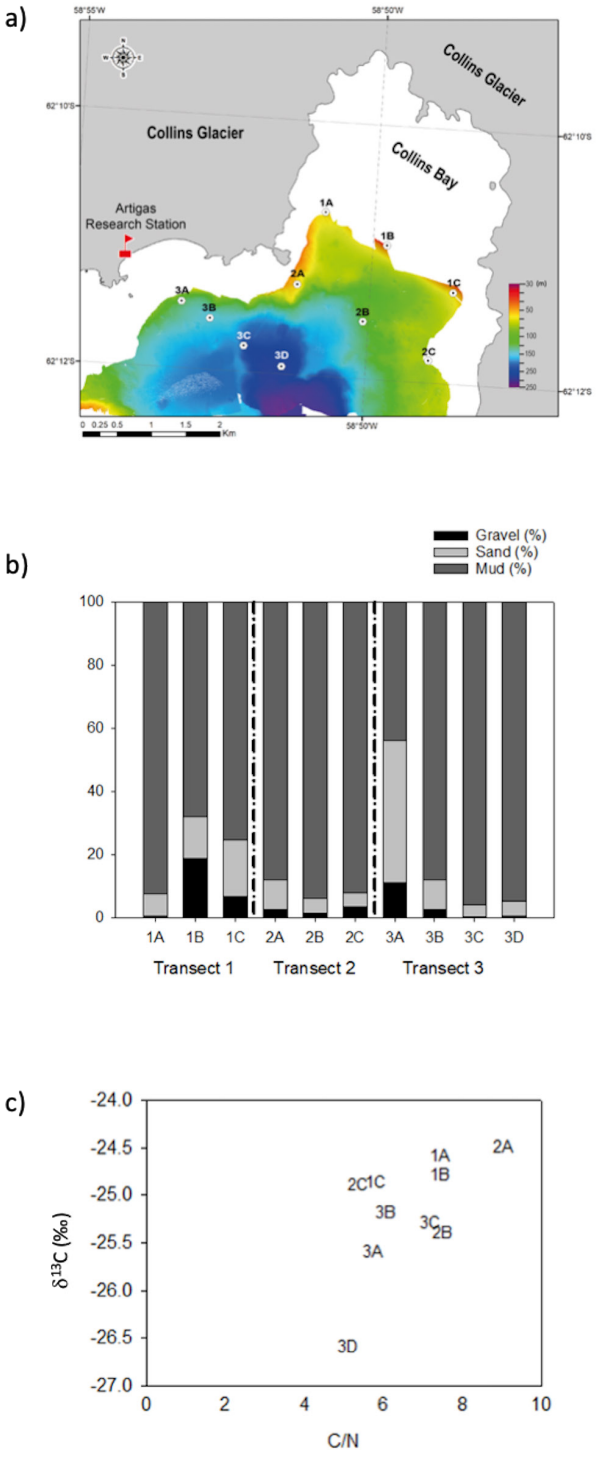

Figure 3. a) Bathymetry (multibeam) of Collins Bay showing the location of the sampling stations. b) Relative contribution of grain-size fractions in the sampling stations of each transect. c) The $\delta^{13}C$ versus C/N ratios in each sampling station.

(transect 1), and only a minor inside-outside gradient can be identified (Fig. 3c).

Biochemical composition of sedimentary organic matter

Total protein (PRT) concentrations in surface sediments from Collins Bay varied from 1,104 to 1,997 μg g^{-1}. Total carbohydrates (CHO) ranged between 374 and 1,119 μg g^{-1}, while total lipids (LIP) varied from 693 to 1,509 μg g^{-1} (Figure 4). PRT concentrations in sediments were very similar among stations, but CHO and LIP showed lower concentrations in stations of transect 1 than in the other stations (Fig. 4). Biopolymeric carbon (BPC) ranged between 1,352 and 2,480 μg C g^{-1}, it also showed lower concentrations in stations of transect 1 than in the others (Fig. 4). As observed to mud, an increment in BPC content occurred from the northern inner fjord (transect 1) and towards the deepest outer sector of the fjord (Fig. 4). In addition, PRT/CHO ratios > 1 and CHO/LIP ratios < 1 were obtained in all stations (Table II).

Composition and distribution of As, major and trace elements, geo-accumulation index (Igeo) and elemental ratios

Concerning productivity proxies, Ba and Ca ranged between 26.1 (station 1C) and 47.6 μg g^{-1} (station 3D) and from 11,429 (station 1C) to 15,508 μg g^{-1} (station 3C), respectively (Table III), both showing an increase from the inner shallow fjord towards the outer deepest fjord (Fig. 5). Amongst terrestrial and fluvial input proxies, Al and Fe did not show a clear pattern (Fig. 5). Their concentrations varied from 29,695 (station 3B) to 35,731 μg g^{-1} (station 2C) and from 33,331 (station 3A) to 49,043 μg g^{-1} (station 2A), respectively (Table III). In contrast, Ti and K increased from the inner shallow fjord (transect 1) towards the outer deepest fjord (Fig. 5), ranging from 910 (station 1C) to 1,501 μg g^{-1} (station 3D) and

Table II. Percentages of grain-size fractions, mean diameter (m) and standard deviation (s), calcium carbonate (CaCO3), total organic carbon (TOC), total nitrogen (TN), carbon/nitrogen ratio (C/N), stable carbon isotopic signatures (δ13C), proteins to carbohydrates ratio (PRT/CHO) and carbohydrates to lipids ratio (CHO/LIP) in the sampling stations of Collins Bay.

Stations	Gravel (%)	Sand (%)	Mud (%)	m (f)	s (f)	Folk & Word definition		CaCO3 (%)	TOC (%)	TN (%)	C/N	δ13C (‰)	PRT/CHO	CHO/LIP
1A	0.6	6.8	92.6	6.2	1.2	Medium Silt	Poorly Sorted	0.32	0.8	0.13	7.41	-24.6	4.55	0.02
1B	18.8	13.1	68.1	3.6	3.8	Very Fine Sand	Very Poorly Sorted	0.21	1	0.16	7.44	-24.8	2.52	0.02
1C	6.6	18.1	75.3	5.3	2.5	Coarse Silt	Very Poorly Sorted	2.41	0.7	0.14	5.82	-24.8	2.67	0.02
2A	2.4	9.5	88.1	6	1.5	Medium Silt	Poorly Sorted	n.d.	1.54	0.2	9.04	-24.5	1.66	0.02
2B	1.4	4.8	93.8	6.3	1.2	Medium Silt	Poorly Sorted	1.4	0.99	0.15	7.5	-25.4	1.41	0.02
2C	3.3	4.4	92.3	6.3	1.4	Medium Silt	Poorly Sorted	2.1	0.99	0.21	5.37	-24.9	1.59	0.04
3A	11.2	45	43.8	4	2.8	Very Fine Sand	Very Poorly Sorted	1.36	0.5	0.1	5.72	-25.6	2.12	0.02
3B	2.6	9.5	87.9	6.1	1.6	Medium Silt	Poorly Sorted	1.42	0.94	0.18	6.06	-25.2	1.31	0.03
3C	0.2	3.9	95.9	6.3	1.1	Medium Silt	Poorly Sorted	0.54	0.94	0.15	7.18	-25.3	2.57	0.02
3D	0.4	4.9	94.7	6.2	1.2	Medium Silt	Poorly Sorted	1.68	0.77	0.18	5.1	-26.6	3.75	0.03

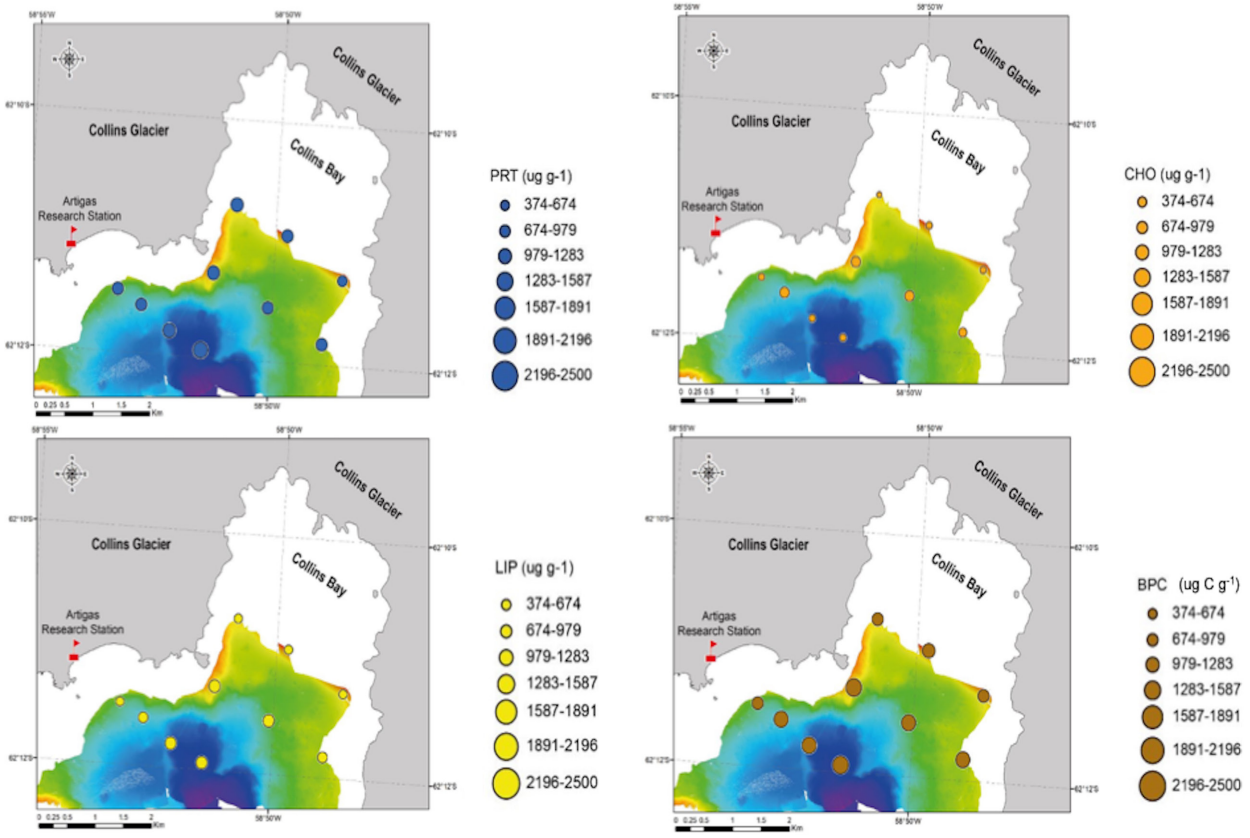

Figure 4. Spatial distribution of proteins (PRT – blue), carbohydrates (CHO - orange), lipids (LIP - yellow) and biopolymeric carbon (BPC - brown) in surface sediments of Collins Bay.

Table III. Total concentrations (mg g-1) of the 20 inorganic elements analyzed in sediments of Collins Bay.

Element	Transect 1			Transect 2			Transect 3			
	1A	1B	1C	2A	2B	2C	3A	3B	3C	3D
Al	32,822	32,323	29,753	35,500	30,601	35,731	31,260	29,695	34,457	35,648
Ag	0.27	0.3	0.18	0.25	0.25	0.23	0.41	0.65	0.36	0.34
As	10.5	9.06	7.14	8.99	6.98	7.19	6.29	11.5	8.68	7.07
Ba	34.9	34.2	26.1	41.6	40.8	43.4	33.2	42.2	45.4	47.6
Ca	12.904	11.661	11.429	13253	12.679	12.556	13.542	12.228	15.508	14.432
Cd	1.14	1.02	1	1.16	0.96	1.35	0.79	0.92	1.1	1.12
Cr	12.8	12.8	11.8	13.7	11.8	14.6	7.85	11.7	14.1	14.2
Cu	70.5	71.7	70.7	63.4	59.6	77.6	51.3	55.7	63.8	64.2
Fe	39,905	48,128	39,614	49,043	41,331	40,828	33,331	43,530	43,552	39,850
K	4.357	3.928	3.157	5.096	4.358	5.017	4.343	4.486	4.875	4.948
Mg	17,670	17,631	16,197	17,736	16,594	19,021	11,441	15,922	17,029	17,056
Mn	358	370	343	351	326	388	260	307	362	359
Mo	0.8	0.48	0.63	0.8	0.67	1.05	0.73	0.59	1.2	0.89
Ni	9.8	10.4	9.31	10.4	10.3	11.5	6.67	9.74	11	11.3
Pb	6.38	6.36	6.68	5.58	5.15	7.11	3.41	4.84	5.62	5.35
Sc	9.19	9.12	8.06	9.89	8.4	10.67	6.93	8.26	9.9	10.02
Sr	82	76.9	63.6	90	78	80.1	123.2	92.1	94.5	88.6
Ti	992	918	910	1,382	1,004	1,250	1,151	1,115	1,408	1,501
V	108	110	98.6	121	95.6	124	89.5	98.8	119	120
Zn	88.5	90.8	80.1	86.2	78.6	98.5	64.3	77.6	85.5	84.6

from 3,157 (station 1C) to 5,096 μg g^{-1} (station 2A), respectively (Table III). Mg presented similar concentrations in most of the stations, excepting in station 3A, where showed its lowest value (11,441 μg g^{-1}) (Table III and Figure 5). An analogous pattern was observed for Mn (Fig. 5). Regarding redox sensitive proxies, Ag ranged between 0.18 (station 1C) and 0.65 μg g^{-1} (station 3B) with higher values in stations of transect 3 than in the other stations (Table III). Cd, which concentrations ranged from 0.79 (station 3A) to 1.35 μg g^{-1} (station 2C), decreased offshore to the outer deepest fjord (Table III and Fig. 5). As, V and Mo did not show a clear pattern, they showed variable concentrations instead (Fig. 5). Cr presented a similar range of concentrations in most of the stations, excepting station 3A, which showed the lowest concentration (7.85 μg g^{-1}) (Table III and Fig. 5).

All elements of anthropogenic concern showed Igeo values between 0 and 1 (Table IV). Therefore, sediment quality status of Collins Bay stations was assigned as unpolluted according to Müller (1969). The lowest concentration of these elements was recorded in station 3A (Fig. 5). Cu, which concentrations ranged from 51.3 (station 3A) to 77.6 μg g^{-1} (station 2C) decreased offshore. Ni presented a similar range of concentrations in most of the stations, excepting station 3A, which showed the lowest concentration equal to

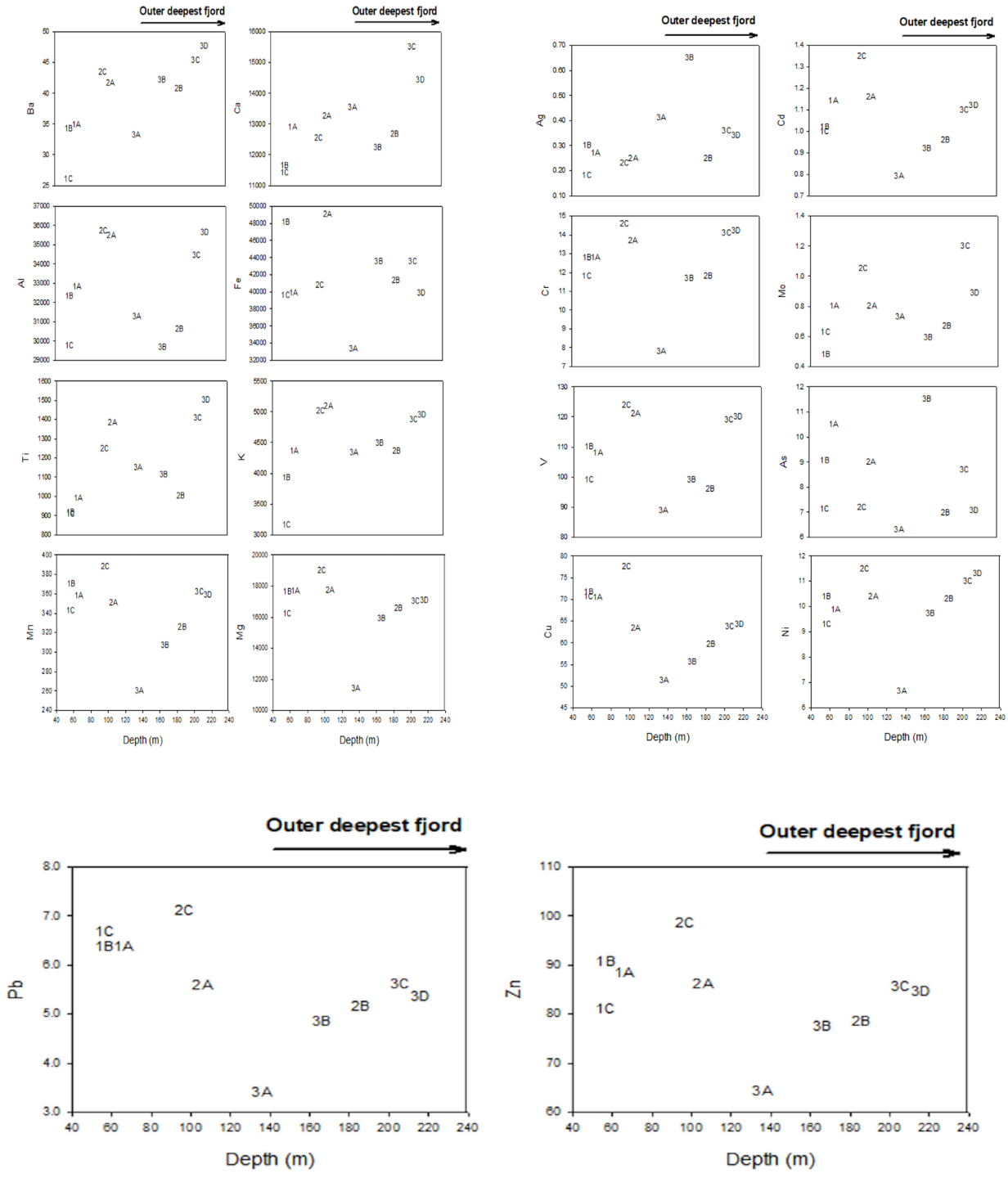

Figure 5. Concentrations of productivity proxies (Ba and Ca), terrestrial and fluvial input proxies (Al, Fe, Ti, K, Mn and Mg), redox sensitive proxies (Ag, Cd, Cr, Mo and V) and elements of anthropogenic concern (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) considered in this study.

6.67 μg g^{-1} (Table III and Fig. 5). Pb and Zn, ranging from 3.41 (station 3A) to 7.11 μg g^{-1} (station 2C) and between 64.3 (station 3A) and 98.5 6 μg g^{-1} (station 2C), respectively (Table III), presented the same pattern of Cu, decreasing offshore to the outer deepest fjord (Fig. 5).

Mn/Al, Mn/Ti and Fe/Ca ratios showed a gradient of decrease from the northern inner fjord (transect 1) towards the deepest outer sector of the fjord (Fig. 6). In contrast, the Ba/Al ratio showed the opposite gradient, increasing from the inner shallow to the deepest outer portion of the fjord, as well as the Ti/Al ratio (Fig. 6). A similar pattern, was observed for the Ag/Al and Mo/Al ratios (Fig. 6).

Statistical analyses

Negative correlation was obtained between $\delta^{13}C$ and depth (Fig. 7). In contrast, Ba, Ca and Ti were positive correlated with depth. Also, negative correlations between mud and coarse sediment fractions (gravel and sand) were obtained (Fig. 7). Among organic biopolymers, CHO, LIP and BPC were positive correlated with mud and organic elements (TOC and TN) (Fig. 7). Instead, PRT were positive correlated with BPC, productivity and fluvial input proxies (Ba, Ca, Ti and K). TOC showed positive correlation with Fe. Sand was negative correlated with several redox (Cd, Cr and V) and anthropogenic inorganic elements (Mn, Ni and Zn), while mud and TN were positive correlated with most of these elements (Fig. 7). The metalloid As, did not showed any correlation with other elements, while most of the anthropogenic elements were positive correlated among them (Fig. 7). PCA results spread the stations into two main groups. One group formed by the stations of transect 1 (to the left) and the other group formed by the stations of transects 2 and 3 (to the right), leaving station 3A in an intermediate place (Fig. 8). PC1 and PC2 together explained 69 % of the total variance. The variables with the highest loadings in PC1 were in decreasing order depth > CHO > LIP > BPC > Ba > Ag > Ti > Mo > K (Fig. 8), whereas the variables with the highest loadings in PC2 were, also in decreasing order, TOC > Pb > TN > Cr > Mg > Cd and Ni (Fig. 8). PCA results indicated higher quantities of CHO, LIP and BPC, linked with higher productivity, fluvial input and redox sensitive proxies, in the stations of the outer deepest fjord than in the stations of the inner

Table IV. Values of the geo-accumulation index (Igeo) for elements of anthropogenic concern in sediments of Collins Bay.

Stations	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Sediment quality based on Müller (1969)
1A	0.49	0.23	0.27	0.41	0.24	0.17	0.35	0.3	0.44	Unpolluted
1B	0.42	0.2	0.27	0.42	0.29	0.17	0.37	0.29	0.45	Unpolluted
1C	0.33	0.2	0.25	0.41	0.24	0.16	0.33	0.31	0.4	Unpolluted
2A	0.42	0.23	0.28	0.37	0.29	0.16	0.37	0.26	0.43	Unpolluted
2B	0.32	0.19	0.24	0.35	0.25	0.15	0.36	0.24	0.39	Unpolluted
2C	0.33	0.27	0.3	0.45	0.24	0.18	0.41	0.33	0.49	Unpolluted
3A	0.29	0.16	0.16	0.3	0.2	0.12	0.24	0.16	0.32	Unpolluted
3B	0.53	0.18	0.24	0.33	0.26	0.14	0.35	0.22	0.39	Unpolluted
3C	0.4	0.22	0.29	0.37	0.26	0.17	0.39	0.26	0.43	Unpolluted
3D	0.33	0.22	0.29	0.38	0.24	0.17	0.4	0.25	0.42	Unpolluted

shallow fjord. In contrast, the inner shallow portion presented higher concentrations of TOC, TN and anthropogenic inorganic elements.

DISCUSSION

Meltwater influence and water column oceanographic settings in Collins Bay

Temperature and salinity in surface waters are similar to those reported in previous years to this area (Venturini et al. 2020), also during the Effective Period of Collins Glacier, when meltwater channels are well formed, and their discharge responds positively to air-temperature raises (Chinarro 2014). Profiles of oceanographic variables with an evident thermocline, a slight halocline and more turbid surface waters denote the occurrence of stratification with a fresher, warmer and turbid superficial water layer in Collins Bay. These conditions have been ascribed to solar radiation heating, meltwater and suspended particles inflow, as well as, active glacier calving and subaqueous melting in Antarctic coastal areas during austral summer (Tian et al. 2015, Meredith et al. 2018, Llanillo et al. 2019, Venturini et al. 2020). Collins Bay has been described as a strong stratified fjord with a dominant two-layered estuarine circulation during the austral summer, partially countered by tidal straining (Llanillo et al. 2019), which support our findings. An enhanced retention of meltwater was observed at the head of Collins Bay during flood tide, and a buoyancy gain through warming and freshening of the surface layer was reported as austral summer progress, influencing the upper 80 m in Collins Bay (Llanillo et al. 2019). According to these authors, the magnitude of these changes is larger than the hydrographic variability due to the oscillating tides, the blowing winds and the fluctuations of the interior density field, having the intraseasonal cycle of the austral summer,

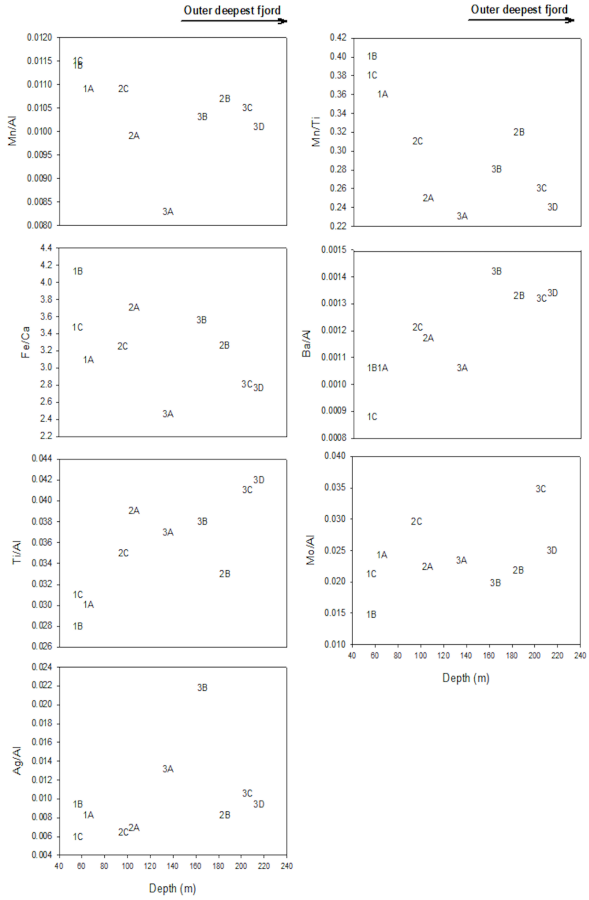

Figure 6. Elemental ratios used as proxies to figure out sources, sedimentation processes and post-depositional alterations of sedimentary particles in Collins Bay.

strong influence on oceanographic variability. However, higher turbidity at surface waters in the inner shallow fjord (transect 1), may be related to frontal ablation inputs from Collins Glacier, owing the close distance of these stations to ice-cliffs. Another explanation could be the meltwater plume with suspended particles turning to the left side due to the Coriolis influence, later keeping at the head of Collins Bay by flood tide. Small supply of suspended particles by meltwater runoff, has been reported to Collins Bay, comparatively to ice-free areas of KGI and near fjords undergoing rapid glacier retreat such as Mariane and Potter Coves (Venturini et al. 2020 and references therein). Collins Bay receives the input of only one meltwater creek, which may

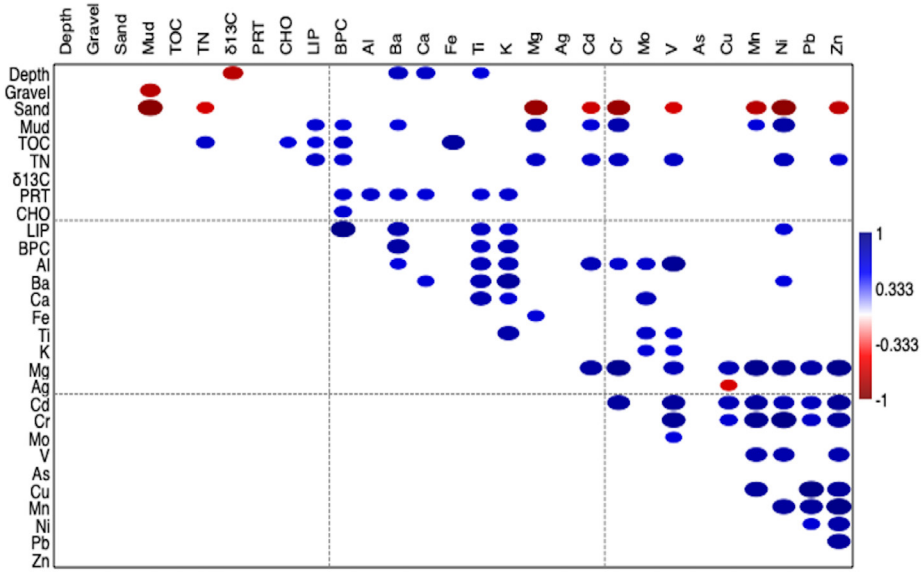

Figure 7. Results of the Pearson correlation performed with depth, oceanographic variables, grain size, bulk geochemical, biochemical and elemental data.

also explain the meltwater influence restricted to the head of the fjord. In addition, saltier waters have been found close to the bottom of Collins Bay, suggesting the intrusion of modified Upper Circumpolar Deep Water (m-UCDW), which promotes salinification, deoxygenation, nutrient enrichment and has larger influence below 80 m (Llanillo et al. 2019). Progressive increase of salinity with depth, and the opposite trend for dissolved oxygen, may be the effect of m-UCDW mixture in the deepest outer fjord. High phytoplankton biomass in the upper water column indicated by fluorescence peaks around 20-25 m depth, are consistent with the predominance of fresh protein-rich suspended organic matter derived from phytoplankton, mainly diatoms, previously recorded in surface waters of Collins Bay (Venturini et al. 2020).

Sedimentation processes, sources and quality of organic particles in sediments of Collins Bay

The predominant muddy nature of seabed sediments in Collins Bay indicates features of low energy environment with relatively high sediment accumulation rates. Due to their bathymetry, landscape and geometry, fjord systems act as natural funnel shape sediment traps. Textural analysis has been used to infer the hydrodynamic conditions of the depositional environment (Bianchi et al. 2020). A modern (^{210}Pb-based) accumulation rate of 5.5 mm yr^{-1} has been estimated for recent sediments of Collins Bay dated from a sediment core taken at 3.4 km distance from the ice front (Boldt et al. 2013). This rate is quite high to sediment accumulation rates reported by these authors for other subpolar fjords in the WAP. Besides, sediment accumulation rate estimated for Collins Bay is similar to that reported in e.g., Andvory Bay another fjord located in the WAP, where lithogenic sediment production is weak, thus, biogenic sediment production is comparatively important (Eidam et al. 2019). High gravel and sand contents in the shallow areas of Collins Bay, both in the northern inner sector (transect 1) and station 3A, corresponds to glaciomarine sedimentation that may be due to the joint effect of meltwater inflow, coastal currents and iceberg scouring. Collins Bay remains covered by sea ice and floating ice in austral winter, active iceberg calving from tidewater glacier terminus has also been reported (Yoon et al. 1998). The

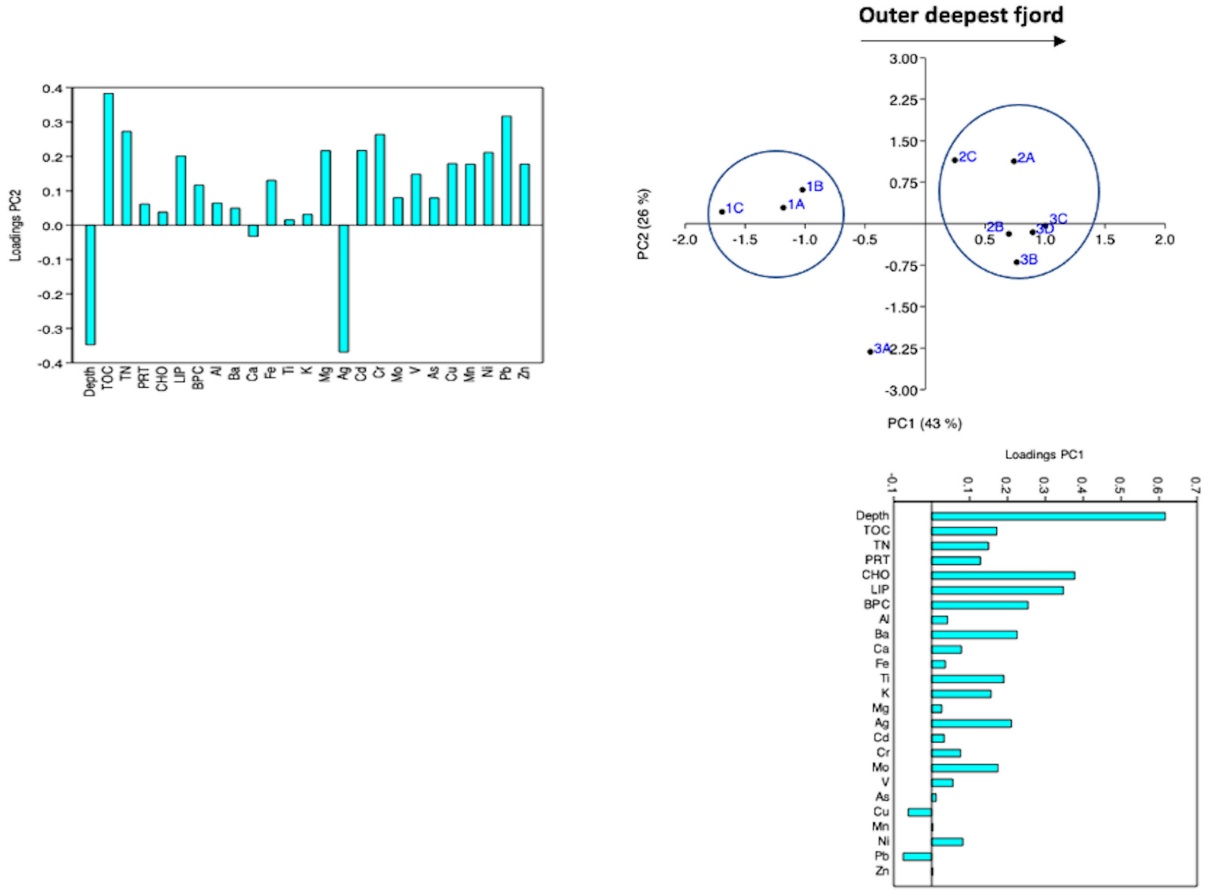

Figure 8. Results of the Principal Components Analysis performed with depth, and biogeochemical data.

rise in mud content towards the deepest outer sector of the fjord is expected, because away from the glacier front and shallower portions of the fjord, where reworking of seafloor sediments by tides, waves and icebergs is strong, pelagic sedimentation and mud deposition increase (Bianchi et al. 2020).

TOC and TN contents, in sediments of Collins Bay are higher than values reported in the near Potter Cove that is undergoing rapid glacier retreat (Pasotti et al. 2014), increased meltwater and land-terminating glacier influence (Meredith et al. 2018). Based on TOC and TN significant positive correlation the same origin for both can be assumed. Since autochthonous and allochthonous organic carbon have different reactivity a geochemical characterization of their sources is required to evaluate the fate of organic carbon in fjord systems (Faust & Knies 2019). The C/N ratio generally ranges between 6 – 10 for fresh living phytoplankton, between 4 – 6 for bacteria and above 12 for terrestrial organisms (Meyers, 1997, Lamb et al. 2006). C/N ratios in sediments of Collins Bay ranged between 5.4 to 9.0 (average 6.6) indicating an autochthonous origin of organic carbon and fresh living phytoplankton as the main source. This value is very close to the Redfield C/N ratio = 6.625, supporting our findings (Redfield 1958). $\delta^{13}C$ signatures (between – 24.5 to – 26.6 ‰) in sediments of Collins Bay are similar to values described for the neighboring Marian Cove in sediment trap studies under low terrestrial particle influx to the nearshore environment

during winter (Khim et al. 2007). $\delta^{13}C$ versus C/N ratios indicate the predominant marine origin of organic carbon in sediments of Collins Bay, with minor terrigenous input, even in the innermost sector of the fjord. These results are consistent with previous findings about suspended POM composition in surface waters of Collins Bay that mainly derived from phytoplankton (diatoms) and sea-ice algae, with no substantial terrestrial inputs (Venturini et al. 2020). The minor terrestrial input may be related to the convergence of the main glaciofluvial channels to a pond that may suffer decreasing meltwater supply in the future (Petsch et al. 2020). However, the formation of at least three glaciofluvial channels directly reaching the sea in Collins Bay have been recently reported (Petsch et al. 2020), which may counteract this minor terrestrial contribution in next decades. In the early stages of detrital decomposition, organic nitrogen is mineralised more rapidly than organic carbon, resulting in an initial C:N ratio rise (Seki et al. 1968). During further degradation of phytoplankton and other organic detritus in surface sediments, bacterial action can introduce nitrogen to the sediment, and consequently, decrease C/N ratios. Likewise, decrease in $\delta^{13}C$ due to the formation of refractory humic compounds has been commonly observed with ongoing degradation (Lamb et al. 2006). Therefore, differences in C/N ratios and $\delta^{13}C$ may be reflecting different stages of marine organic particles degradation in stations of Collins Bay. The smooth decreasing gradient to depleted $\delta^{13}C$ from the inner shallow fjord towards the outer deepest fjord, may be linked to great organic carbon degradation during settling and in the sediments of the deepest outer sector.

Present PRT, CHO, LIP and BPC concentrations are comparable to those reported in sediments next to recently emerged ice-free areas in Potter Cove (Pasotti et al. 2014). Although, they are higher than those reported to shallow marine sediments along the Terranova Bay, Ross Sea, a system in the Antarctic continent, which has short spring-summer-time periods of vertical flux of primary organic matter and faecal pellets to bottom sediments (Baldi et al. 2010). PRT predominance over CHO and LIP in nearshore and deep-sea Antarctic sediments has been previously reported, and assumed, as fresh high nutritive organic matter produced by phytoplankton that is exported to bottom sediments (Isla et al. 2006, Lee et al. 2009, Pasotti et al. 2014). Also, PRT accumulation in superficial sediments has been associated to both, anaerobic microbial activities faster fermenting CHO than amino-acids (Baldi et al. 2010), and the tendency of PRT to combine with refractory compounds (Covazzi-Harriague et al. 2007). Unlike to PRT concentrations that were similar in all stations of Collins Bay, CHO and LIP showed lower concentrations in stations of transect 1 than in the other stations. Diatom aggregates and fecal pellets of zooplankton are supposed to be the most important carriers of PRT and LIP to Antarctic seabed sediments (Kim et al. 2015), while high CHO concentrations have been attributed to degraded phytoplankton detritus (Pusceddu et al. 2009). Also, decreased lipid production by phytoplankton has been related to the reduction of light intensity in the water column (Lee et al. 2012). So, less zooplankton grazing jointly with small lipid production by phytoplankton in the shallow inner portion of study area, where high hydrodynamic conditions, meltwater influence and turbidity occur, may be a possible explanation for the lower CHO and LIP concentrations than in seabed sediments of the outer deepest fjord.

Positive correlation between BPC and mud, as well as, the same distributional pattern of these variables, increasing from the northern inner fjord (transect 1) and station 3A towards the deepest outer sector of the fjord, indicate pelagic

sedimentation of biogenic labile organic carbon and high benthic-pelagic coupling in Collins Bay. The seasonal pulse of labile organic carbon to bottom sediments is a well-documented process in different regions of Antarctica, which play a relevant role in regulating the carbon cycling, supporting benthic communities the entire year, and connecting pelagic and benthic biogeochemical processes (Fabiano & Pusceddu 1998, Isla et al. 2006, Mincks et al. 2005, Zenteno et al. 2019). PRT/CHO ratios > 1 and CHO/LIP ratios < 1 in all the stations are in agreement with the prevalence in the sediments of labile organic carbon, shaped during early stage of a phytoplankton bloom and high amounts of freshly produced organic compounds (Baldi et al. 2010, Pasotti et al. 2014). Biopolymeric composition revealed the predominance of fresh marine protein-rich sedimentary POM in the seafloor of Collins Bay that denotes high quality food resource for marine benthic heterotrophic organisms.

Also, positive correlation of PRT with productivity proxies (Ba and Ca) and fluvial input proxies (Ti and K) indicate boosting of primary production by meltwater intrusion, but also, suggest sediment-laden meltwater as another potential source of protein-rich particles in sediments of Collin Bay. Meltwater plumes from glaciers can enhanced micronutrient supply to nearshore areas and transport lithogenic particles derived from subglacial erosion and ice-free surface outwash (Meredith et al. 2018). Recently, organic matter dominated by biogenic sources, mostly vegetal with small microbial mats and petrogenic contributions has been reported in soils near Collins Bay (Vega-García et al. 2021). Therefore, the combination of PRT with refractory terrestrial compounds may explained high PRT concentrations in the inner stations (transect 1) of the fjord.

Inorganic geochemical proxies of particle sources, sedimentation processes and redox conditions in surface sediments of Collins Bay

Overall, total concentrations of most inorganic elements found in this study are similar to those reported by other authors in surface marine sediments of Collins Bay and have been attributed to natural sources such as erosion and volcanic activities (Vodopivez et al. 2019, Delhaye et al. 2023). The exceptions were Cr and Mn, which presented lower concentrations in our study. Recently, Delhaye et al. (2023) reported a consistent increment in Cr concentrations around several areas of KGI comprising Collins Bay, which may be related to anthropogenic activities, but they need to be further investigated. Also, different depositional and accumulation regimes of inorganic elements may explain that concentrations of most elements (excepting Mn), were slightly higher in muddy sediments of our study than in coarse nearshore marine sediments of Collins Bay and North Cove reported by Bueno et al. (2018). Based on Igeo values (between 0 and 1) surface marine sediment of Collins Bay can be considered unpolluted with levels of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn similar to those reported by former authors and found in other unpolluted areas of KGI (Ribeiro et al. 2011, Bueno et al. 2018, Vodopivez et al. 2019, Delhaye et al. 2023 and references therein). Therefore, main sources of these elements may be related with geochemical composition of volcanic rocks, weathering processes and glacial melt-water inputs to Collins Bay. Tidewater glaciers are assumed to introduce significant amounts of detrital material below sea level at the glacial terminus (Domack & Ishman 1993, Wagner et al. 2015). In addition, elevated concentrations of Fe, Cu, Mn, Pb and Zn in suspended particulate matter near sources of glacial melt-water, have been attributed to great input of lithogenic

particles into the neighboring Marian Cove (Lee et al. 2008), which sharply decreased with increasing distance from the melt-water sources. Further, uneven distributions of heavy and trace metals, with maximum concentrations of Zn, Ni, and Pb close to the Dome summit, have been recently reported to the Collins Glacier. However, the distribution of Cu and Cd have more a local character. The most likely processes bringing these elements to the dome are mixed organo-lithogenic genesis with influence of anthropogenic activities (Nizamutdinov et al. 2022). Therefore, distributional patterns of most of these elements with a gradient of decrease from the shallow inner fjord towards the outer deepest fjord, suggest that they are associated with the deposition of detrital material and lithogenic particles supplied after Collins Glacier melting by both, frontal ablation and runoff.

Ba and Ag accumulation in surface sediments of the Southern Ocean has been linked to the export of primary production from the water column (Wagner et al. 2015). Besides, high Ag/Al ratios indicate the importance of export production on sedimentary redox conditions (Wagner et al. 2013). Diminish of elemental ratios such as Mn/Al, Mn/Ti and Fe/Ca and the rise of Ba/Al has been related to reduced terrestrial inputs and increased amount of primary production contributions (Martínez-Ruiz et al. 2015). The decline of Mn/Al, Mn/Ti and Fe/Ca ratios and the rise of the Ba/Al ratio indicate that the continental and freshwater supply to seabed sediments of Collins Bay decrease from the shallow inner to the outer deepest fjord, while the deposition of material derived from primary production increase. This is consistent with the positive correlation of most of inorganic elements with mud and TN and the pattern of increasing pelagic sedimentation of biogenic particles towards the outer deepest sector of Collins Bay showed by grain size and organic proxies.

CONCLUSIONS

The biogeochemical composition of surface marine sediments of Collins Bay reflects the oceanographic and sedimentary controls on their supply and distribution.

Collins Bay is an Antarctic fjord with high marine inflow and low glacial melting runoff, which is dominated by marine organic matter, while the minor contribution of terrestrial organic carbon decreases to its outer deepest portion in the seaward direction. The predominance of fresh marine protein-rich sedimentary POM in the bottom sediments of Collins Bay denotes high quality food resource for marine benthic heterotrophic organisms. Marine sediments of Collins Bay can be considered unpolluted with inexistent levels of anthropic influence. The distribution patterns of most of the trace metals and elements studied (gradient of decrease from the shallow inner fjord towards the outer deepest fjord) are suggesting its association with the deposition of detrital material and lithogenic particles supplied by Collins Glacier melting.

Multivariate analysis evidenced two main groups of sampling stations, one characterized by higher quantities of CHO, LIP and BPC, linked with higher productivity, fluvial input and redox sensitive proxies (outer deepest stations) and the other from most inner stations characterized by higher concentrations of TOC, TN and anthropogenic inorganic elements.

In the end, this work provides a first comprehensive biogeochemical characterization of surface marine sediments of Collins Bay that would be used as baseline information for interpreting downcore sedimentary reconstructions and future climate-induce changes. Fjords have been recognized as important areas for carbon burial and therefore as a major component of global carbon cycles and budgets. Thus, it is essential to understand

the origin, transport, and character of OM entering fjords to accurately constrain carbon burial rates.

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