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Constraining the radiocarbon reservoir age for the Southern Ocean using whale bones salvaged from early 20th century whaling stations

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ABSTRACT

Radiocarbon dating is arguably the most common method for dating Quaternary deposits. However, accurate age assignments using radiocarbon dating are dependent on knowing the radiocarbon reservoir. For the coastal waters across Antarctica, the radiocarbon reservoirs show significant variation, ranging from 700 to 6000 years depending on the material dated and the period in question. In this study, we examine the radiocarbon reservoir age for the shallow waters of the Southern Ocean using 23 whale bones salvaged from commercial whaling operations on or near the Western Antarctic Peninsula between 1904 and 1916. The species origin of the bones had been identified previously as humpback, fin, or blue whales using sequences of mitochondrial (mt)DNA. We find an average reservoir age of 1050 ± 135 years for these 23 whale bones, with a <100-year difference in the reservoir age by species. A comparison between our results and other studies through the Holocene suggest that the Southern Ocean surface water radiocarbon reservoir age is of a similar magnitude across much of Antarctica and has not significantly changed for the last 14,000 years. Combining our new ages with existing data sets provides insight to the stability of the Southern Ocean marine radiocarbon reservoir age, enhancing our understanding of ocean ventilation and upwelling dynamics throughout the Holocene.

1. Introduction

The Southern Ocean plays a pivotal role in Earth's thermohaline circulation and climate through ventilation of deep bottom waters (Broecker et al., 1998; Hellmer and Beckmann, 2001; Skinner et al., 2010), absorption and redistribution of heat (Morrison et al., 2016; Sallée, 2018), and facilitating the Antarctic Circumpolar Current (Klinck and Nowlin Jr, 2001). Due to the Southern Ocean's active upwelling and limited primary productivity in surface waters due to iron and seasonal light deficiency, many nutrients in the deep carbon-rich water brought to the surface are left unutilized (Martin, 1990; Coale et al., 2004; Fung et al., 2000; Boyd et al., 2001; Banse, 1996; Mitchell et al., 1991). This allows for exchange of carbon in the surface water and atmosphere before transport back to the deep ocean, enhancing radiocarbon reservoirs (Sigman et al., 2010; Li et al., 2020). In the Southern Ocean, the upwelling of old deep-waters and the relatively short residence times of surface waters have created the largest radiocarbon reservoir ages of anywhere on Earth (Key et al., 2004). Radiocarbon reservoir ages with values up to 6000 years have been reported in radiocarbon-dated sediments, while other regions of Antarctica have shown reservoir ages as little as 700 years (Hall et al., 2010; Pudsey and Evans, 2001; Sugden and John, 1973; Gordon and Harkness, 1992). Surface water radiocarbon reservoir ages in the Southern Ocean can act as an end member for major deep-water masses and provide information about ocean water circulation and mixing (Hall et al., 2010; Robinson et al., 2005). Constraining present and past reservoir ages allows us to gain information about ocean circulation and mitigates limitations on interpreting Antarctic chronologies. Due to the scarcity of terrestrial organic matter in Antarctica, many radiocarbon dates originate from marine material, subjecting them to this reservoir effect.

To calculate a radiocarbon reservoir age, one straight-forward approach is to date modern organisms with the offset representing the

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reservoir age (Hua, 2015; Hua et al., 2020; O'Connor et al., 2010; Petchey, 2009; Southon et al., 2002). However, the advent of nuclear bomb testing, which introduced a significant amount of anthropogenic ^{14}C into the atmosphere, and the so-called Suess effect from the burning of fossil fuels, largely altered the radiocarbon content of the atmosphere and oceans over the last century (Suess, 1955; Broecker and Walton, 1959; Reimer et al., 2004). Thus, the offset in ^{14}C age of modern or post-bomb (~1950) organisms does not accurately reflect past radiocarbon reservoirs. To overcome this complication, we obtained 25 whale bones collected from known locations of past whaling operations that occurred in the early 20th century around the Western Antarctic Peninsula (WAP, Fig. 1). DNA had previously been extracted from these whale bones and used to identify them to species (Sremba et al., 2015, 2023). These whales were killed between 1910 and 1915. We date these bones of a known age to determine the pre-bomb, modern Southern Ocean surface water radiocarbon reservoir age and compare our findings to that of other radiocarbon reservoir age estimates across Antarctica through the Holocene/Late Pleistocene. We also examine the reservoir age by whale species and harvest site to determine if these factors contribute to significant differences that would make separate reservoir age values by species or location within the WAP necessary. Establishing a radiocarbon reservoir age for the Southern Ocean is crucial for accurately interpreting Quaternary records, such as changes in Southern Ocean ventilation (Li et al., 2020), and even the deep ocean radiocarbon reservoir age (Rae et al., 2018; Burke and Robinson, 2012).

A comprehensive understanding of Southern Ocean dynamics is essential for interpreting broader implications of the global ocean's role in climate regulation.

2. Background

2.1. Radiocarbon reservoirs

A radiocarbon reservoir develops in waters (or other systems) in which the $^{14}C/^{12}C$ ratio is not in equilibrium with that of the atmosphere. This disequilibrium can arise due to a variety of factors including deep oceanic circulation residence times (Orsi et al., 1999), old carbon sources (Domack et al., 1989; Domack, 1992), and inhibition of ocean-atmospheric exchange due to sea-ice (Gordon and Harkness, 1992). For the waters around Antarctica, all three of these processes are likely operating, leading the Southern Ocean to having some of the largest radiocarbon reservoirs on the planet (Key et al., 2004; Hall et al., 2010).

Proposed reservoir values for the Southern Ocean have usually been based on small sample sizes (<10), and often have relied on the same few historical samples with known ages before 1950 (Stuiver, 1981; Geyh and Wirth quoted in Whitehouse et al., 1988; Mabin, 1985; Whitehouse et al., 1988; Berkman and Forman, 1996; Gordon and Harkness, 1992; Curl, 1980; Hall and Perry, 2004; Björck et al., 1991; Key et al., 2004, Tables 1 and 2). As Antarctic samples of known
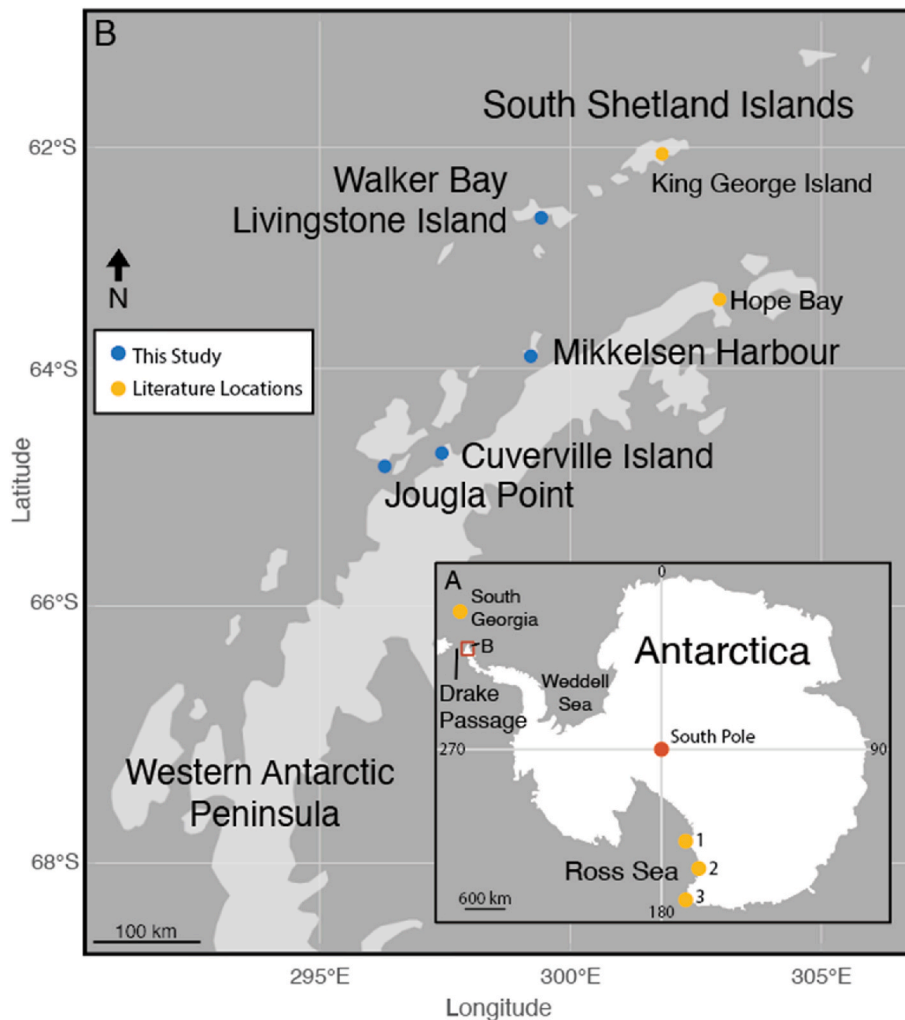

Fig. 1. Map of whale bone collection locations in this study (blue), literature sample locations (orange), and important Antarctic locations such as the Ross and Weddell Sea. 1 = McMurdo Sound & Ice Shelf and Cape Royds. 2 = Terra Nova Bay, Hell's Gate Ice Shelf, and Inexpressible Island. 3 = Cape Adare.

Table 1

Lab Number	Material	Location	Latitude	Longitude	Year Collected (age if different)	14C yr BP ± 1 sigma	References
AA 14785	marine biogenic carbonates	near McMurdo	68°47′S	90°35′E	1917	1215±57	Berkman and Foreman, 1996
LU-3101	penguin bone	Hope Bay	63°24′S	56°59′E	1903	1280±50	Bjork et al., 1991
DIC-367	whalebone	South Shetlands	60°05′S	58°23′E	1974 (1904)	1000±45	Curl (1980)
–	penguin flesh	Cape Royds	78°30′S	166°14′E	1904	915±75	Geyh and Wirth quoted in Whitehouse et al., (1988)
–	flew mew of prey	Cape Adare	71°30′S	170°24′E	1902	1125±90	Geyh and Wirth quoted in Whitehouse et al., (1988)
NZ-6856	penguin bones	Inexpressible Island	74°54′S	163°39′E	1912	1160	Geyh and Wirth quoted in Whitehouse et al., (1988)
NZ-6863	seal bones and flesh	Inexpressible Island	74°54′S	163°39′E	1912	1285	Geyh and Wirth quoted in Whitehouse et al., (1988)
NZ-6864	sealflesh	Inexpressible Island	74°54′S	163°39′E	1912	1260	Geyh and Wirth quoted in Whitehouse et al., (1988)
NZ-6872	charcoal from seal blubber stove	Inexpressible Island	74°54′S	163°39′E	used 1912	1240±45	Geyh and Wirth quoted in Whitehouse et al., (1988)
SRR-4055	whalebone	South Georgia	54°21′S	36°20′E	1982 (pre-nuclear)	1160±50	Gorden and Harkness, 1992
SRR-4056	whalebone	South Georgia	54°21′S	36°20′E	1982 (pre-nuclear)	1010±50	Gorden and Harkness, 1992
SRR-4057	whalebone	South Georgia	54°21′S	36°20′E	1982 (pre-nuclear)	1550±60	Gorden and Harkness, 1992
AA-46814	whalebone	King George Island	62°02′S	58°21′W	during whaling 1820–1910 (they assumed 1865)	1410 ± 43	Hall and Perry, 2004
AA-46814	whalebone	King George Island	62°02′S	58°21′W	during whaling 1820–1910 (they assumed 1865)	1450 ± 47	Hall and Perry, 2004
NZ-6399A	Penguin bone	Inexpressible Island	74°54′S	163°39′E	1912	1065±50	Mabin (1985)
NZ-6327A	Weddell seal bone	Inexpressible Island	74°54′S	163°39′E	1912	1760±50	Mabin (1985)
QL-171	Weddell seal	Inexpressible Island	74°54′S	163°39′E	1912	1390±40	Stuiver et al. 1981
QL-173	Emperor penguin	Inexpressible Island	74°54′S	163°39′E	1912	1300±50	Stuiver et al. 1981
NZ-6842A	penguin bone and flesh	Inexpressible Island	74°54′S	163°39′E	1912	1060±45	Whitehouse et al., 1988
	Seals Average					1424±200 (n = 4)	Berkman and Foreman, 1996 (based on data from Gordon and Harkness, 1992)
	Penguins Average					1130±134 (n = 6)	Berkman and Foreman, 1996 (based on data from Gordon and Harkness, 1992)

Lab number code key: QL = Quaternaru Isotope Laboratory, University of Washington, Seattle USA; NZ = Institute of Nuclear Sciences, DSIR, Lower. Hunt New Zealand; SRR = NERC Radiocarbon Laboratory, East Kilbride, Scotland; DIC = Dicarb Radioisotope Company, Oklahoma, USA; LU = Radiocarbon Dating Laboratory, Lund, Sweden; AA = University of Arizona Mass Spectrometry Lab, Arizona, USA.

Table 2

Reservoir age estimates for the Southern Ocean and specific areas of Antarctica proposed in previous studies.

Reservoir Age 14C yr BP	Reference	Region	Material Dated
1000 ± 45	Curl (1980)	McMurdo Sound	Whalebone
1000–1300	Stuiver, 1981	McMurdo Sound	Shell
1200–1400	Stuiver, 1981	Terra Nova Bay	Shell
1200–1300	Björck et al., 1991	Inexpressible Island	Penguin Bone
1000 ± 45	Gordon and Harkness, 1992	McMurdo Sound	Whalebone
1300 ± 100	Berkman and Forman, 1996	South Georgia Island	Seal and Penguin
1325–1365	Hall and Perry, 2004	South Shetland Islands	Whalebone
1100	Key et al., 2004	Southern Ocean	–
1144 ± 120	Hall et al. (2010)	Ross Sea	Solitary Coral
~950	Li et al. (2020)	Drake Passage	Deep-Sea Coral

*Reservoir Age of Björck et al. (1991) is a combination of ages from samples collected by Stuiver (1981) and Mabin (1985).
Reservoir age of Gordon and Harkness (1992) is taken directly from Curl (1980).

collection age before 1950 are extremely hard to come by, the combining and recycling of samples is a good way to increase our knowledge of radiocarbon reservoir information but means that the same limited number of samples are influencing reservoir age estimates.

Some studies such as Hall et al. (2010) and Li et al. (2020) have also used paired U–Th/^{14}C dating to find reservoir offsets, allowing the use of larger sample populations without known ages at the time of collection. Hall et al. (2010) found evidence for a near constant radiocarbon reservoir age for the last 6000 years using paired U–Th/^{14}C dating from solitary coral from the Ross Sea. However, Li et al. (2020), using a similar approach but with deep-sea corals from the Drake Passage, found that the Southern Ocean reservoir age fluctuated through time, particularly during the late deglacial. Their study suggests a B-Atmosphere (similar to ΔR but accounting for changing atmospheric ^{14}C through time) of up to 2100 years during the Last Glacial Maximum and early deglacial (Li et al., 2020), a value found in similar studies from other locations farther north within the Southern Ocean (e.g. Sikes et al., 2000; Van Beek et al., 2002; Siani et al., 2013; Hines et al., 2015). However, their late Holocene data shows a much younger reservoir age for shallow samples (~600 years; very similar to Hall et al., 2010 updated value of 635 years) versus deep-sea samples (1060 years; Li et al., 2020). More estimates of the ^{14}C reservoir age from other geographic locations and ocean depths are needed to further refine our understanding of the differences in the marine radiocarbon reservoir age by depth and through time.

2.2. Antarctic Peninsula whale bones

Although commercial sealing commenced in the 1820's across the South Shetland Islands and northern Antarctic Peninsula, whaling activities did not start in earnest until 1904 (Hart, 2006). Over the next 60 years, whale populations were hunted and nearly driven to extinction (Rocha et al., 2014). The number of whales taken around the South

Shetland Islands reached over 2000/year during the 1910's (Brown, 1963). During the early 1900's most of these whales were processed using floating factories anchored in the shallow and protected bays of the South Shetland Islands and Northern Antarctic Peninsula (Hart, 2006). These floating factories would clean the whales of their blubber and discard the carcasses into the shallow waters, where the whale bones would drift ashore and be caught in the littoral system (Hart, 2006) thus populating the beaches of these old whaling bays with thousands of whale bones. By 1910, the number of carcasses started to attract the attention of government officials, particularly those of Great Britain who licensed whaling in the region at the time, with a call to fully utilize the whale carcasses (Hart, 2006). Shortly after that call, more land-based operations opened and with the introduction of cookers to process the meat and bones lead to the use of much of the meat and bone of the whales and a reduction in waste left to accumulate on the beaches (Hart, 2006). However, the First World War led to an increase in waste as resources to utilize the whole whale were lost to the war effort, resulting in a large increase in waste and bones accumulating in the shores (Hart, 2006). Following the war, the full use of the carcasses was re-instigated and even mandated (Hart, 2006). In the 1920's, pelagic factory ships were introduced leading to the decline of the on-land and shallow factory ships (in concert with the depletion of whale numbers in shallow waters), and the dwindling of whale bones introduced to the shallow littoral systems of the Antarctic Beaches. By the 1928/1929 season, the traditional harbors of the South Shetland Islands and northern Antarctic Peninsula were all but deserted (Hart, 2006).

2.3. Carbon sources and residence time

Research into the influence of species on radiocarbon reservoir age is constrained by the availability of samples; however, studies have shown that species diversity can influence the reservoir age needed for an effective age correction (Dury et al., 2022). This variation is primarily attributed to differences in carbon sources, such as species that feed in shallow versus deep waters. Given that baleen whales, including humpback, blue, fin, and minke whales, obtain carbon through digestion of their primary food source, Antarctic krill (*Euphausia superba*), as well as other pelagic animals and plankton (Savoca et al., 2021; Modest et al., 2021; Weinstein and Friedlaender, 2017), it is unlikely that species variation will significantly impact radiocarbon reservoir age, but this assumption has yet to be tested.

Krill, which primarily live near the water's surface, are abundant in the Southern Ocean where baleen whales spend their summer/autumn months (January–June) feeding before migrating north for the winter to calve/breed in warmer waters (Modest et al., 2021). Baleen whales rarely feed along their migratory routes or on these lower-latitude breeding grounds (Modest et al., 2021; Chittleborough, 1965; Dawbin and Norris, 1966), which means that the carbon they store is representative of their feeding grounds in the Southern Ocean and not a "mean" for the water along their migratory routes.

The movements of baleen whales while foraging is closely related to the depth and density of krill across a range of spatial and temporal scales (Nichols et al., 2022). Throughout the Antarctic summer krill are broadly distributed over the continental shelf but as autumn approaches, krill move inshore and coalesce in nearshore bays in high densities (Nicol, 2006; Nowacek et al., 2011). To maximize their energy efficiency, whales feed when and where high-density patches are available; during summer months whales feed nearly continuously in near surface waters and by autumn whales feed almost exclusively at night (Friedlaender et al., 2013, 2016; Nichols et al., 2022).

When carbon-dating whales, the standard matter used is bone collagen (Taylor, 1992; Calabrisotto et al., 2013). In humans, most bone collagen is locked in during the growth period, around the time a person reaches 20 years of age (Geyh, 2001), so when carbon-dating human bones the bone residence time must be subtracted. Mangerud et al. (2006) took this into account when carbon-dating whale bones from the

North Sea; however, at that time there had been no investigations into the residence time of whale bones. To address this, Mangerud et al. (2006) used humans as a representation of all mammals with the caveat that unlike humans, whales continue growing throughout their lives. Humpback, fin, and blue whales all have estimated lifespans of 80–90 years (Chittleborough, 1965; Branch et al., 2007; Malige et al., 2022; Lockyer, 1977; Arrigoni et al., 2011). The whale bone reservoir age implies that the bone should reflect the sea reservoir age at the time in which the carbon was fixed in the collagen at the time of the whale's death (Mangerud et al., 2006). To minimize the bone reservoir age, the outer part of the bone should be sampled, as it is the most recently formed.

3. Samples and methods

3.1. Whale bone collection

Twenty-five whale bones were collected by Robert Pitman and Peter Wilson in February and March of 2016 under permit ACA 2016-006 (Table 3, Fig. 2). These bones were collected from old whaling stations/sites across the Antarctic Peninsula as part of a biological study to examine the impacts of whaling on genetic populations in Antarctica (Sremba, 2017). Bones of 4 species were collected across 4 sites (Fig. 1). Bone samples were identified to species through DNA extraction and sequencing of the mitochondrial DNA control region following methods in Sremba et al. (2015, 2023). In total, 12 samples were collected at Mikkelson harbor (3 fin, 6 humpback, and 3 blue whales), 9 at Jougla Point (6 fin, 2 humpback, and 1 blue whale), 3 at Walker Bay (2 humpback and 1 minke whale), and 1 at Cuverville Island (humpback).

3.2. Prep and measurement for ^{14}C dating

Sample preparation and measurements were completed at the UCI W. M. Keck Carbon Cycle Accelerator Mass Spectrometry (KCCAMS) Facility at the University of California Irvine. The outermost portion of the bone was sampled to ensure the most recently produced collagen was collected. Collagen was extracted from the bones using a modified Longin method (Longin, 1971) followed by ultrafiltration (Brown et al., 1988). The bone was first mechanically cleaned, and then decalcified in 1N HCl. The presence of contaminating humics was not suspected, so no base treatment was applied. The resulting crude collagen extract was then hydrolyzed to gelatin at 60 °C and pH 2, and the gelatin was ultrafiltered to select a high molecular weight fraction (>30 kDa). The purified gelatin extract was then freeze dried in a vacuum centrifuge. All samples were combusted to CO2 and then graphitized and pressed into sample holders for Accelerator Mass Spectrometer (AMS) analysis using a National Electrostatics Corporation (NEC 0.5 MV 1.5SDH-2) AMS.

3.3. Calculation of the marine reservoir age and statistics

The marine reservoir age signifies the disparity between a sample's radiocarbon age from a defined marine source and the concurrent atmospheric ^{14}C age (Reimer et al., 2004). The global value used for the Holocene Marine20 curve for 1910 is 607 ± 64 years; however, regional differences in surface water reservoir ages require the inclusion of an offset value for age calibration, known as ΔR (Heaton et al., 2020). To incorporate calendar age uncertainty into this calculation, we used the online program *deltar* for calculating ΔR and the uncertainty of each sample (CALIB: Delta R Program, accessed 2023; Reimer and Reimer, 2017). This program uses the formula

$$\Delta R(t) = {}^{14}Cm - Marine20C(t) \tag{1}$$

where ^{14}Cm is the measured radiocarbon age of the known age sample and Marine20C(t) is the radiocarbon age of Marine20 at time t (Reimer and Reimer, 2017). All reported errors in this study are expressed at the

Table 3

Sample ID	Location	Year of Collection	Species	UCI AMS Code	d13C (‰)	±	Fraction Modern	±	D14C (‰)	±	14C yr BP	±1	Delta R[a]
WB_01	Mikkelsen Harbor	1910±6	Humpback	270243	−19.2	0.1	0.8754	0.0018	−124.6	1.8	1070	20	463 ±40
WB_02	Mikkelsen Harbor	1910±6	Fin	270244	−17.5	0.1	0.8899	0.0016	−110.1	1.6	935	15	328 ±30
WB_03	Mikkelsen Harbor	1910±6	Humpback	270245	−20.6	0.1	0.8635	0.0016	−136.5	1.6	1180	15	573 ±30
WB_04	Mikkelsen Harbor	1910±6	Humpback	270246	−17.6	0.1	0.8712	0.0016	−128.8	1.6	1110	15	503 ±30
WB_05	Mikkelsen Harbor	1910±6	Blue	270247	−20.9	0.1	0.8632	0.0017	−136.8	1.7	1180	20	573 ±40
WB_06	Mikkelsen Harbor	1910±6	Blue	270248	−21.4	0.1	0.8622	0.0017	−137.8	1.7	1190	20	583 ±40
WB_07	Mikkelsen Harbor	1910±6	Humpback	270249	−17.5	0.1	0.8835	0.0017	−116.5	1.7	995	20	388 ±40
WB_08	Mikkelsen Harbor	1910±6	Humpback	270250	−18.8	0.1	0.8755	0.0017	−124.5	1.7	1070	20	463 ±40
WB_09	Mikkelsen Harbor	1910±6	Blue	270251	−21.0	0.1	0.8647	0.0016	−135.3	1.6	1170	15	563 ±30
WB_10	Mikkelsen Harbor	1910±6	Humpback	270252	−18.4	0.1	0.8765	0.0016	−123.5	1.6	1060	15	453 ±30
WB_11	Mikkelsen Harbor	1910±6	Fin	270253	−18.8	0.1	0.8879	0.0016	−112.1	1.6	955	15	348 ±30
WB_12	Mikkelsen Harbor	1910±6	Fin	270254	−20.4	0.1	0.8756	0.0016	−124.4	1.6	1065	15	458 ±30
WB_13	Jougla Point	1910±6	Humpback	270255	−19.0	0.1	0.8683	0.0016	−131.7	1.6	1135	15	528 ±30
WB_14	Jougla Point	1910±6	Fin	270256	−15.9	0.1	0.9072	0.0017	−92.8	1.7	785	15	178 ±30
WB_15	Jougla Point	1910±6	Fin	270257	−17.0	0.1	0.8987	0.0016	−101.3	1.6	860	15	253 ±30
WB_16	Jougla Point	1910±6	Fin	270258	−16.5	0.1	0.9049	0.0019	−95.1	1.9	805	20	198 ±40
WB_17	Jougla Point	1910±6	Fin	270259	−20.2	0.1	0.8670	0.0015	−133.0	1.5	1145	15	538 ±30
WB_18	Jougla Point	1910±6	Humpback	270260	−19.0	0.1	0.8901	0.0016	−109.9	1.6	935	15	328 ±30
WB_19	Jougla Point	1910±6	Fin	270261	−19.3	0.1	0.8862	0.0016	−113.8	1.6	970	15	363 ±30
WB_20	Jougla Point	1910±6	Fin	270262	−17.5	0.1	0.8834	0.0016	−116.6	1.6	995	15	388 ±30
WB_21	Jougla Point	1910±6	Blue	270263	−21.2	0.1	0.8632	0.0016	−136.8	1.6	1180	15	573 ±30
WB_22	Cuverville Island	1910±6	Humpback	270264	−19.7	0.1	0.8807	0.0018	−119.3	1.8	1020	20	413 ±40
WB_23	Walker Bay. Livingston Island	1910±6	Humpback	270242	−19.0	0.1	0.8466	0.0016	−153.4	1.6	1340	15	733± 30

[a] Calculated ucing Calib deltar (Reimer and Reimer, 2017) with Marine20 curve.

Fig. 2. Photographs of blue whale bone samples at Mikkelsen Harbor (WB_05 & WB_06) and Jougla Point (WB_21).

confidence level of 1σ unless stated otherwise.

Parametric tests were used to evaluate the statistical significance of differences between groupings of samples for species and location. These tests included a one-way analysis of variance (ANOVA), multi-way analysis of variance (ANOVAN), Tukey's honest significant difference criterion test (Tukey's HSD), and *t*-test. All statistical tests within this study were completed in MATLAB using the statistics and machine learning toolbox (The MathWorks Inc, 2022). All data was evaluated for normality using a chi squared goodness of fit test.

3.4. Whale bone age assignment

Although historical accounts suggest whaling continued in this region until 1929, analysis of whale species composition of the collection compared with whale catch history suggest that almost all the whale bones on the Antarctic beaches used in this study were killed between 1904 and 1916 with a X^2 value of 1.27 that with 3 degrees of freedom leads to a p = 0.735 (Sremba, 2017). This is supported by the high number of humpback whales, which were nearly hunted to extinction in the region by 1915 (Hart, 2006). To account for the period of whaling activities in this region, we assign a collection age of 1910 ± 6 C.E. to the whalebones used in this study.

A lag in the bone collagen's absorption of carbon could result in a sea surface reservoir age that varies with whale age and could represent a time before the whale's death. To examine this possibility, we investigate periods 10, 20, and 30 years prior to our proposed collection age. To

do this, we adjust time t in the ΔR calculation to a starting date of 1900, 1890, and 1880 to look at differences in the resulting surface reservoir age values. The error margin on the year was kept the same ($\pm$ 6 years) for all calculations. This allowed an examination of the effect that lag from the whale bone collagen may have on the resulting carbon reservoir age value.

3.5. Literature samples

In order to compare samples from our study with those from the literature, we compiled a list of radiocarbon samples of similar known collection age from various locations around Antarctica, taken from organisms that would have inhabited the surface water <400 m deep (Stuiver, 1981; Geyh and Wirth quoted in Whitehouse et al., 1988; Mabin, 1985; Whitehouse et al., 1988; Berkman and Forman, 1996; Gordon and Harkness, 1992; Curl, 1980; Hall and Perry, 2004; Björck
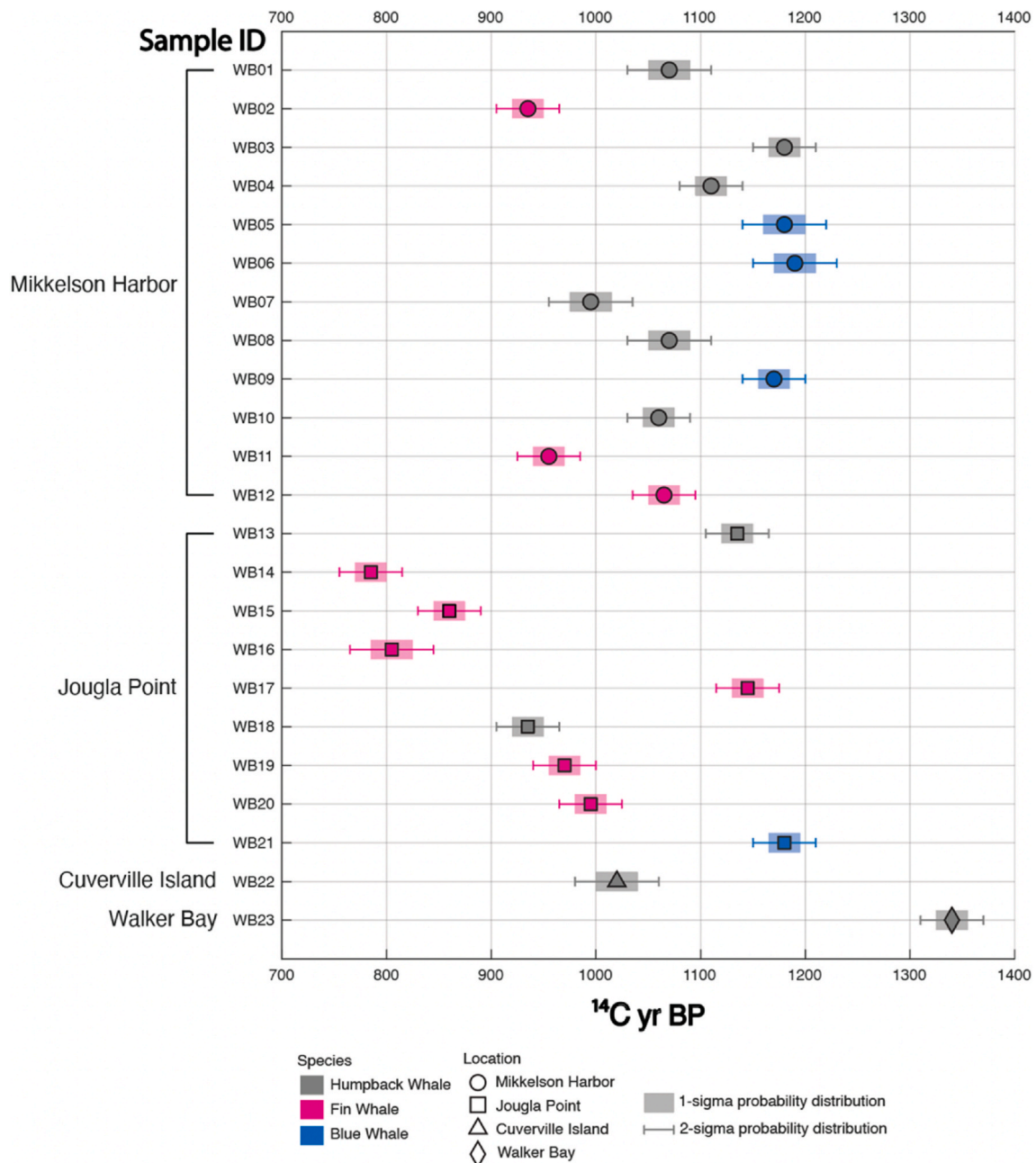

Fig. 3. Whale bone ^{14}C age plotted with species and location information differentiated by shape and color.

et al., 1991, Table 1). We separated these samples into two groups, one representing the Ross Sea (Stuiver, 1981; Geyh and Wirth quoted in Whitehouse et al., 1988; Mabin, 1985; Whitehouse et al., 1988; Berkman and Forman, 1996), and one the WAP (Gordon and Harkness, 1992; Curl, 1980; Hall and Perry, 2004; Björck et al., 1991). We compared these two groups of literature samples to our samples using a T-test.

We also divided the literature samples into groups based on dated material. We compared our samples (whalebones) to 17 previously-dated dated whalebones (Hall, 2010; Gordon and Harkness, 1992; Curl, 1980; Hall and Perry, 2004), 5 seal samples (Stuiver, 1981; Mabin, 1985; Geyh and Wirth quoted in Whitehouse et al., 1988), and 6 penguin samples (Stuiver, 1981; Geyh and Wirth quoted in Whitehouse et al., 1988; Mabin, 1985; Whitehouse et al., 1988; Björck et al., 1991). We compared these three groups of previously studied samples to our samples by examining the weighted average of each group's reservoir age.

4. Results

Of the 25 samples processed, 23 were successfully radiocarbon dated (Fig. 3). The single minke whale sample was unable to be graphitized, so the sample was not measured, and collagen was not able to be extracted from one humpback whale bone. The minke whale sample was further treated for the presence of sulfur compounds, but this treatment did not result in successful graphitization. Both samples were from Walker Bay, on Livingston Island (Fig. 1).

4.1. Intraspecies

The average uncorrected age of all species is 1050 ± 135 BP (Table 2). Average age by species ranges from 946 ± 117 BP for fin whales, 1091 ± 111 BP for humpback whales, and 1180 ± 8 BP for blue whales (Table 4). Blue whale ages contained a difference between the oldest and youngest sample of only 20 years, while the humpback whales had a 405-year difference, and fin whales a 360-year difference.

Using an ANOVA test, which compared the radiocarbon age with species of whale, we found that the radiocarbon ages of different species show a small but significant difference (p = 0.026). The pairwise comparison results of a Tukey's HSD test revealed that humpback and blue whale values are significantly different from fin whales (p = 0.0187 and p = 0.0039, Table 5), but not from each other (p = 0.3515, Table 5).

4.2. Location

Average age by location ranges from 978 ± 148 BP for Jougla Point and 1081 ± 88 BP for Mikkelsen Harbor (Table 4). Samples from Jougla Point exhibited a 360-year difference between the oldest and youngest sample, while samples from Mikkelsen Harbor exhibited a 255-year

Table 4
Average age and error by species and location.

Species	Average Age (^{14}C yr BP)	1σ	# of Samples
All Species	1050	135	23
Fin Whales	946	117	9
Humpback Whales	1091.5	111	10
Blue Whales	1180	8	4
Location			
Jougla Point	978	148	9
Fin only	926	136	6
Humpback only	1040	141	2
Blue only	1080	–	1
Mikkelsen Harbor	1081	88	12
Fin only	985	70	3
Humpback only	1080	61	6
Blue only	1080	10	3
Cuverville Island (Humpback)	1020	–	1
Walker Bay (Humpback)	1340	–	1

Table 5
P values associated with each statistical analysis completed using all data and with the removal of outliers. Bold represents values that show statistical significance. Abbreviations stand for: RS = Ross Sea, WAP = Western Antarctic Peninsula, TS = This Study, WB = Walker Bay, JP = Jougla Point, MH = Mikkelsen Harbor, CI = Cuverville Island, F = fin whale, H = humpback whale, and B = blue whale. RS 1760 refers to a Ross Sea sample with a radiocarbon age of 1760 years (Mabin, 1985). WB Humpback refers to the humpback whale sample in this study collected at Walker Bay (WB_23).

Statistical Analysis	Comparison	P-value	P-value
		All Data	Remove RS 1760
T-test	RS: WAP	0.7376	0.3315
T-test	RS: TS	**0.004**	**0.0115**
T-test	WAP:TS	**0.0035**	–
		All Data	Remove WB Humpback
ANOVAN	Species (X1)	**0.0061**	**0.0061**
ANOVAN	Location (X2)	0.0544	0.5575
ANOVAN	X1:X2	0.9068	0.9068
ANOVA - Species	P value	**0.026**	**0.0011**
ANOVA - Species	Humpback: Fin	**0.018691**	**0.031145**
ANOVA - Species	Humpback: Blue	0.35154	**0.010757**
ANOVA - Species	Fin: Blue	**0.0039977**	**0.0010319**
ANOVA - Location	P value	**0.0376**	0.1659
ANOVA - Location	WB: MH	0.18505	–
ANOVA - Location	WB: JP	**0.040536**	–
ANOVA - Location	WB: CI	0.25096	–
ANOVA - Location	MH: JP	0.22889	0.14359
ANOVA - Location	MH: CI	0.9571	0.87021
ANOVA - Location	JP: CI	0.98699	0.94128

difference.

Using an ANOVA test, we compared the radiocarbon age to location of the whale bones and found that the radiocarbon ages from bones at different locations have a significant difference when species is not considered (p = 0.0376, Table 5). The pairwise comparison results of a Tukey's HSD test revealed that no locations significantly differ from Cuverville Island or Mikkelsen Harbor, but that the means of bones from Jougla Point and Walker Bay are significantly different (0.0405, Table 5).

To determine if species has an impact on the ANOVA test by location, we compared the reservoir age by location using only whale bones of the same species. This included blue and fin whale bones from Mikkelsen Harbor and Jougla Point, and humpback whale bones from all four locations. Bones of blue whales from Mikkelsen Harbor exhibited a significant difference from both fin (p = 0.0088) and humpback whale bones (p = 0.0308) from Mikkelsen Harbor. Bones of fin whales from Jougla Point also exhibited a significant difference from humpback (p = 0.0304) and blue whale bones (0.0174) from Mikkelsen Harbor. No other species groups at any location showed significant differences between each other. Some of this significant difference between bones of different species within each location may account for the small but statistical difference seen between the locations themselves.

4.3. Both variables

Using an ANOVAN test, we tested the effect of both grouping variables (species and location) on the mean of our radiocarbon ages (Table 5). Responses were significantly different between species (p 0.0061), but not location (p = 0.0544). This result is similar to both prior ANOVA tests, which showed significant differences in both groups. The interaction of these two variables is not significant (p = 0.968). In a comparison of the combinations of the two grouping variables, the only significant difference was the fin whale bones at Jougla Point and the humpback whale bone at Walker Bay (p = 0.0412).

4.4. Outliers

Sample WB_23, the humpback whale bone at Walker Bay, is the only

sample from this location that was able to be dated. The age returned for this whale bone was 1340 ± 15 BP, about 200 years more than any other humpback whale sample. Considering this difference, we explored the effects of this potential outlier on our analysis (Table 5). Sample WB_23 was removed from the statistical analysis and all tests were rerun. Without sample WB_23, no statistical difference was found between locations in any test. The test result for ANOVAN species did not change. In the ANOVA comparison, bones from the humpback and blue whale comparison changed from not significantly different (p = 0.3515) to significantly different (p = 0.0107). This finding aligns with the greater ages and smaller range of the blue whale samples compared to the rest of the humpback whale samples.

4.5. Delta R

Individual ΔR values computed for each sample range from 178 ± 30 years (WB_14) to 733 ± 30 years (WB_23) relative to our assumed collection year of 1910 ± 6. Our average ΔR for all samples is 443 ± 135 years. When computing ΔR with the assumption of a 10, 20, and 30 year lag between the death of the whale and the incorporation of seawater carbon into its bone collagen (e.g. the carbon was sequestered 10, 20, and 30 years before the whales death), we found values of 437 ± 33 years for a 10 year lag, 426 ± 135 years for a 20 year lag, and 417 ± 135 years for a 30 year lag. This shows a 26-year difference between the 1910 and 1880 reservoir age values, which falls into the error of the original 443 ± 135 year result. While it is possible that the collagen collected could have a slight lag in the radiocarbon reservoir age it is representing, the change to the reservoir age produced does not significantly alter the results.

5. Discussion

5.1. Comparison of ^{14}C ages and reservoir estimates from other locations

Previously published radiocarbon ages from both the WAP and Ross Sea were compared to the radiocarbon ages from this study and each other using a *t*-test (Table 5). The results revealed intriguing patterns: while previously published ages within each location did not exhibit statistically different means (11 years), our study displayed a small but significant difference when compared to both groups (198 years for the Ross Sea and 209 years for the WAP). Specifically, when comparing the 12 historical samples from the Ross Sea to our results, the obtained p-value was 0.0040 (Stuiver, 1981; Geyh and Wirth quoted in Whitehouse et al., 1988; Mabin, 1985; Whitehouse et al., 1988; Berkman and Forman, 1996). Similarly, the comparison with the 7 historical samples studied earlier from the WAP yielded a p-value of 0.0035 (Gordon and Harkness, 1992; Curl, 1980; Hall and Perry, 2004; Björck et al., 1991).

Comparing the historical Ross Sea samples to other previously published WAP samples via *t*-test returned a p-value of 0.7376, meaning a high probability that the data comes from two independent random samples with equal means at the default 5% significance level. Much like this study, one historical sample from the Ross Sea has a much older age than the rest. This sample was reported by Mabin (1985) and is ~370 years older than any other historical sample reported. Without the inclusion of this sample in the comparison, the statistical difference between this study and that of the Ross Sea increased to p = 0.01, lowering the significance level of the difference (Table 5).

Multiple radiocarbon and paired U/Th ages of deep-sea corals have been collected in the Drake Passage by Li et al. (2020). Li et al. (2020) found a Holocene reservoir age of approximately 950 years. We recalculated the reservoir age for subgroups of their ages. One subgroup included samples above 400m water depth, representing the water masses accessible to feeding whales during their lifetimes. The second subgroup encompassed ages younger than 11,000 years to focus solely on samples originating within the Holocene. However, all Holocene-aged samples were collected at a depth of 816m, exceeding

the diving capabilities of whales. Moreover, samples above 400m depth dated older than the Holocene, a time period of vastly different oceanic and atmospheric conditions (Clark and Mix, 2002). Consequently, drawing definitive conclusions between the comparison between reservoirs obtained from the Drake Passage corals and our bones proves challenging due to these differences in depth and oceanic conditions. The <400m depth samples exhibited an average reservoir age value of 1014 ± 183 years, falling within error of our value of 1050 ± 135. However, the Holocene age samples averaged 447 ± 96 years, which likely reflects the different water masses the ages are sampling.

Hall et al. (2010) obtained a radiocarbon reservoir age for the Ross Sea of 1144 ± 120 years based paired U/Th and radiocarbon ages of solitary corals obtained from a floating ice shelf. Their reservoir age of 1144 years agrees well with older estimates obtained from pre-bomb historical samples (1131 ± 125 years; Berkman and Forman, 1996; Mabin, 1985; Stuiver, 1981, Table 5), and overlaps with our reservoir age of 1050 ± 135 years. However, Hall et al.'s (2010) samples date from modern (post-bomb) to ~6500 years of age. Only two samples from Hall et al. (2010) are both pre-bomb and had a raw ^{14}C age under 2000 years (K78-66 A[2] and K81–1C[3]), similar to the samples in this study. The reservoir age of these two samples was found to be 1077 ± 30 years, showing even higher similarly to the reservoir age found in this study.

5.2. Comparison of ^{14}C reservoirs by organism

To examine reservoir age differences among different ^{14}C dated material within Antarctica we use a weighted average, considering the weight of associated error margins for each sample included. The weighted average of our 23 whale bones samples is 1045 ± 10 years, compared to the weighted average of 16 other pre-bomb whalebone samples from Antarctica of 1198 ± 7 years (Hall, 2010; Gordon and Harkness, 1992; Curl, 1980; Hall and Perry, 2004). This results in a minimum difference of 136 years, which falls within the 2-sigma error (1050 ± 270) of our proposed reservoir age.

When compared to values from other animal samples, we find the weighted average of 5 pre-bomb seal samples to be 1387 ± 26 years (Stuiver, 1981; Mabin, 1985; Geyh and Wirth quoted in Whitehouse et al., 1988), and 6 pre-bomb penguin samples to be 1130 ± 23 years (Stuiver, 1981; Geyh and Wirth quoted in Whitehouse et al., 1988; Mabin, 1985; Whitehouse et al., 1988; Björck et al., 1991). The seal weighted average was skewed by a single sample from Inexpressible Island, reported by Mabin (1985) with an age of 1760 yr BP, 370 years older than any other historical seal sample. However, we suspect possible contamination in this outlier such as fine particles of other material or chemical alteration, as it deviates greatly from the rest of the samples collected on Inexpressible Island in the same year. When excluding this sample, the refined seal reservoir age value (1294 ± 26) may be a more accurate representation of the group. This adjusted seal reservoir age value, along with the penguin reservoir age value, both fall within the 2-sigma error of our proposed reservoir age (1050 ± 270).

Comparing our reservoir age to the paired ^{14}C and U/Th coral databases of Li et al. (2020) and Hall et al. (2010), we observed a closer alignment with Hall et al.'s (2010) value for the Ross Sea (1131 ± 125 years), compared to Li et al.'s (2020) value in the Drake Passage (~950 years). This discrepancy can be attributed to differences in sample ages and water depths within the Li et al. (2020) dataset, as discussed in section 5.1. Hall et al.'s (2010) dataset, featuring solitary corals from the basal ice of the McMurdo and Hells Gate Ice shelves, closely mirrored the sample conditions of our study, reflecting the properties of the open Ross Sea surface waters. Overall, our analysis did not reveal a significant difference in reservoir age based on sample material.

5.3. ^{14}C reservoir variability through time

Hall et al. (2010), found a constant surface reservoir age for the last 6000 years (Fig. 4). They speculate that this is due to approximate
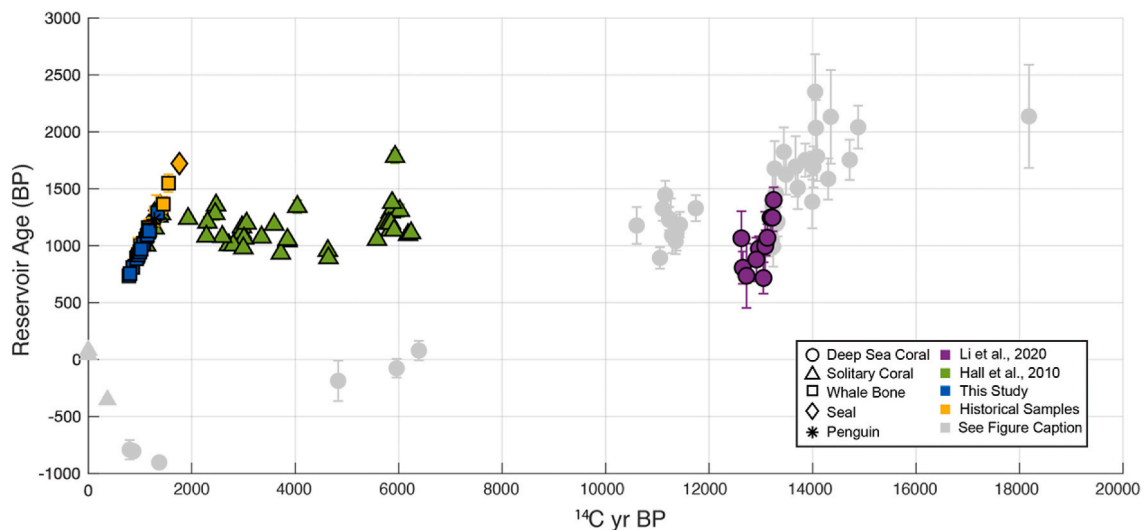
Fig. 4. Reservoir ages plotted again raw radiocarbon age for samples from this study, Li et al. (2020), Hall et al. (2010), and historical samples (Stuiver et al., 1981; Geyh and Wirth quoted in Whitehouse et al., 1988; Mabin, 1985; Whitehouse et al., 1988; Berkman and Forman, 1996; Gordon and Harkness, 1992; Curl, 1980; Hall and Perry, 2004; Björck et al., 1991). Error bars represent 1 sigma error. Light grey data points represent post-bomb samples from Hall et al. (2010), and samples from the shallow group of Li et al. (2020) which exceeded 400m depth.

consistency in the composition of Atlantic and Pacific waters that make up the Southern Ocean, and in air-sea exchanges (Hall et al., 2010). To extend Hall et al.'s (2010) findings we consider two groups of the shallow deep-sea coral data from Li et al. (2020): 1.) the entire shallow group (up to 1012m depth), and 2.) only samples above 400m depth to ensure different water masses were not intermingled in the surface reservoir age estimate. In both cases, we see no significant change in trend from the present to 14,000 years (with R^2 values of 0.18 for the case including only <400m samples, and 0.006 for the case including all samples), indicating that the ^{14}C Southern Ocean surface reservoir age has stayed relatively constant throughout this period. It is possible that complementary changes in air-sea exchange and ocean circulation could result in a constant Southern Ocean surface reservoir; however, it is more likely that the conditions remained close to constant throughout this time (Hall et al., 2010). Hall et al. (2010) suggests this would be possible if changes in the relative fraction of the Atlantic input into the Southern Ocean stayed under 25% its modern value. The lack of significant change in the surface water radiocarbon reservoir over the last 14,000 years suggests this input has not fluctuated significantly throughout the Holocene.

6. Conclusion

Twenty-three whalebones with an age between 1904 and 1916 were used to investigate the radiocarbon reservoir age of the Southern Ocean. Our analysis revealed an average reservoir age of 1050 ± 135 years and ΔR of 443 ± 135 years for these whale bones. A small but statistically significant variation was found between bones of different species, specifically between bones from fin and blue whales, and bones from fin and humpback whales. With the inclusion of all samples, variation by location was seen between Walker Bay (one sample, humpback) and Jougla Point. However, the very small difference suggeststhat location and species did not contribute to an overwhelming difference in radiocarbon age for the WAP, making separate reservoir estimates unnecessary. Given the uniformity in the carbon source for these whale species, our observations align with established variations in reservoir ages across diverse organisms. In conjunction with DNA sequencing to identify species, these results provide a valuable contribution to the understanding of radiocarbon reservoir ages in Antarctica.

When comparing our data to previous studies of ^{14}C surface reservoir ages across Antarctica, we found small but statistically significant

differences (p values < 0.05) between radiocarbon reservoirs from our study, the Ross Sea, and the WAP. When one outlier was removed from the analysis, reservoir differences between our study and the Ross Sea became insignificant (p = 0.01). We observed no significant difference in the reservoir ages of different commonly dated materials including whalebone, seal, penguin, and coral, including all available ^{14}C data from shallow (<400m) waters across Antarctica. Overall, our findings align closely with Hall et al. (2010) Holocene reservoir age value from the Ross Sea, showing good alignment between reservoir ages of Southern Ocean surface waters across Antarctica. It was difficult to draw conclusions from a comparison with data from the Drake Passage as the dataset of Li et al. (2020) differed significantly in sample age and depth of collection. However, by only examining the shallow coral ages of Li et al. (2020), we observed a near-constant surface reservoir value over the last 14,000 years, strengthening our understanding of the overall shallow Southern Ocean radiocarbon reservoir age. Continued efforts to refine reservoir age estimations through diverse and extensive datasets are essential for advancing our knowledge of the Quaternary history of Antarctica, particularly in the face of its rapid warming, potential contributions to sea-level rise, and the role of the Southern Ocean in climate regulation.

Author contributions

Conceptualization: ARS, AF, Data curation: ARS, CD, Formal Analysis: CD, Funding acquisition: ALS, ARS, CSB, Investigation: CD, JS, ALS, CSB, Methodology: ARS, JS, CD, Resources: ALS, CSB, Supervision: ARS, Visualization: CD, Writing – original draft: CD with input from ARS, AF, and the rest of the authors, Writing – review & editing: CD with input from ARS and the rest of the authors, CD = Claire Divola, ARS = Alexander R. Simms, ALS = Angela Sremba, CSB═C. Scott Baker, AF = Ari Friedlaender, JS = John Southon.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

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