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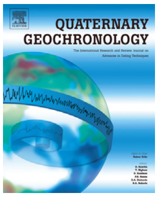

Seasonal radiocarbon reservoir ages for the 17th century James River, Virginia estuary

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ABSTRACT

This study utilizes a combined stable isotope and ^{14}C dating approach to determine the radiocarbon reservoir age correction, ΔR, for the James River, Virginia estuary from 17th century *Crassostrea virginica* shells of known collection dates. ΔR, which can vary spatially and temporally, is a locality-specific adjustment applied to the global ocean reservoir, R, to further account for the offset between the atmospheric and marine ^{14}C calibration curves. To assess the temporal variability in ΔR, continuous δ^{18}O sampling along the oyster shell hinge provides a seasonal record throughout the oyster's life. This is then used to identify sampling locations for ^{14}C measurements based on calcite precipitated during the Summer (>19 °C) and Fall through Spring (F-Sp, <15 °C) months. The resulting seasonal ΔR values range from -151 ± 46 to $+109 \pm 55$ ^{14}C years (260 years) due to changes in the contribution and age of dissolved inorganic carbon (DIC) from marine and freshwater sources in the James River estuary. The F-Sp samples display a larger ΔR range than the Summer samples, as do the shells precipitated during drought conditions (1606–1612) when compared to shells from the remainder of the 17th century. The largest intrashell ΔR variability, 195 ^{14}C years, is similarly found in a drought shell and is attributed to variability caused by the extreme regional 1606–1612 drought. Early land use changes related to European development and farming practices also altered the age of DIC in the James River estuary. We estimate that the soil inorganic carbon (SIC) contributing to freshwater DIC ranged from 0 to ~1800 years old and reflected both the drought and land use changes that occurred during the 17th century. Using only the Summer samples, which represent the majority of shell calcite, we obtain a mean $\Delta R = -32 \pm 11$ ^{14}C years (1σ) for 17th century James River estuary ΔR at the very onset of European colonization. Employing a seasonally resolved sampling method will provide the greatest constraint on ^{14}C measurements in an estuarine environment where multiple carbon sources can fluctuate on seasonal timescales and as a result of large scale environmental change.

1. Introduction

Radiocarbon (^{14}C) is one of the most important dating tools used by geologists and archaeologists to reconstruct the timing of changes in Earth and human history over the past 50,000 years. ^{14}C can be used in the traditional sense of assigning a date to a specific event, but it is also used as a tracer for processes such as ocean circulation, changes in air-sea equilibration, and upwelling (Druffel et al., 2004; Andrus et al., 2005; Ferguson et al., 2013), as well as carbon flow through terrestrial ecosystems (Gaudinski et al., 2000; Trumbore, 2000; Raymond et al., 2004). As a result, extensive research has been devoted to refining the ^{14}C technique, including intercalibrating radiocarbon with absolute geochronometers such as U/Th (Bard et al., 1990; Fairbanks et al., 2005; Reimer et al., 2013), constraining carbon source variations in ^{14}C from different environments (Hogg et al., 1998; Ascough et al., 2010; Rick et al., 2012), and selection of the most appropriate datable material (Ingram and Southon, 1996; Hogg et al., 1998; Kennett et al., 2002; Ascough et al., 2005b).

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Interpretations of ^{14}C data from identifiable terrestrial fossils are generally straightforward because photosynthesis incorporates $^{14}CO_2$ directly from the atmosphere (Anderson et al., 1947). Because the residence time of atmospheric CO_2 is ~4–10 years (Craig, 1957; Levin and Hesshaimer, 2000), the initial ^{14}C content of terrestrial material is closely linked to the atmospheric $^{14}C/^{12}C$ ratio. Dating organic carbon from plants and animals in aquatic environments is more complicated due to a mixing of carbon pools with different ages. Lakes, estuaries, and oceans each contain dissolved inorganic carbon (DIC) with ^{14}C content that is often lower than the atmosphere. The difference between the atmospheric $^{14}C/^{12}C$ ratio and the co-occurring $^{14}C/^{12}C$ content of a carbon pool is known as the radiocarbon reservoir effect (Stuiver and Polach, 1977; Stuiver and Braziunas, 1993).

The magnitude and sign of the ^{14}C reservoir effect varies depending on environment. Freshwater lake samples often appear older than their true calendar age because the DIC pool contains a fraction of carbonate-derived ‘dead’ carbon (carbon that lacks ^{14}C because its age exceeds ~50 kyr) from groundwater that interacts with surrounding bedrock (Deevey et al., 1954; Broecker and Walton, 1959). There may also be slow atmosphere-water mixing rates resulting from stratification or ice cover (Abbott and Stafford, 1996). Oceanic environments are also depleted in ^{14}C with respect to the atmosphere because the deep oceanic carbon reservoirs require millennia to circulate before interacting with the atmosphere again (Broecker and Peng, 1982). The oceanic ^{14}C surface reservoir effect is referred to as the global ocean reservoir, R, and is considered to have an average age of ~400 years (Stuiver and Braziunas, 1993). Processes such as changes in ocean circulation rate, upwelling, or mixing of water masses can cause regional offsets from 400 years (Goodfriend and Flessa, 1997; Kennett et al., 1997; Ferguson et al., 2013), thereby necessitating the use of locality-specific reservoir age corrections, referred to as ΔR (Stuiver and Braziunas, 1993), to compute radiocarbon ages.

The magnitude of ΔR varies spatially and temporally and must be established to compute a more accurate age of marine sample material (see review by Ascough et al., 2005a). In estuaries, river and seawater DIC mix to produce a final inorganic carbon pool that is a function of the DIC concentration and radiocarbon age of each component (Ingram and Southon, 1996; Ulm, 2002; Culleton et al., 2006; Russell et al., 2010; Lougheed et al., 2016). Sources of ^{14}C in freshwater rivers, ranging in age from modern to radiocarbon-dead, include atmospheric ^{14}C, inorganic carbon derived from remineralized soil organic carbon, and carbon from the interaction of water with bedrock (Hope et al., 1994; Raymond et al., 1997, 2000, 2004; Hossler and Bauer, 2012, 2013). These latter two comprise the soil inorganic carbon (SIC) component of the freshwater DIC pool. Within an estuary, the relative proportions of marine and freshwater-derived ^{14}C will change depending on the amount of freshwater input and marine incursion, which can be calculated if salinity is known.

Attempts have been made to deconvolve the marine and estuarine inorganic carbon system to determine region specific ΔR. These include combining ^{14}C data from paired terrestrial and aquatic material (Kennett et al., 1997; Ingram, 1998; Ascough et al., 2005b), quantifying ^{14}C and U/Th ages from the same samples (Bard et al., 1990; Yu et al., 2010), or dating marine organisms such as mollusks from archaeological sites of known calendar age (Colman et al., 2002; Culleton et al., 2006; Rick et al., 2012; Rick and Henkes, 2014). Application of paired terrestrial and aquatic materials allow for the direct determination of ΔR if contemporaneity can be assumed. Unfortunately, the coeval nature of such samples is often difficult to confidently confirm in paired marine and terrestrial deposits. The combined use of U/Th dating and ^{14}C measurements to establish ΔR introduces its own set of assumptions and uncertainties (Edwards et al., 1987). Historically dated archaeological sites allow the direct comparison of estuarine ^{14}C measurements to specific time periods, thereby reducing the uncertainties when computing ΔR for a defined watershed.

Accuracy in determining the radiocarbon reservoir ages applied to estuarine mollusks (e.g., Eastern oyster, *Crassostrea virginica*) is critical for archaeological studies of early North American sites that predate the historical record. Of particular importance in defining ΔR are issues related to monthly, seasonal, and interannual changes in the estuarine carbon system which can vary with decadal changes in regional precipitation patterns and/or watershed land-use modifications (Ingram and Southon, 1996; Brush, 2001; Raymond and Bauer, 2001b). A suite of archaeological sites available from Virginia's James River estuary are uniquely suited to quantify variations in ΔR from 17th century estuarine waters because the burial date of their *C. virginica* oyster shells can be established from the historical record (Fig. 1, Table 1). These sites include three Jamestown Fort era wells (1607–1624, Kelso and Straube, 2004; Hudgins et al., 2008; Schmidt and Straube, 2012) and trash pits from Nansemond Pallizado (1636–1646; Luccketti, 2010; Pecoraro, 2015) and Bacon's Castle (1676; Luccketti, 1990; Dean, 2005). The sealed wells and trash pits were used because the archaeology supports material deposition during unique time periods of week(s) to about three months (Luccketti, 1990; Kelso and Straube, 2004; Hudgins et al., 2008; Schmidt and Straube, 2012; Pecoraro, 2015). These sites are representative of the James River geographic range of oyster habitat (Haven and Fritz, 1985; Harding et al., 2010).

Previous radiocarbon studies of mollusks from freshwater and marine environments recommend homogenizing shell $CaCO_3$ for ^{14}C analyses to smooth short term (tidal, days, or weeks; e.g. physiological processes) and sub-annual (months; e.g. seasonal upwelling or productivity) variability that may be present (Hogg et al., 1998; Culleton et al., 2006). However, this variability can impart significant uncertainty to an age determination because ^{14}C content in a system may differ seasonally (Druffel et al., 2004;

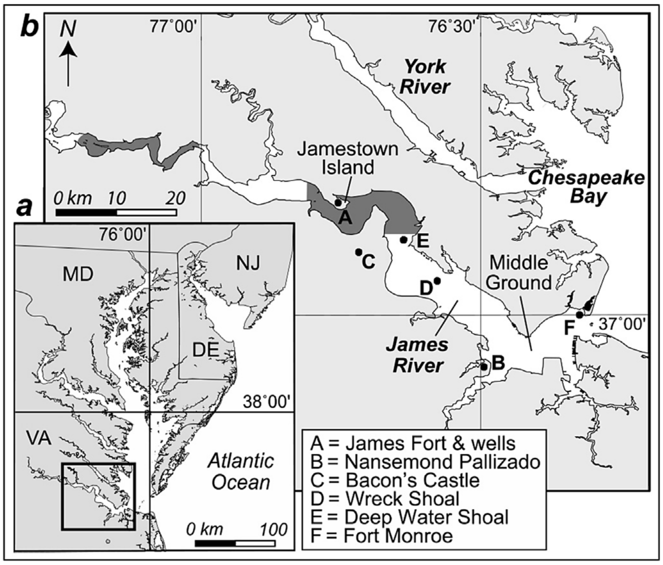

Fig. 1. Map of (a) Chesapeake Bay and (b) James River estuary showing the location of archaeological oyster and water collection localities used in this study (modified from Harding et al., 2010). Shaded areas of the river indicate the fresh-salt water transition zone today (downriver shading) and during the drought that spanned 1606–1612 (upriver shading). Deep Water Shoal (site E) is the modern limit for oyster survival based on their minimum salinity tolerance of 5–7 psu (Shumway, 1996; Mann et al., 2009).

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