Proceedings of the Geologists' Association 125 (2014) 14–19

Contents lists available at ScienceDirect

Proceedings of the Geologists' Association

journal homepage: www.elsevier.com/locate/pgeola

Sodium and strontium in mollusc shells: preservation, palaeosalinity and palaeotemperature of the Middle Pleistocene of eastern England

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ARTICLE INFO

Article history:
Received 25 July 2013
Received in revised form 18 October 2013
Accepted 26 October 2013
Available online 21 November 2013

Keywords:
Sodium
Strontium
Mollusc shells
Palaeosalinity
Pleistocene

ABSTRACT

This paper revisits the utility of sodium (Na) content in aragonite and calcite mollusc shells as an indicator of palaeosalinity. The data come mainly from a related suite of Middle Pleistocene marine and freshwater fossils that have been subject to broadly similar diagenetic histories. Environmental salinity is re-affirmed as the primary factor in determining the sodium content of modern and ancient mollusc shells: values <2000 ppm Na are generally indicative of non-marine environments while values >2000 Na ppm are typically from marine shells. There is a positive relationship between Na (salinity) and Sr which is a helpful discriminator of palaeosalinity in the fossil data set. The Na and Sr data give confidence that the fossil shells have not suffered pervasive diagenetic alteration and that the marine fossils lived in fully marine conditions. Oxygen isotope values in the best-preserved, fully marine fossil shells, suggest Middle Pleistocene 'eastern England' seawater temperatures were broadly similar to those of the modern North Sea.

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1. Introduction

Fossils preserved in ancient sediments have long been used as an important source of palaeoenvironmental information, helping identify a huge range of open marine, estuarine and non-marine conditions. Where well-preserved, some fossils skeletons, particularly marine ones, are used to reconstruct palaeotemperature information, often through the use of oxygen isotope thermometry. This short contribution discusses fossil geochemistry and is centred mainly on a stratigraphically related set of both marine and freshwater material from the Middle Pleistocene (~500–800 ka) of north Norfolk, UK. We concentrate mainly on molluscan aragonite, the survival of which, in itself, suggests good preservation. The particular focus is on the use of sodium (Na) and strontium (Sr) substitution in the molluscan aragonite as an indicator of both preservation, but also palaeosalinity. Where good preservation is proven we use stable oxygen isotope thermometry to infer likely Middle Pleistocene seawater temperatures and compare these to present day conditions.

The use of trace element substitution in calcium carbonate shells is a well established technique for assessing degree of diagenetic alteration (e.g. Brand and Morrison, 1987). Sodium content, in-particular, has been proposed both as an indicator of post depositional alteration and potentially as a proxy for palaeosalinity. Modelling and fluid inclusion data suggest that Na concentrations in the oceans have not changed significantly over Phanerozoic time (Demicco et al., 2005), such that well-preserved Na contents in Phanerozoic fossil carbonate shells should record values similar to those from modern shells.

Early research on modern marine oyster and barnacle shells suggested that water salinity had the strongest control on calcium carbonate Na content (Rucker and Valentine, 1961; Pilkey and Harriss, 1966; Gordon et al., 1970). Brackish water fossil shells have also been shown to contain lower Na contents than their fully marine counterparts (e.g. Brand, 1987). The database on modern carbonates was much extended by Land and Hoops (1973) who found that overall, marine aragonitic and Mg-calcitic sediments and shells contained >1000 ppm Na; actual contents varied with organism type, suggesting that a biochemical vital effect modulated Na uptake. Subsequently, Okumura and Kitano (1986) ascertained that most aragonite molluscs contained between 2000 and 6000 ppm Na. Comparative study of modern and Pleistocene carbonates by Land and Hoops (1973) also showed that meteoric diagenetic alteration of carbonates lowered Na and other trace element contents. Further work on Palaeozoic carbonates (Veizer et al., 1977) established that Na contents were higher in hypersaline dolostone facies than normal marine facies despite their likely overall lowering by post depositional alteration.

Despite this early promise, by the mid-1980s the technique had not found widespread utility; caution with the approach was urged (Brand and Morrison, 1987) not least because the data was often

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http://dx.doi.org/10.1016/j.pgeola.2013.10.005

ambiguous; biochemical effects were poorly understood, a considerable portion of the Na content in calcium carbonate minerals was potentially associated with NaCl-containing liquid inclusions, or adsorbed to non-carbonate contaminant portions such as silicate and Fe–Mn crusts (Veizer, 1983).

In this paper we look again at Na in calcium carbonate shells, mainly biogenic aragonites. We make observations on a suite of related marine and freshwater fossils that have been subject to broadly similar diagenetic histories. The results, particularly the relationship between Na and Sr contents, are given context by comparisons with modern marine and freshwater shells, in some cases the exact same species as the fossil ones.

2. Material

The study focuses primarily on the Wroxham Crag and Cromer forest Bed Formations (Middle Pleistocene) of north Norfolk (Fig. 1; locality and details of the stratigraphy are given in the appropriate references below). The preservation of ancient biogenic aragonite in these sequences is in itself somewhat enigmatic; aragonite is prone to post-depositional groundwater dissolution and calcitization, yet in some horizons this Middle Pleistocene aragonite survives in what appear to be rather porous sandy and conglomeratic sediments.

The oldest material comes from the basal 'stone bed' of the marine Mundesley Member of the Wroxham Crag at Weybourne (Fig. 1; 52°56′56.3″ N; 1°18′48.1″ E), which lies beneath sediments with reversed magnetic polarity and attributed to the Matuyama reversed Chron (Hallam and Maher, 1994); i.e. >780 ka. The 'stone bed' is patchily-rich in marine molluscs, particularly *Arctica islandica*, and the member is thought to have formed in tidal shallow seawater (Pawley et al., 2004). The West Runton Freshwater Bed (Fig. 1.; WRFB; 52°56′29.8″ N; 1°15′12.1″ E) is an intercalated freshwater deposit within the Wroxham Crag/Cromer forest Bed Formations (Gibbard et al., 2010), generally believed to be >500 ka and <780 ka, possibly deposited in Marine Isotope Stage (MIS) 15 or 17 (see for example, discussion in Brough et al., 2010). The lower part of the bed is rich in non-marine molluscs that lived in a slow-flowing, vegetated stream environment (Preece and Parfitt, 2000; Gibbard et al., 2010). The 'monkey gravel', directly overlying the WRFB at West Runton, is a gravelly, muddy sand containing the bivalve *Mya truncata* in life position and indicating a return to marine conditions. To extend both the marine and freshwater data sets we also analysed material from: (1) MIS 7 and ?MIS 11 shallow marine marls from, respectively, Agrilliou Bay (38°0′36.5″ N; 22°54′43.5″ E; Turner et al., 2010) and the Corinth Canal, central Greece (37°56′23.9″ N, 22°58′49.4″ E; Collier and Leeder, 2007); and (2), freshwater gastropods *Lymnaea peregra* from the Holocene (~10,500 years BP; Garnett et al., 2006) Caerwys tufa, North Wales (Fig. 1; 53°14′13.1″ N; 3°18′23.2″).

To constrain likely baseline Na contents, modern marine and freshwater mollusc shells were also analysed: these included; (1) marine bivalves (*Ensis ensis*, *Ostrea edulis*, *Mytilus edulis*, *Pecten* sp.) and gastropods collected from An Cruinn-leum beach, north of Applecross Village, Scotland (Fig. 1; 57°28′6.4″ N; 5°51′38.0″ E), from Cley-next-the-Sea beach, Norfolk (Fig. 1; 52°57′57.4″ N; 1°2′53.3″ E), and the bivalve *A. islandica* from ~20 m depth in the southern North Sea; (2) modern freshwater shells (*Dreissena polymorpha*, *Unio pictorum*, *Anadonta anatina*) from the River Bure, near Horning, Norfolk (52°41′40.4″ N; 1°27′57.1″ E). Two species of tank grown freshwater gastropods were also studied.

3. Method

3.1. Sample preparation

The surface of shell samples was scraped with a scalpel, and episodically dipped in 10% HCl for a few seconds to remove

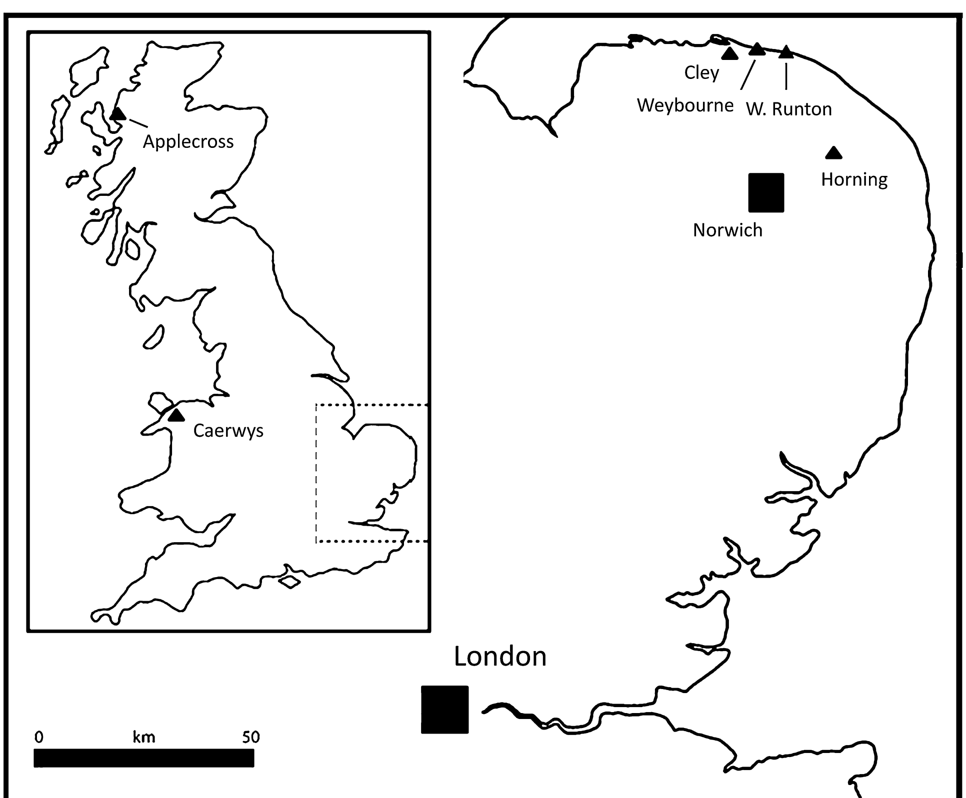

Fig. 1. Locality map of East Anglia, and inset of Great Britain, locating all of the British sample sites. Co-ordinates for each site are given in Section 2.

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