



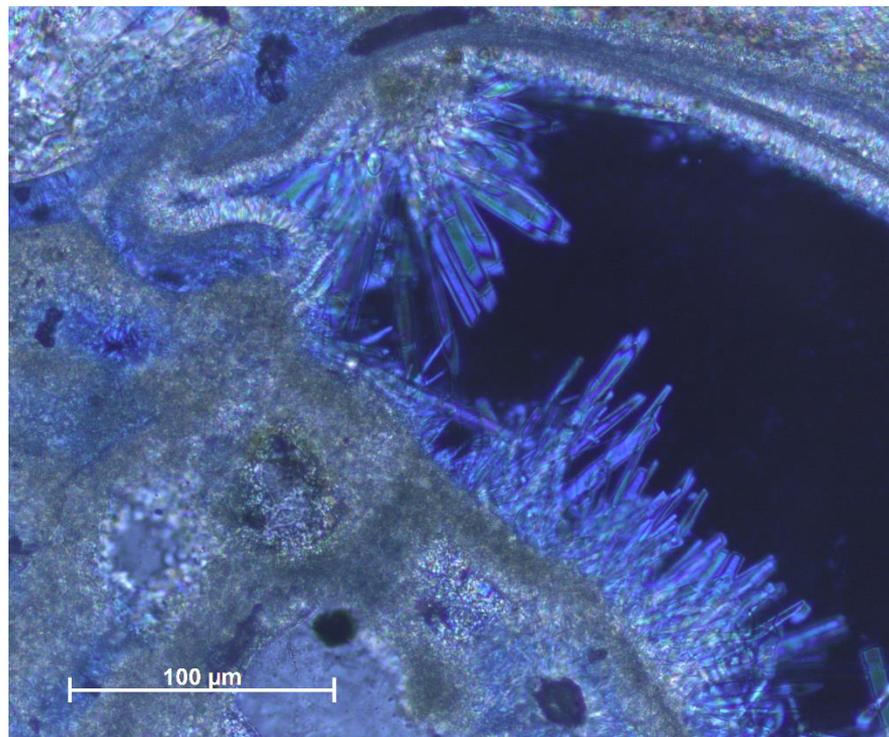
**British  
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# Analysis of methane-derived authigenic carbonates (MDAC) from the Croker Carbonate Slab, CEND 23/25 Survey. Stage 2 Radiometric dating

Land, Soil and Coast Programme

Commissioned Report CR/17/028





BRITISH GEOLOGICAL SURVEY

LAND, SOIL AND COAST PROGRAMME

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Optical photomicrograph of aragonite needles on micrite from sample GT066.

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# Foreword

This report is the published product of the second stage of a study by the British Geological Survey (BGS) commissioned by the Centre for Environment, Fisheries and Aquaculture Science (Cefas) on behalf of the Joint Nature Conservation Committee (JNCC), to date methane derived authigenic carbonate (MDAC) samples using radiometric dating methods. Cefas recovered a suite of 30 samples of carbonate-cemented sediment from within, and in the vicinity of, the Croker Carbonate Slabs (Candidate Special Area of Conservation / Site of Community Importance (cSAC/SCI)) of the mid Irish Sea as part of a multidisciplinary survey (Cefas/JNCC cruise CEND 23/15). Following completion of Stage 1 (Field et al., 2016), this report presents the radiometric dating analyses carried out on a selected sub-set of samples.

This work was carried out under Cefas purchase order 20038258: contract reference MPM023-15. The specific objectives of the BGS study were as follows:

The scope of the current work (Stage 2) is defined in the analysis specification provided by Chris Jenkins of Cefas to Antoni Milodowski of the British Geological Survey (Cefas / JNCC document “*Methane-Derived Authigenic Carbonate (MDAC) Sample Analysis Specification*” 13 January 2016). The completed Stage 1 of the analytical programme (Field et al., 2016) undertaken by the BGS included the following tasks defined in the Cefas / JNCC specification:

- Carbon ( $\delta^{13}\text{C}$ ) and Oxygen ( $\delta^{18}\text{O}$ ) stable isotopic compositions of cement material, calculated via a mass spectrometer, to establish the origin of the cement,
- Preparation of thin sections, imaging and analysis,
- Scanning Electron Microscope (SEM) to be conducted with Energy Dispersive Spectrometer (EDS) analysis to establish the proportions of minerals present in the sample,
- X-ray diffraction mineralogy profile of samples to confirm the nature of any carbonate cements.

These results established that the samples collected during the CEND 23/15 survey, are indeed MDAC.

The original specification (op. cit.) also requested that the following be considered after the programme of MDAC characterisation:

- Strontium isotope ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) analysis to establish the source of pore water fluids,
- Uranium-thorium dating of aragonite crusts,
- $^{14}\text{C}$  dating of enclosed shell material.

This was subsequently refined in discussion between JNCC, Cefas, Dr Alan Judd and BGS at a meeting held at JNCC in Peterborough on 22<sup>nd</sup> November 2016.

## $^{14}\text{C}$ dating

It was decided not to proceed further with  $^{14}\text{C}$  because the  $^{14}\text{C}$  reservoir in the MDAC system would be significantly diluted or entirely dominated by “dead” (i.e. geologically-old) carbon deriving from the methane, which is the predominant carbon source. This is a major issue with  $^{14}\text{C}$  dating of MDAC that has been recently discussed in the literature (Prouty et al., 2016).

## $^{87}\text{Sr}/^{86}\text{Sr}$ ratio analysis

Strontium isotope analysis will also have issues associated with strontium from mixed sources. Strontium isotope ratio ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) analyses can provide insights into the fluid source and flow

pathway for carbonate precipitation. However, the strontium isotope ratio in these MDAC deposits may potentially be derived from more than one source which may affect:

- The  $^{87}\text{Sr}/^{86}\text{Sr}$  of strontium in solution within the formation fluid discharging through the sea floor. This may further be modified by rock-water interaction processes along its geological flow-path;
- The  $^{87}\text{Sr}/^{86}\text{Sr}$  of strontium in solution in seawater, which will reflect the ambient  $^{87}\text{Sr}/^{86}\text{Sr}$  at a particular time.

The MDAC matrix contains intimately admixed assemblage of comminuted calcium carbonate bioclastic fragments (bivalve shells, foraminifera etc.), which may have a  $^{87}\text{Sr}/^{86}\text{Sr}$  reflecting the ambient marine  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, and authigenic magnesian calcite which may include  $^{87}\text{Sr}/^{86}\text{Sr}$  derived from formation fluid and seawater. As these are impossible to separate physically or chemically for the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio analysis, the analytical results will give a mixed  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio that is difficult to evaluate. Therefore, to minimise this, the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope analyses were limited to the analysis of material that could be separated as *relatively pure* authigenic carbonate – i.e. essentially aragonite from five MDAC samples that contain areas of pure aragonite that can be realistically sub-sampled as a pure phase. In addition three subsamples of late calcareous encrusting biota (e.g. serpulid and bryozoan encrustations) were analysed to provide a reference value for the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the marine Irish Sea seawater signature, against which the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the aragonite cements can be compared.

#### Uranium-thorium dating

Age dating analysis was carried out of a subset of nine MDAC samples, previously analysed by petrographic and stable isotope methods in Stage 1 (Field et al, 2016). The samples collected are ‘grab’ samples, and therefore have limited in-situ, contextual, and stratigraphical information, and therefore the analytical approach was designed to provide a broad indication of the age of the deposit.

## Acknowledgements

Mr John Fletcher (BGS, Thin Section Laboratory) is gratefully acknowledged for preparing the polished blocks from the MDAC samples.

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## Summary

This report describes the results from the second stage of a programme of work undertaken by the British Geological Survey (BGS), carried out on methane-derived authigenic carbonate (MDAC) samples that was commissioned by the Centre for Environment, Fisheries and Aquaculture Science (Cefas), on behalf of the Joint Nature Conservation Committee (JNCC). This work was carried out under Cefas purchase order 20038258: contract reference MPM023-15. The purpose of this Stage 2 study was to use radiometric techniques to: a) establish the source of pore water fluids, and b) to provide a broad indication of the age of the deposit. These analyses were carried out on a sub-set of the samples recovered by Cefas and JNCC from the seabed as part of a multidisciplinary survey (CEND 23/15) to Croker Carbonate Slabs cSAC/SCI between 24<sup>th</sup> October and 6<sup>th</sup> November 2015, and to ascertain whether the carbonate cements represent MDAC. These samples were collected from an area of active methane seeps, designated as a Candidate Special Area of Conservation (cSAC: UK0030381) and Site of Community Importance (SCI) following identification under the Annex I of the 1992 EC Habitats Directive; in particular, the Annex I habitat *Submarine structures made by leaking gases* (Whormersley et al., 2008). The Croker Carbonate Slabs are located in the mid-Irish Sea (centroid latitude N 53.4725°, longitude W 5.238055556°), approximately 30 km west of Anglesey, comprising a total area of 66 km<sup>2</sup>. The seabed surface lies in approximately 70 m water depth on top of the slabs in the north, descending to approximately 100 m below sea level at their base in the southwest corner (JNCC, 2012).

The specific tasks within this Stage 2 of the BGS analytical programme were as follows:

1. Strontium isotope ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) analysis of aragonite in five of the samples to establish the source of pore water fluids.
2. Strontium isotope ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) analysis of a subset of three samples of late calcareous encrusting biota (e.g. serpulid and bryozoan encrustations) to provide a reference value for the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the marine Irish Sea seawater signature, against which the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the aragonite cements can be compared.
3. Uranium-thorium age dating analysis of a subset of nine MDAC samples, previously analysed by petrographic and stable isotope methods in Stage 1 to provide a broad indication of the age of the deposit.

Strontium isotope ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) analysis indicates the aragonite and calcareous encrusting biota were precipitated in seawater comparable to present day seawater (Elderfield, 1986).

The U-Th analyses indicate that all micrite domains have undergone some form of open system behaviour, the most common of which would be the loss of soluble U through leaching, and therefore no accurate age information has been preserved in the Croker Slab micrites.

However, analytical data from aragonite subsamples from GT106 and GT141 were able to provide radiometric ages. The aragonite subsamples from GT106 resulted in three statistically equivalent dates of around 5 ka with the most precise date ( $4.8 \pm 0.2$  ka) obtained from the cleanest subsample, A. Two additional subsamples from sample GT141 (C and D) exhibited measured ( $^{230}\text{Th}/^{232}\text{Th}$ ) above the threshold value of 2, and therefore were also interpreted as single dates corrected using a theoretical detrital U-Th isotope composition, resulting in statistically equivalent ages of  $12.3 \pm 3.0$  ka and  $17.0 \pm 5.5$  ka. Initial modelled ( $^{234}\text{U}/^{238}\text{U}$ ) values for all five aragonite subsamples are between 1.147 and 1.161 which, given their respective uncertainties are consistent with a seawater U signature.

## 1 Introduction

The British Geological Survey (BGS) was contracted by the Centre for Environment, Fisheries and Aquaculture Science (Cefas), to undertake a mineralogical and petrological study of thirty samples of diagenetic, carbonate-cemented sediment samples. These were recovered by Cefas and JNCC from the seabed as part of a multidisciplinary survey (CEND 23/15) to Croker Carbonate Slabs cSAC/SCI (Figure 1) between 24<sup>th</sup> October and 6<sup>th</sup> November 2015. The mineralogical and petrological study (Stage 1) confirmed these carbonate-cemented samples to be Methane-Derived Authigenic Carbonate (MDAC).

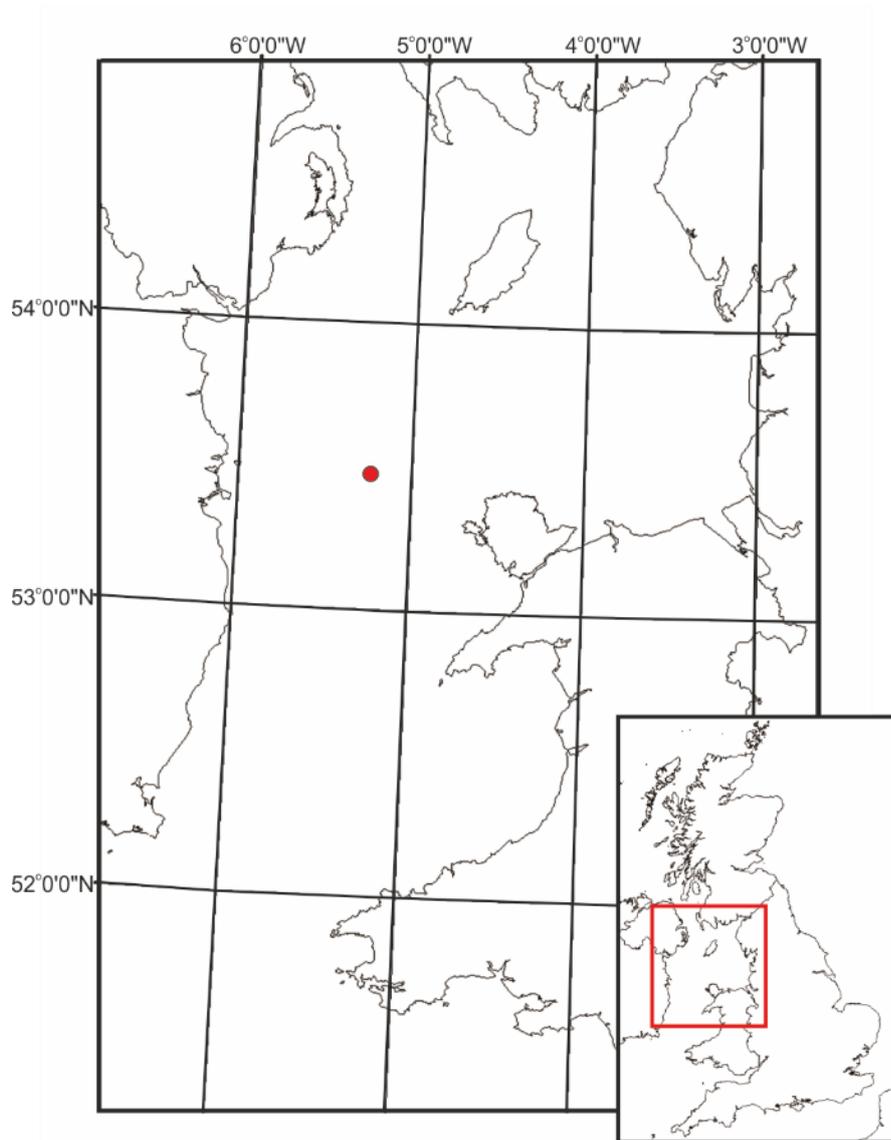
The specific objectives and tasks of this Stage 2 of the BGS study (under Cefas purchase order 20038258, contract reference MPM023-15) are detailed below:

Strontium isotope ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) Ratio Analysis was carried out on 5 samples of “pure” aragonite cement and 3 “reference” samples of late-stage encrustations by bryozoan and / or serpulid worms from the external surfaces of the MDAC samples (to provide a reference for the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the ambient seawater component).

U-Th age Dating Analysis of nine samples was carried out using the method described below (Analytical Method):

- Sample selection. Nine samples were selected with the best potential for age dating analysis, to provide a broad spread across the available samples. Five were identified as suitable aragonite-dominated samples, and five were identified as suitable micritic samples with one sample (GT106) being selected as suitable for both aragonite-dominated and micrite-dominated;
- From each sample, sub-sampled material was obtained by micro drilling;
- A single date uranium-thorium dating method using three single point analyses on clean carbonate to potentially provide a single date per analyses was carried out on sample GT106;
- A modal date uranium-thorium dating method, using two analyses per model date was carried out on the nine samples (see Table 1).

This report provides the results of the above radiometric dating of the selected MDAC samples.



**Figure 1. Location of the Croker Carbonate Slabs SCI/cSAC shown by the red dot (centrum N 53.4725°, W 5.238°). The red box in the insert map of the UK shows the approximate area of the enlargement. Map derived from Ordnance Survey data © Crown Copyright and database rights 2016. Ordnance Survey Licence No. 100021290.**

## 1.1 GENERAL

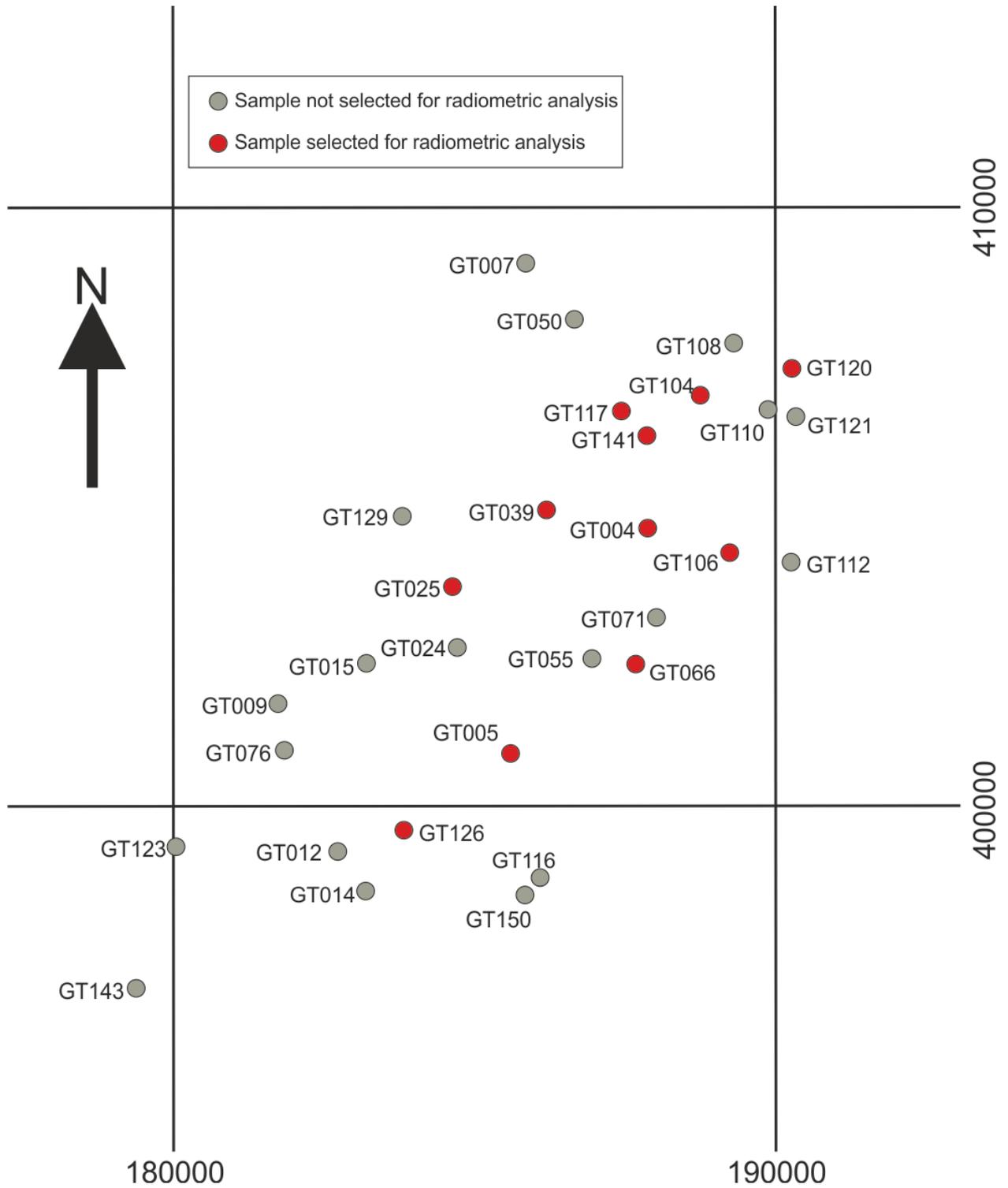
The Centre for Environment, Fisheries and Aquaculture Science (Cefas) and the Joint Nature Conservation Committee (JNCC) undertook a survey of the Mid Irish Sea area (Cruise CEND 23/15) to assess the geomorphology, and the distribution and range of seabed habitats. Interest was focussed on identifying and delineating habitats listed under Annex I of the 1992 EC Habitats Directive; in particular, the Annex I habitat *Submarine structures made by leaking gases* (Whormersley et al., 2008). These features are considered to be of important ecological significance and there is a requirement to adequately characterise these features in order to develop appropriate conservation management plans for such habitats in UK offshore waters. The structures consist of carbonate-cemented sediments that are believed to have a Methane-Derived Authigenic Carbonate (MDAC) origin.

## 1.2 SAMPLES

Thirty-two samples of potential MDAC material were provided to the BGS, recovered from the seabed using grab sampling. Thirty of these were characterised under Stage 1. Following on from Stage 1, a sub-set of the most suitable samples were selected for radiometric dating in Stage 2. The sample selection was based on: a) suitability for dating, and b) providing broad geographical representation. The selected samples are detailed in Table 1 and their locations are shown in Figure 2.

**Table 1. List of MDAC sub-samples selected by BGS for radiometric dating. The number of analyses for U-Th are shown in brackets.**

Station no	Sample no	<sup>87</sup> Sr/ <sup>86</sup> Sr late-stage encrustations	<sup>87</sup> Sr/ <sup>86</sup> Sr Aragonite	U-Th Aragonite	U-Th High magnesian calcite micrite
160A2	GT004				X (4)
169A2	GT005				X (4)
173A2	GT025	X (surface shell fragments)			
156A3	GT039	X (surface shell fragments)			X (4)
166A3	GT066		x	X (4)	
153A2	GT104		x	X (4)	
162A5	GT106		x	X (3: single date method)	X (4)
	GT117	X (surface serpulid castings)			
150A1	GT120		x	X (4)	
186A1	GT126				X (4)
154A2	GT141		x	X (6)	



**Figure 2. Distribution of those samples selected for radiometric analysis from the Croker Carbonate Slabs area.**

### 1.3 GEOLOGICAL BACKGROUND

The location of the study area (Figure 1) is similar to that described by Milodowski et al., (2009) in an earlier study of MDAC from the Croker Carbonate Slabs area of the Irish Sea. The geological background of the study area is summarised by Whormersley et al. (2008). The study area is underlain by inclined strata of Carboniferous (Dinantian and Westphalian) age. These bedrocks have been weathered and form an irregular unconformity surface that is between 20 to 60 m below the seabed. Carboniferous strata are overlain by the shallow-dipping or sub horizontal sediments of the Quaternary Prograded Facies of the Western Irish Sea Formation, formed during deglaciation of the Irish Sea after the last glacial maximum. The Quaternary sediments are themselves cut by several trenches and scarps that are presumed by Whormersley et al. (2008) to be related to ongoing erosion at the sea floor by tidal currents, possibly augmented by gas escape at the seabed.

A thin veneer of gravely sand containing shell fragments covers much of the study area. This is the active layer being mobilised at the seabed in the current hydrological regime. Larger sediment wave forms are present in the area, with crests running east-west for up to 1 km, but these may not be active. MDAC has previously been identified beneath the active layer, and may be exposed and undercut by seabed erosion (Milodowski et al., 2009).

## 2 Analytical methods

### 2.1 STRONTIUM ISOTOPE ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) RATIO ANALYSIS

Strontium isotope ratio ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) analyses can provide insights into the fluid source and flow pathway for carbonate precipitation. However, the strontium isotope ratio in these MDAC deposits may potentially be derived from more than one source:

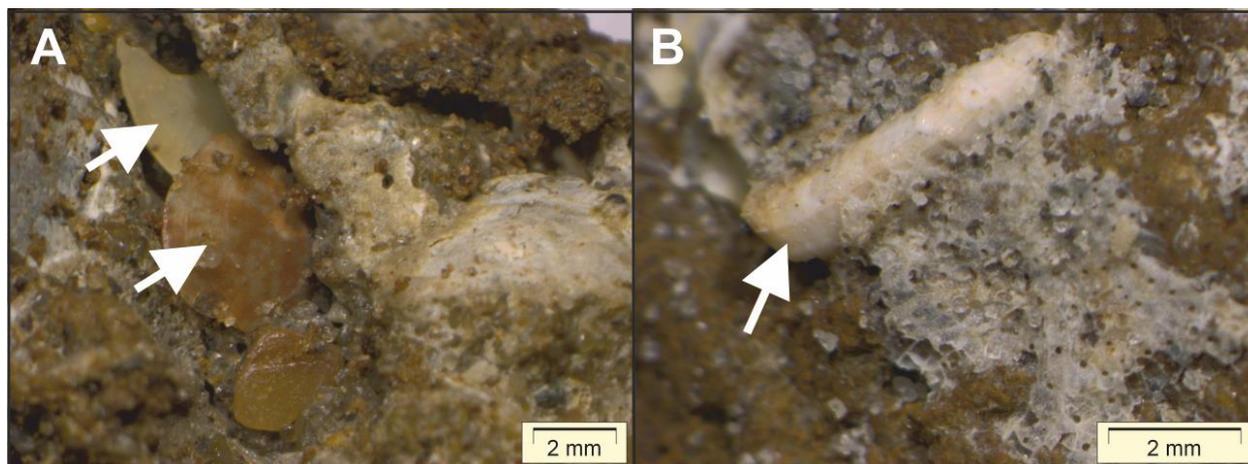
- The  $^{87}\text{Sr}/^{86}\text{Sr}$  of strontium in solution within the formation fluid discharging through the sea floor. This may further be modified by rock-water interaction processes along its geological flow-path;
- The  $^{87}\text{Sr}/^{86}\text{Sr}$  of strontium in solution in seawater, which will reflect the ambient  $^{87}\text{Sr}/^{86}\text{Sr}$  at a particular time.
- $^{87}\text{Sr}/^{86}\text{Sr}$  of strontium liberated to sediment porewaters as a result of diagenetic dissolution of unstable detrital minerals in the sediments on the sea bed.

The MDAC matrix contains intimately admixed assemblages of comminuted calcium carbonate bioclastic fragments (bivalve shells, foraminifera etc.), which may have a  $^{87}\text{Sr}/^{86}\text{Sr}$  reflecting the ambient marine  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, and authigenic magnesian calcite which may include  $^{87}\text{Sr}/^{86}\text{Sr}$  derived from formation fluid and seawater. As these are impossible to separate physically or chemically for the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio analysis, the analytical results would give a mixed  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio that would be difficult to evaluate. Therefore, the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope analysis was limited to material which could be separated as *relatively pure* authigenic carbonate – i.e. essentially aragonite from the small number of MDAC samples that contain areas of relatively coarse, discrete aragonite that could be realistically sub-sampled as a pure phase. In addition, subsamples of late calcareous encrusting biota (e.g. serpulid and bryozoan encrustations) were analysed to provide a reference value for the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the ambient marine Irish Sea seawater signature, against which the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the aragonite cements can be compared.

A total of eight samples of 1-10 mg of pure aragonite and reference late calcareous biota encrustations were carefully hand-picked or micro-drilled from either the polished blocks prepared for Stage 1, or direct from the “raw” hand-specimen samples (as appropriate).

These include three samples of late stage (i.e. post-sediment lithification) encrustations by serpulid worms, or shelly fragments on the surface of the samples (detailed in Table 1). The samples were

taken from GT025, GT039 and GT117 by carefully breaking off pieces of the mollusc shells or encrustations using tweezers and ensuring the fragments were free of any host carbonate sediment material. Examples of two of the three samples before sampling are shown in Plate 1.



**Plate 1. Optical micrographs showing late state shelly material and encrustations used as reference samples of the ambient seawater component. A) small bivalve mollusc shells (arrowed) on the surface of sample GT039, and B) a serpulid worm casting (arrowed, and bryozoan encrustation, not sampled) on the surface of GT117.**

The remaining five samples of relatively pure aragonite cement were micro drilled from the polished blocks of GT066, GT104, GT106, GT120 and GT141.

The recovered material was carefully rinsed in milliQ H<sub>2</sub>O to remove any surface contamination, and subsequently leached in dilute (10% acetic acid) at c. 60°C in order to dissolve carbonate material.

The leachates were evaporated to dryness and then converted to nitrate using 200 µm of 16M HNO<sub>3</sub>.

Strontium was separated using Sr-SPEC ion exchange resin, then loaded onto outgassed single Re-filaments and analysed in a Thermo Scientific Triton thermal ionisation mass spectrometer. The mass spectrometer was operated in multidynamic mode, and 100 measurement cycles were completed for each sample.

## 2.2 URANIUM-THORIUM AGE DATING ANALYSIS

### 2.2.1 General principles

The U-Th age dating method is based on the co-precipitation of uranium (present in solution in seawater or formation fluid) with calcium in the authigenic calcium carbonate. Ideally, a pure carbonate sample will not contain any <sup>230</sup>Th at the time when it precipitates, because Th is highly insoluble and not present in the mineralising porewater, and therefore the accumulation of <sup>230</sup>Th over time through the radioactive decay of uranium (from <sup>238</sup>U to <sup>234</sup>U to <sup>230</sup>Th) in the authigenic calcium carbonate will provide a measure of the age of the sample. In order for the method to provide reliable age data it is imperative that the sample behaves as a closed system with respect to U and Th, that is to say that, except for the in situ radioactive decay of U to Th, no additional U or Th is added to or removed from the sample after precipitation.

The assumption of zero initial <sup>230</sup>Th at the time of precipitation is seldom valid for MDAC that precipitate below the sediment-water interface. Consequently, in order to obtain an accurate date, it is necessary to quantify and account for any amount of initial <sup>230</sup>Th present in the sample (i.e. <sup>230</sup>Th that did not result from the in-situ decay of U). This initial <sup>230</sup>Th is typically carried by detrital particles

(mostly silicates) incorporated into the fine-grained carbonate matrix. Because these detrital particles originate from the weathering of older rocks exposed on nearby land masses they can typically be assumed to have reached secular equilibrium (see Text Box 1) with respect to the  $^{238}\text{U}$  decay chain, and consequently their U-Th composition can be approximated using calculated values for average continental crust (e.g. Wedepohl, 1995). Carbonates precipitating in large bodies of water carry one additional complication: over time, the  $^{234}\text{U}$  dissolved in the water column decays to  $^{230}\text{Th}$  (i.e. the same decay process that occurs within the carbonates themselves). Because Th is highly insoluble, this water-borne  $^{230}\text{Th}$ , often referred to in the literature as hydrogenous Th, will be adsorbed onto the outer surface of particles dispersed or suspended floating in the water column (e.g. clay minerals). Consequently, detrital material incorporated in marine carbonates, such as MDAC, contains excess hydrogenous Th relative to the composition of the average continental crust, with the proportion of hydrogenous Th increasing with water depth (i.e. the longer a particle takes to sink from the sea surface to the sea floor, the more hydrogenous  $^{230}\text{Th}$  it will adsorb). However, given the shallow water depth in the Croker Carbonate Slab area, the impact of hydrogenous  $^{230}\text{Th}$  is likely to be relatively small. Therefore, the theoretical detrital U-Th composition based on average continental crust values (i.e.  $(^{232}\text{Th}/^{238}\text{U}) = 1.2 \pm 50\%$ ), and secular equilibrium with respect to the  $^{238}\text{U}$  decay chain (i.e.  $(^{230}\text{Th}/^{238}\text{U}) = 1 \pm 50\%$  and  $(^{234}\text{U}/^{238}\text{U}) = 1 \pm 50\%$ ), is likely to be adequate to correct data from individual analyses. The large uncertainties associated with theoretical detritus isotope compositions are necessary to account for natural variations in sediment composition. These uncertainties are propagated into the final age uncertainty, and their impact increases with the amount of detrital material incorporated in the carbonate sample. Consequently, theoretical detrital compositions are only suitable for correcting data from relatively pure carbonate samples, as their application to samples with a high proportion of detrital material would result in calculated age uncertainties in the region of  $\pm 100\%$ , rendering the results essentially useless.

Two approaches have been taken: a single analysis methodology, and a two-point, modal age methodology, which are detailed below.

**Text box 1****Activity ratios and secular equilibrium**

In U-Th dating, the U and Th composition of a sample is usually expressed in terms of activity ratios, denoted by round brackets. The activity ratio of a pair of isotopes is the ratio of their respective abundances in the sample, multiplied by the ratio of their respective decay constants. For example:

$$\left(\frac{{}^{230}\text{Th}}{{}^{234}\text{U}}\right) = \frac{{}^{230}\text{Th}}{{}^{234}\text{U}} * \frac{\lambda_{230}}{\lambda_{234}}$$

Where  ${}^{230}\text{Th}$  and  ${}^{234}\text{U}$  are the amounts of isotopes present in the sample and the  $\lambda$  values are the respective decay constants.

The concept of secular equilibrium applies to isotope pairs from the same decay chain, specifically when a long-lived isotope, such as  ${}^{238}\text{U}$  (half-life of  $4.5 \times 10^9$  years) decays to a comparatively short-lived isotope, such as  ${}^{230}\text{Th}$  (half-life of  $7.5 \times 10^4$  years) which is itself radioactive. Assuming no  ${}^{230}\text{Th}$  is present initially, the amount of  ${}^{230}\text{Th}$  in the sample increases gradually over time until a point is reached where the rate of production of  ${}^{230}\text{Th}$  (through the decay of  ${}^{238}\text{U}$  via  ${}^{234}\text{U}$ ) is equal to the rate at which  ${}^{230}\text{Th}$  decays in turn. This is referred to as secular equilibrium at which point the relevant activity ratios are equal to 1, and remain constant over time:

$$\left(\frac{{}^{230}\text{Th}}{{}^{238}\text{U}}\right) = 1 \text{ and } \left(\frac{{}^{234}\text{U}}{{}^{238}\text{U}}\right) = 1$$

U-Th dating measures the age of a sample by determining how far its isotope composition has evolved from an initial state with zero in situ produced  ${}^{230}\text{Th}$  towards secular equilibrium. After ca. 600000 years, the activity ratios of the sample become indistinguishable from the secular equilibrium value of 1 at the level of precision afforded by state-of-the-art mass spectrometers – this marks the upper age limit of the U-Th method.

The distinction between pure and detritus-rich carbonates is usually made based on the samples ( ${}^{230}\text{Th}/{}^{232}\text{Th}$ ) activity ratio – in this case  ${}^{232}\text{Th}$  is used as a proxy for the amount of silicate detritus because it is absent from pure carbonate due to the insolubility of Th, and being a long-lived radioactive isotope (half-life of ca.  $14 \times 10^9$  years) it can be regarded as essentially stable over the age range datable by the U-Th method. In our experience, the above approach of correcting data from a single analysis methodology using a theoretical detrital composition is suitable for samples with ( ${}^{230}\text{Th}/{}^{232}\text{Th}$ )>2 (e.g. Prouty et al., 2016, Crémère et al., 2016a, 2016b).

For samples with ( ${}^{230}\text{Th}/{}^{232}\text{Th}$ )<2 it becomes necessary to use statistical methods that rely on the analyses of multiple, closely spaced subsamples to determine the age of a carbonate domain. In this case, a line fitted through data from at least two analyses is used to account for the mixing of detrital and authigenic components and produce a “model age” and associated parameters related to the initial state of the system, namely the initial ( ${}^{234}\text{U}/{}^{238}\text{U}$ ) of the fluid from which the carbonate precipitated, and the initial ( ${}^{230}\text{Th}/{}^{232}\text{Th}$ ) of the detritus incorporated in the sample, thereby circumventing the need to make assumptions about the isotope composition of the detrital silicate fractions. However, in order for this approach to work, the subsamples underpinning each age must meet certain criteria:

- The carbonate in all subsamples must be of the same age – this may be difficult to achieve in samples where a clear growth direction cannot be established, because ideally subsamples should be distributed perpendicular to the growth direction rather than parallel to it.
- The detrital material incorporated in each subsample must have the same U-Th composition.
- The carbonate / detritus ratio must vary across different subsamples – this variation is necessary in order to generate enough spread in the results to allow a line to be fitted with reasonable confidence.
- As in the single analyses approach above, all subsamples must behave as closed systems for U and Th.

If any of the above criteria are not met, an accurate age cannot be calculated. This will be evident from the fact that the modelling returns implausible values for the age and/or initial parameters of the

samples. This includes negative values for any of the parameters, or initial values that conflict with our knowledge of the samples. For example, MDACs are expected to crystallise from seawater, or

pore-waters enriched in  $^{234}\text{U}$  relative to seawater, and therefore their modelled initial ( $^{234}\text{U}/^{238}\text{U}$ ) is expected to fall at or above the mean seawater value of 1.1466 (Robinson et al., 2004). A modelled initial ( $^{234}\text{U}/^{238}\text{U}$ ) that falls significantly below the seawater value would indicate that the model age may not be accurate. Because MDACs are complicated materials when it comes to U-Th dating, a reasonable expectation would be that around 50% of attempts to calculate a model age will fail. Consequently, we typically opt for a conservative approach wherein each model age is underpinned by two analyses (because increasing the number of subsamples would not increase the likelihood of success) and rely on reproducibility of data from each sample or group of sample as an additional test of accuracy.

### 2.2.2 Sample processing

A total of 41 subsamples weighing between 0.63 and 3.64 mg were micro-drilled from polished blocks previously prepared for Stage 1. Initial plans for Stage 2 called for 15 analyses of pure aragonite, to be corrected using a theoretical detritus isotope composition, which would have resulted in 15 U-Th dates. However, closer inspection of the samples revealed that although aragonite is present in five of the MDAC slabs provided, in most cases it is intermixed with silicate detritus to an extent where obtaining pure carbonate samples is not feasible. Therefore we elected to collect only three subsamples from sample GT106, which contained the cleanest aragonite domains in this sample set, to be interpreted as single analyses. The remaining 38 subsamples are distributed as closely spaced pairs across aragonite domains from samples GT066 (n=4), GT104 (n=4), GT120 (n=4), GT141 (n=6) and micrite domains from samples GT004 (n=4), GT005 (n=4), GT039 (n=4), GT106 (n=4) and GT126 (n=4).

Analytical protocols for the separation and purification of U and Th from MDAC samples were aimed at ensuring the complete dissolution of the detrital material incorporated in the samples and the oxidation of organic material liable to produce isobaric interferences during measurements of Th isotope ratios (Shen et al., 2002). All evaporation steps took place in a closed EvapoClean device, to minimize cross-contamination and reduce fall-in blanks. Samples were dissolved in  $\sim 8\text{ M HNO}_3$ , spiked with a mixed  $^{229}\text{Th}$ - $^{236}\text{U}$  isotopic tracer, left to equilibrate overnight and dried down. Samples were re-dissolved in a mixture of  $\text{HClO}_4:\text{HF}:\text{HNO}_3$  (1:2:2.5), using  $\sim 50\ \mu\text{l}$  HF per estimated mg of detrital material, dried down, re-dissolved in  $8\text{ M HCl}$  and dried down again, to ensure the conversion of residual fluorides to chlorides. Pre-concentration of U and Th through Fe co-precipitation and initial separation on  $0.6\text{ ml}$  columns using  $\text{AG-1} \times 8$  anion exchange resin were done following the procedure of Edwards et al. (1987). Th fractions were further purified using a second pass through  $\text{AG-1} \times 8$  resin and were filtered using  $0.22\text{-}\mu\text{m}$  pore-size syringe filters to remove resin particles. Both U and Th fractions were oxidized twice in  $2\text{ ml}$   $16\text{ M HNO}_3$  and  $0.2\text{ ml}$   $30\% \text{ H}_2\text{O}_2$ , and dissolved in  $0.5\text{ ml}$   $0.1\text{ M HCl}$  and  $0.035\text{ M HF}$ . Before mass spectrometry analyses, all samples were filtered to remove particles originating from the beakers used for sample preparation.

Isotope ratio measurements were made on a Thermo Neptune Plus multi-collector ICP-MS, using sample-standard bracketing protocols outlined in Cr mi re et al. (2016). U-Th age calculations were performed using in-house Microsoft Excel spreadsheets using the  $^{230}\text{Th}$  and  $^{234}\text{U}$  decay constants of Cheng et al. (2013).

## 3 Results

### 3.1 STRONTIUM ISOTOPE ANALYSES

The results of the strontium isotope ratio ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) analyses are provided in Appendix 1.

Eleven analyses of the NBS987 Sr standard across the time of analysis gave a value for  $^{87}\text{Sr}/^{86}\text{Sr}$  of  $0.710253 \pm 0.000006$  (8.2 ppm, 1-sigma). Data are normalised to a value of 0.710250 for this standard. Five seawater standards analysed with the samples gave  $^{87}\text{Sr}/^{86}\text{Sr} = 0.709179 \pm 0.000004$

(normalised to NBS987 = 0.7102500; 5.8 ppm, 1-sigma). This is identical to the value of  $0.709179 \pm 0.000002$  obtained for seawater by Mokadem et al. (2015).

The analysed aragonite samples give values for  $^{87}\text{Sr}/^{86}\text{Sr}$  ranging from 0.709192 – 0.709221 (average  $0.709202 \pm 0.000012$ ). The surface encrustations give values of 0.709182 – 0.710198, averaging  $0.709192 \pm 0.000007$ . These results indicate that the samples precipitated from sediment porewaters of similar composition to present day seawater, with very limited addition of Sr from a more radiogenic (i.e. higher  $^{87}\text{Sr}/^{86}\text{Sr}$ ) source. Sample GT120 has the highest value ( $0.709221 \pm 0.000005$ ).

### 3.2 U-Th ANALYSES

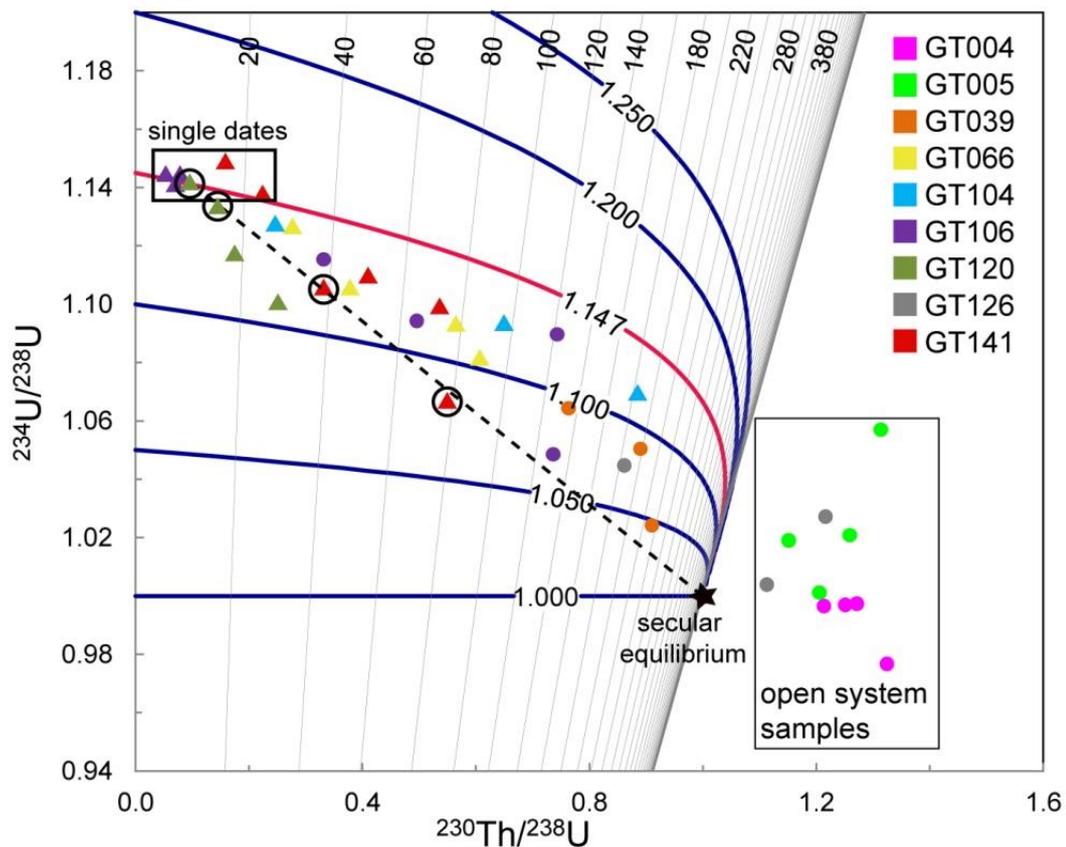
The results of U-Th analyses of MDAC samples from the Croker Carbonate Slab area are summarised in Appendix 2 and plotted in Figure 3.

The three aragonite subsamples (A, B and C) from sample GT106 contained 3.9 – 4.4 ppm of U, and their ( $^{230}\text{Th}/^{232}\text{Th}$ ) values were between 2.8 and 12.3, confirming that they are suitable for interpretation as single analyses corrected using a theoretical detrital isotope U-Th composition. This approach resulted in three statistically equivalent dates of around 5 ka with the most precise date ( $4.8 \pm 0.2$  ka) obtained from the cleanest subsample, A. Two additional subsamples from sample GT141 (C and D) which were drilled for the purpose of obtaining a model age, exhibited measured ( $^{230}\text{Th}/^{232}\text{Th}$ ) above the threshold value of 2, and therefore were also interpreted as single dates corrected using a theoretical detrital U-Th isotope composition, resulting in statistically equivalent ages of  $12.3 \pm 3.0$  ka and  $17.0 \pm 5.5$  ka. Initial modelled ( $^{234}\text{U}/^{238}\text{U}$ ) values for all five aragonite subsamples are between 1.147 and 1.161 which, given their respective uncertainties are consistent with a seawater U signature.

A further 16 subsamples were allocated to obtaining two-point model ages from aragonite domains in samples GT066, GT104, GT120 and GT141 (four subsamples from each) with the intention of producing eight U-Th dates. Of these, only two pairs of subsamples yielded usable age information: subsamples A and B from sample GT120 ( $4.1 \pm 0.2$  ka), which is statistically equivalent to single dates derived from the aragonite domains of sample GT106 (see above) and subsamples E and F from sample GT141 which gave an age of  $16.1 \pm 0.7$  ka, statistically equivalent to the single date derived from subsample D ( $17.0 \pm 5.5$  ka) of the same sample. All other aragonite subsamples, and all subsamples drilled from micrite domains of samples GT004, GT005, GT039, GT106 and GT126 failed to provide usable age information. The evolution diagram in Figure 3 provides some explanation for this failure:

- All micrite subsamples from samples GT004 and GT005, as well as two out of three subsamples from GT126 plot on the right side of the diagram, in a space that lies outside any possible evolution pathways for the U-Th composition of a carbonate sample (see figure caption for explanation). This indicates that the respective micrite domains have undergone some form of open system behaviour, the most common of which would be the loss of soluble U through leaching, and therefore no accurate age information is preserved by these samples.
- The subsamples used for single age determinations plot at or above the evolution curve for carbonate precipitating from seawater, and the four subsamples used for two-point model ages (circled in black) plot on or close to a theoretical mixing line between a ca. 10 ka old carbonate sample and detrital material in secular equilibrium (dashed line in Figure 3). All other subsamples that failed to provide reliable age information plot between the seawater evolution curve and the mixing line (except for two subsamples from sample GT120 which plot below the mixing line. This is consistent with most subsamples recording some degree of open system behaviour as preferential loss of U over insoluble Th would shift the isotope composition of the samples towards the right (i.e. higher ( $^{230}\text{Th}/^{238}\text{U}$ ) values) and preferential loss of more mobile  $^{234}\text{U}$  over  $^{238}\text{U}$  would shift compositions downward (i.e. towards lower ( $^{234}\text{U}/^{238}\text{U}$ ) values). In other words, we estimate that the majority of the aragonite samples and all the micrite samples analysed from the Croker Carbonate Slab record a level of open system

behaviour. This was sufficient to disturb their U-Th systematics and preclude age interpretation, but not necessarily enough to shift them all the way to the right side of the diagram where open system behaviour would be obvious.



**Figure 3. U-Th evolution diagram. Triangles/circles mark subsamples drilled from aragonite/micrite domains. Blue and red curves represent theoretical evolution pathways for the U-Th isotope composition of a pure carbonate sample as a function of the samples initial ( $^{234}\text{U}/^{238}\text{U}$ ) which corresponds to the labels on the curves. Note that all curves converge towards a point where  $(^{230}\text{Th}/^{238}\text{U})=(^{234}\text{U}/^{238}\text{U})=1$ , marked by the black star, which corresponds to secular equilibrium, and also marks the theoretical composition of detrital material included in the MDAC. The red curve labelled 1.147 marks the theoretical evolution of a carbonate sample that precipitated from seawater. Results from clean MDAC are expected to plot in close proximity to, or slightly above this curve. The grey lines mark how far the composition of a sample has evolved starting from the time of precipitation, when  $(^{230}\text{Th}/^{238}\text{U})=0$ . For example, a zero age sample precipitating from seawater would plot at the intercept of the red evolution curve on the y axis (where  $(^{230}\text{Th}/^{238}\text{U})=0$ ). Over time, the composition of the sample would evolve from right to left along the red curve, and reach its intersection with the line labelled 20 after 20 kyr, and the intersection with the line labelled 40 after 40 kyr. The black dashed line represents a theoretical mixing line between a ca. 10 ka old carbonate precipitating from seawater, and detrital material in secular equilibrium. Subsamples circled in black have been used to calculate two-point model ages.**

## 4 Summary and conclusions

The strontium analyses and the U-Th model ages obtained both point to modern-day formation of the MDAC. The strontium isotope values obtained range from 0.709182 to 0.709221. This is

consistent with MDAC precipitation from porewaters where Sr is dominantly sourced from present day seawater ( $0.709179 \pm 0.000002$ ; Mokadem et al. 2015), with a minor component from a more radiogenic source. Although, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of seawater has varied little over the past 40 ka (Mokadem et al., 2015).

The U-Th radiometric ages obtained from the authigenic aragonite analyses, which represent the latest cement in the MDAC (Field et al., 2016) indicate relatively recent ages of formation ( $<17 \pm 5.5$  ka). The youngest age obtained was from sample GT120 of  $4.1 \pm 0.2$  ka. These age data are consistent with the strontium data, indicating a relatively young formation (i.e. since the last glacial maximum,  $\sim 24$  ka), consistent with precipitation from porewaters similar to present day seawater compositions.

## Appendix 1

**Table 2. Strontium isotope ratio ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) analyses.  $^{87}\text{Sr}/^{86}\text{Sr}$  \* represents the measured value normalised to a value of 0.710250 for NBS987.**

SAMPLE	Type	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$ *	$\pm$ 2SE	$^{88}\text{Sr}/^{86}\text{Sr}$	$\pm$ 2SE	$^{84}\text{Sr}/^{86}\text{Sr}$	$\pm$ 2SE	$^{85}\text{Rb}/^{86}\text{Sr}$	$\pm$ 2SE
GT141	Aragonite	0.709207	0.709204	0.000006	8.317277	0.001483	0.056938	0.000014	0.000006	0.000003
GT104	Aragonite	0.709195	0.709192	0.000005	8.309575	0.000561	0.056976	0.000005	0.000004	0.000003
GT066	Aragonite	0.709202	0.709199	0.000008	8.462130	0.002495	0.055940	0.000018	0.000003	0.000004
GT106	Aragonite	0.709195	0.709192	0.000007	8.497520	0.002277	0.055686	0.000017	-0.000002	0.000003
GT120	Aragonite	0.709224	0.709221	0.000005	8.452711	0.005265	0.055988	0.000038	0.000002	0.000003
	Mean		0.709202							
	$\pm$ 1 sigma		0.000012							
GT025-1	Shell fragments	0.709201	0.709198	0.000006	8.478346	0.004091	0.055822	0.000029	0.000004	0.000002
GT025-2	Shell fragments	0.709185	0.709182	0.000007	8.476044	0.020084	0.055836	0.000135	0.000003	0.000003
GT039	Shell fragments	0.709195	0.709192	0.000007	8.501166	0.001984	0.055670	0.000013	0.000006	0.000004
GT117	Serpulid castings	0.709197	0.709194	0.000005	8.400428	0.000635	0.056352	0.000005	0.000000	0.000002
	Mean		0.709192							
	$\pm$ 1 sigma		0.000007							
Seawater Standard		0.709180	0.709177	0.000005	8.305544	0.000280	0.057012	0.000003	0.000003	0.000003
Seawater Standard		0.709184	0.709181	0.000005	8.316390	0.000312	0.056947	0.000004	0.000008	0.000003
Seawater Standard		0.709182	0.709179	0.000004	8.303791	0.000705	0.057036	0.000007	0.000010	0.000002
Seawater Standard		0.709176	0.709173	0.000007	8.346156	0.001335	0.056730	0.000012	0.000013	0.000004
Seawater Standard		0.709187	0.709184	0.000004	8.396021	0.000554	0.056390	0.000005	0.000523	0.000015
	Mean		0.709179							
	$\pm$ 1 sigma		0.000004							
	ppm		5.8							

SAMPLE	Type	87Sr/86Sr	87Sr/86Sr *	± 2SE	88Sr/86Sr	± 2SE	84Sr/86Sr	± 2SE	85Rb/86Sr	± 2SE
NBS987		0.710248		0.000005	8.371875	0.002223	0.056544	0.000014	0.000010	0.000003
NBS987		0.710248		0.000006	8.356134	0.005167	0.056664	0.000034	0.000004	0.000003
NBS987		0.710262		0.000007	8.383975	0.001022	0.056461	0.000008	0.000009	0.000004
NBS987		0.710247		0.000006	8.351181	0.004461	0.056661	0.000025	0.000016	0.000004
NBS987		0.710250		0.000006	8.326794	0.002432	0.056861	0.000017	0.000012	0.000004
NBS987		0.710247		0.000006	8.350963	0.003006	0.056693	0.000020	0.000018	0.000006
NBS987		0.710247		0.000007	8.345943	0.003916	0.056723	0.000027	0.000089	0.000006
NBS987		0.710258		0.000006	8.366094	0.002018	0.056589	0.000013	0.000009	0.000004
NBS987		0.710256		0.000006	8.358011	0.002587	0.056632	0.000016	0.000004	0.000004
NBS987		0.710259		0.000005	8.382972	0.000762	0.056468	0.000007	0.000008	0.000003
NBS987		0.710258		0.000005	8.334437	0.004308	0.056804	0.000030	0.000007	0.000003
	Mean	0.710253								
	± 1 sigma	0.000006								
	ppm	8.2								

**Table 3.** Results of U-Th dating of MDAC from the Croker Carbonate Slab area. Italicized values in brackets indicate uncertainties quoted at the 95% confidence level, which are specified as percentage values for columns under the ‘Measured activity ratios’ heading, and as absolute values for columns under the ‘Age interpretation’ heading. The suffix ‘i’ indicates initial values obtained from single-point age calculations, and two-point age modelling. Note that all ( $^{234}\text{U}/^{238}\text{U}$ )<sub>i</sub> ratios are consistent with sample precipitation from seawater.

Sample ID	Weight (mg)	U (ppm)	Th (ppm)	Measured activity ratios				Age interpretation			Notes
				$(^{230}\text{Th})$ $(^{232}\text{Th})$	$(^{232}\text{Th})$ $(^{238}\text{U})$	$(^{230}\text{Th})$ $(^{238}\text{U})$	$(^{234}\text{U})$ $(^{238}\text{U})$	Age (ka)	$(^{234}\text{U})$ $(^{238}\text{U})$ <sub>i</sub>	$(^{230}\text{Th})$ $(^{232}\text{Th})$ <sub>i</sub>	
GT004 A	1.14	0.57	2.05	1.1	1.17187 (0.25)	1.2714 (0.53)	0.9973 (0.60)	-	-	-	Fractions A and B – open system behaviour, no age information
GT004 B	1.43	0.34	1.18	1.2	1.13044 (0.15)	1.3245 (0.62)	0.9768 (0.40)	-	-	-	
GT004 C	1.74	0.30	0.87	1.3	0.96265 (0.21)	1.2135 (0.68)	0.9966 (0.45)	-	-	-	Fractions C and D – open system behaviour, no age information
GT004 D	2.03	0.70	4.28	0.6	2.00058 (0.07)	1.2508 (0.40)	0.9970 (0.22)	-	-	-	
GT005 A	1.45	0.36	1.58	0.9	1.45587 (0.51)	1.3135 (0.73)	1.0570 (0.74)	-	-	-	Fractions A and B – open system behaviour, no age information
GT005 B	2.32	0.42	1.77	0.9	1.38295 (0.24)	1.2054 (0.50)	1.0012 (0.45)	-	-	-	
GT005 C	3.52	0.36	0.83	0.15	0.75333 (0.16)	1.1514 (0.43)	1.0190 (0.37)	-	-	-	Fractions C and D – open system behaviour, no age information
GT005 D	3.64	0.21	0.81	1.0	1.22404 (0.16)	1.2591 (0.48)	1.0208 (0.38)	-	-	-	
GT039 A	1.65	0.50	1.23	1.1	0.81187 (0.14)	0.8898 (0.53)	1.0504 (0.34)	-	-	-	Fractions A and B – possible open system behaviour, no age information
GT039 B	2.20	0.64	1.20	1.5	0.61206 (0.08)	0.9101 (0.45)	1.0242 (0.23)	-	-	-	
GT039 C	2.36	0.55	0.94	1.4	0.55379 (0.09)	0.7632 (0.47)	1.0644 (0.27)	-	-	-	Fraction D – open system behaviour, no age information
GT039 D	1.61	0.93	0.96	2.7	0.34013 (0.08)	0.9076 (0.44)	0.9379 (0.25)	-	-	-	
GT066 A	1.08	1.50	0.93	1.9	0.20369 (0.09)	0.3781 (0.91)	1.1051 (0.22)	-	-	-	Fractions A and B – possible open system behaviour, no age information
GT066 B	1.94	2.93	4.51	0.5	0.50487 (0.06)	0.2766 (0.45)	1.1264 (0.15)	-	-	-	
GT066 C	1.25	2.18	1.95	1.9	0.29459 (0.12)	0.5646 (0.46)	1.0930 (0.29)	-	-	-	Fractions C and D – possible open system behaviour, no age information
GT066 D	1.90	2.49	5.21	0.9	0.68815 (0.07)	0.6066 (0.37)	1.0814 (0.18)	-	-	-	
GT104 A	0.95	1.36	0.60	1.7	0.14409 (0.13)	0.2458 (1.14)	1.1273 (0.29)	-	-	-	Fractions A and B – possible open system behaviour, no age information
GT104 B	0.97	1.51	2.16	1.4	0.46881 (0.14)	0.6492 (0.53)	1.0931 (0.32)	-	-	-	
GT104 C	1.02							-	-	-	

Sample ID	Weight (mg)	U (ppm)	Th (ppm)	Measured activity ratios				Age interpretation			Notes
				$\frac{^{230}\text{Th}}{^{232}\text{Th}}$	$\frac{^{232}\text{Th}}{^{238}\text{U}}$	$\frac{^{230}\text{Th}}{^{238}\text{U}}$	$\frac{^{234}\text{U}}{^{238}\text{U}}$	Age (ka)	$\frac{^{234}\text{U}}{^{238}\text{U}}_i$	$\frac{^{230}\text{Th}}{^{232}\text{Th}}_i$	
GT104 D	2.07	0.80	1.67	1.3	0.68637 (0.10)	0.8852 (0.45)	1.0689 (0.26)	-	-	-	Fraction C lost during sample preparation – no age information
GT106 A	3.14	3.93	0.05	12.3	0.00432 (0.06)	0.0530 (0.56)	1.1442 (0.13)	4.8 (0.2)	1.147 (0.003)	0.83 (0.59)	
GT106 B	2.43	4.06	0.34	2.8	0.02766 (0.06)	0.0775 (0.57)	1.1430 (0.13)	5.4 (1.5)	1.149 (0.012)	0.83 (0.60)	
GT106 C	1.53	4.41	0.35	3.0	0.02637 (0.06)	0.0785 (0.61)	1.1444 (0.15)	5.7 (1.5)	1.150 (0.011)	0.83 (0.60)	
GT106 D	1.07	0.56	0.96	1.3	0.55988 (0.43)	0.7433 (0.72)	1.0897 (0.73)	-	-	-	Fractions D and E – possible open system behaviour, no age information
GT106 E	1.59	0.78	1.62	1.1	0.68444 (0.12)	0.7364 (0.50)	1.0486 (0.29)	-	-	-	
GT106 F	1.68	1.41	1.20	1.2	0.27986 (0.09)	0.3315 (0.54)	1.1154 (0.24)	-	-	-	Fractions F and G – possible open system behaviour, no age information
GT106 G	1.33	1.23	1.28	1.4	0.34273 (0.12)	0.4956 (1.08)	1.0943 (0.29)	-	-	-	
GT120 A	1.46	2.31	0.32	2.1	0.04612 (0.07)	0.0955 (0.88)	1.1413 (0.17)	4.1 (0.2)	1.152 (0.006)	1.196 (0.039)	Age and initial values based on fractions A and B
GT120 B	1.20	2.59	0.70	1.6	0.08860 (0.08)	0.1444 (0.95)	1.1330 (0.22)	-	-	-	
GT120 C	1.52	1.90	0.57	1.8	0.09831 (0.07)	0.1746 (0.65)	1.1173 (0.20)	-	-	-	Fractions C and D – possible open system behaviour, no age information
GT120 D	2.47	1.92	1.56	0.9	0.26567 (0.06)	0.2508 (0.52)	1.1000 (0.16)	-	-	-	
GT126 A	2.36	0.35	1.09	1.2	1.01886 (0.42)	1.2163 (1.04)	1.0272 (0.71)	-	-	-	Fractions A and B – open system behaviour, no age information
GT126 B	2.49	0.63	1.35	1.6	0.70320 (0.12)	1.1127 (0.51)	1.0039 (0.32)	-	-	-	
GT126 C	2.30	0.47	1.04	1.2	0.72494 (0.24)	0.8611 (0.68)	1.0447 (0.46)	-	-	-	Fraction D lost during sample preparation – no age information
GT126 D	2.59							-	-	-	
GT141 A	0.98	0.86	0.76	1.8	0.29182 (0.26)	0.5358 (1.16)	1.0986 (0.47)	-	-	-	Fractions A and B – possible open system behaviour, no age information
GT141 B	1.07	0.53	0.44	1.5	0.27372 (0.19)	0.4096 (1.01)	1.1095 (0.39)	-	-	-	
GT141 C	0.63	1.55	0.23	3.3	0.04841 (0.16)	0.1581 (1.04)	1.1484 (0.36)	12.2 (3.0)	1.161 (0.023)	0.82 (0.63)	
GT141 D	0.73	1.63	0.41	2.7	0.08299 (0.24)	0.2237 (1.64)	1.1375 (0.49)	17.0 (5.5)	1.155 (0.042)	0.81 (0.67)	
GT141 E	0.97	1.35	0.78	1.6	0.21070 (0.16)	0.3307 (0.88)	1.1053 (0.31)	16.1 (0.7)	1.142 (0.007)	0.96 (0.24)	Age and initial values based on fractions E and F
GT141 F	0.91	0.93	1.35	1.2	0.47546 (0.15)	0.5494 (0.72)	1.0666 (0.34)				

## Glossary

<i>BGS</i>	British Geological Survey.
<i>BSEM</i>	Backscattered electron microscopy.
<i>Cefas</i>	Centre for Environment, Fisheries and Aquaculture Science.
<i>JNCC</i>	Joint Nature Conservancy Committee.
<i>EDS</i>	Energy-dispersive spectroscopy.
<i>EDXA</i>	Energy-dispersive X-ray spectroscopy.
<i>MDAC</i>	Methane-Derived Authigenic Carbonate.
<i>SAC</i>	Special Area of Conservation.
cSAC	Candidate Special Area of Conservation.
<i>SCI</i>	Site of Community Importance.
<i>SEM</i>	Scanning electron microscope / microscopy.

## References

British Geological Survey holds most of the references listed below, and copies may be obtained via the library service subject to copyright legislation (contact [libuser@bgs.ac.uk](mailto:libuser@bgs.ac.uk) for details). The library catalogue is available at: <https://envirolib.apps.nerc.ac.uk/olibcgi>.

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