Analytical methods applied to samples of suspected MDAC

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1. X-RAY DIFFRACTION ANALYSIS

Whole rock X-ray diffraction (XRD) analysis was undertaken on 30 samples to confirm the identification of the carbonate cements. For XRD analysis, approximately 10 mm^3 lumps of the rock were ground in pestle and mortar and a c.3 g portion of the ground material was then wet-micronised under acetone for 10 minutes, dried, disaggregated and back-loaded into standard stainless steel sample holders to prepare random-orientated powder mounts for analysis.

XRD analysis was carried out using a PANalytical X'Pert Pro series diffractometer equipped with a cobalt-target tube, X'Celerator detector and operated at 45 kV and 40 mA. The random powder mounts were scanned from 4.5-85 °2θ at 2.06 °2θ/minute. Diffraction data were initially analysed using PANalytical X'Pert Highscore Plus version 4.1 software coupled to the latest version of the International Centre for Diffraction Data (ICDD) database followed by mineral quantification applying the Rietveld refinement method using PANalytical Highscore Plus software.

2. PETROGRAPHIC ANALYSIS

Polished section and polished block preparation

Polished thin sections for petrographic analysis were prepared from small blocks, approximately 40 x 25 x 15 mm, that were sawn from the MDAC samples. The blocks were impregnated with epoxy-resin under vacuum in order to stabilise the material for polished section preparation. A blue dye was added to the epoxy-resin prior to vacuum impregnation to differentiate between porosity originally present within sample and any artefacts of the sectioning process (e.g. grain plucking), when subsequently observed by transmitted-light microscopy. These resin-impregnated blocks were then sliced, and the slice polished to produce polished thin sections 30 μm thick bonded onto 45 x 28 mm glass microscope slides with a colourless epoxy-resin. The thin sections were finished by polishing with 0.45 μm diamond paste.

The residual counterpart resin-impregnated block to each thin section slice was also polished. This block was then used for microsampling, by microdrilling, of selected areas and types of carbonate mineral material for stable isotope analysis as described below.

Optical microscopy

The polished thin sections were initially scanned, using a digital flatbed scanner, to provide reference images of the whole section/block area. The polished sections were then examined by optical microscopy under plane-polarized light (PPL) and cross-polarized light (XPL) condition, using a Zeiss AxioImager A2m polarizing microscope equipped with a bespoke Zeiss AxioCam ICC5 digital camera. Representative images of key features were recorded in TIFF format at a resolution of 2452 x 2056 pixels, using the Zeiss AxioVision SE64 software package (Release 4.9.1).

Scanning electron microscopy and electron probe microanalysis

Backscattered scanning electron microscopy (BSEM) was used to make detailed high-resolution petrographical observations of the polished thin sections. BSEM analyses were carried out using a FEI QUANTA 600 environmental scanning electron microscope (ESEM) fitted with an Oxford Instruments INCA Energy 450 energy-dispersive X-ray microanalysis (EDXA) system with an Oxford Instruments X-MAX 50 mm^2 Peltier-cooled (liquid nitrogen free) silicon drift detector (SSD). This X-ray detector is capable of operating at very high input X-ray count rates (up to $\sim 10^6$ counts per second). The polished sections were coated with a nominally 25 nm thick film of carbon, prior to examination in the ESEM instrument, to make them electrically-conductive. Carbon-coating was carried out using an EMITECH 960L evaporation-coating unit.

The ESEM instrument was operated in conventional high vacuum mode, with a routine electron beam accelerating voltage of 20 kV, and beam probe currents of between 0.71 and 1.2 nA, and a working distance of 10 mm. SEM and BSEM photomicrographs were recorded as 8-bit greyscale TIF digital image over a range of magnifications at a resolution of 1024 x 884 pixels. Image brightness in BSEM images is related to the average atomic number of the phases observed (Goldstein *et al*., 1981), and this therefore allows differentiation of the minerals observed in polished sections on the basis of the image brightness. Prior to BSEM examination, the polished surface of the thin section was made electrically conductive by coating with a thin layer of carbon (25 nm thick) by vacuum evaporation of carbon.

Mineral/phase identification was aided by micro-chemical information routinely obtained from simultaneous observation of semi-quantitative EDXA spectra recorded from features of interest. EDXA data was acquired and processed using the Oxford Energy INCA Suite Version 5.04 Issue 21a+SP2 (2012)

software package. The EDXA system used is capable of detecting elements from atomic number 4 (boron) to atomic number 92 (uranium), and has detection limits of the order of 0.2 to 0.5 wt. % for most common major elements (sodium to iron). Quantitative energy-dispersive electron probe microanalysis (ED-EPMA) of the carbonate cements observed in polished thin section was also undertaken using the same instrumentation. Quantitative ED-EPMA were preformed using a 20 kV electron beam, 1.2 nA beam currents at a working distance of 10 mm. EDXA spectra were processed and quantified using the INCA analysis software package detailed above. The EDXA system was calibrated by reference to individual element X-ray spectra recorded from pure metal, oxide and known mineral standards that are normalised against the X- ray spectrum from pure cobalt recorded under the same operational conditions. Cobalt is subsequently used as an internal reference against which sample spectra are normalised.

3. STABLE ISOTOPE ANALYSIS

One hundred and fifty sub-samples of MDAC were analysed to determine oxygen and carbon isotope ($\delta^{18}O$ and $\delta^{13}C$) composition of the carbonate components. These included bulk cement samples and targeted subsamples, recovered by microsampling discrete areas of the polished blocks that contained (or were dominated by) specific generations or types of carbonate (including bioclasts and cement types). The areas for microsampling were initially identified from optical microscopy and SEM observations carried out previously on the corresponding polished thin sections. This methodology has been very successfully used in previous studies to sample and analyse discrete generations of carbonate mineralisation in intergrown polymineralic or multi- generation carbonate cements (Milodowski *et al*., 2005).

Microsampling was undertaken using a diamond-tipped microdrill, whilst observing the block sample in reflected light under an optical microscope. The microdrill was capable of drilling, and retrieving material from areas as small as 100 μm. However, in order to obtain sufficient material for analysis areas up to 1 mm diameter were drilled. After microdrilling, the microdrilled areas in each block were examined by BSEM-EDXA to verify the mineralogical identity of the material sampled for stable isotope analysis.

Approximately 50-100 micrograms of carbonate are used for isotope analysis using an IsoPrime dual inlet mass spectrometer plus Multiprep device. Samples are loaded into glass vials and sealed with septa. The automated system evacuates vials and delivers anhydrous phosphoric acid to the carbonate at 90 °C. The evolved CO_2 is collected for 15 minutes, cryogenically cleaned and passed to the mass spectrometer. Isotope values ($d^{13}C$, $d^{18}O$) are reported as per mille (‰) deviations of the isotopic ratios ($^{13}C/^{12}C$, $^{18}O/^{16}O$) calculated to the VPDB (Vienna Pee Dee Belemnite) scale using a within-run laboratory standard calibrated against NBS-19. The Calcite-acid fractionation factor applied to the gas values is 1.00798 dolomite-acid =1.00873 and aragonite 1.00782. Due to the long run time of 21 hours a drift

correction is applied across the run, calculated using the standards that bracket the samples. The Craig correction is also applied to account for $d^{17}O$. The average analytical reproducibility of the standard calcite (KCM: Keyworth carbonate marble) is 0.08‰ for $d^{13}C$ and $d^{18}O$.

4. STRONTIUM ISOTOPE (87Sr/86Sr) RATIO ANALYSIS

Strontium isotope ratio ($^{87}Sr/^{86}Sr$) 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 $^{87}Sr/^{86}Sr$ 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 $^{87}Sr/^{86}Sr$ of strontium in solution in seawater, which will reflect the ambient $^{87}Sr/^{86}Sr$ at a particular time.
- $^{87}Sr/^{86}Sr$ 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 $^{87}Sr/^{86}Sr$ reflecting the ambient marine $^{87}Sr/^{86}Sr$ ratio, and authigenic magnesian calcite which may include $^{87}Sr/^{86}Sr$ derived from formation fluid and seawater. As these are impossible to separate physically or chemically for the $^{87}Sr/^{86}Sr$ isotope ratio analysis, the analytical results would give a mixed $^{87}Sr/^{86}Sr$ ratio that would be difficult to evaluate. Therefore, the $^{87}Sr/^{86}Sr$ 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 $^{87}Sr/^{86}Sr$ of the ambient marine Irish Sea seawater signature, against which the $^{87}Sr/^{86}Sr$ 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. 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.

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_2O 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_3.

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.

5. URANIUM-THORIUM AGE DATING ANALYSIS

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 ^{230}Th at the time when it precipitates, because Th is highly insoluble and not present in the mineralising porewater, and therefore the accumulation of ^{230}Th over time through the radioactive decay of uranium (from ^{238}U to ^{234}U to ^{230}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 ^{230}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 ^{230}Th present in the sample (i.e. ^{230}Th that did not result from the in-situ decay of U). This initial ^{230}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 with respect to the ^{238}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}U dissolved in

the water column decays to ^{230}Th (i.e. the same decay process that occurs within the carbonates themselves). Because Th is highly insoluble, this water-borne ^{230}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}Th it will adsorb). However, given the shallow water depth in the Croker Carbonate Slab area, the impact of hydrogenous ^{230}Th is likely to be relatively small. Therefore, the theoretical detrital U-Th composition based on average continental crust values (i.e. (^{232}Th/^{238}U) = 1.2 ± 50%), and secular equilibrium with respect to the ^{238}U decay chain (i.e. (^{230}Th/^{238}U) = 1 ± 50% and (^{234}U/^{238}U) = 1 ± 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 ± 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.

The distinction between pure and detritus-rich carbonates is usually made based on the samples (^{230}Th/^{232}Th) activity ratio – in this case ^{232}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 x 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}Th/^{232}Th)>2 (e.g. Prouty et al., 2016, Crémière et al., 2016a, 2016b).

For samples with (^{230}Th/^{232}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}U/^{238}U) of the fluid from which the carbonate precipitated, and the initial (^{230}Th/^{232}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}U relative to seawater, and therefore their modelled initial ($^{234}U/^{238}U$) is expected to fall at or above the mean seawater value of 1.1466 (Robinson et al., 2004). A modelled initial ($^{234}U/^{238}U$) 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.

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 ~8 M HNO_3, spiked with a mixed ^{229}Th-^{236}U isotopic tracer, left to equilibrate overnight and dried down. Samples were re-dissolved in a mixture of $HClO_4$:HF:HNO_3 (1:2:2.5), using ~50 µl HF per estimated mg of detrital material, dried down, re-dissolved in 8 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 ml columns using AG-1 × 8 anion exchange resin were done following the procedure of Edwards et al. (1987). Th fractions were further purified using a second pass through AG-1 × 8 resin and were filtered using 0.22-µm pore-size syringe filters to remove resin particles. Both U and Th fractions were oxidized twice in 2 ml 16 M HNO_3 and 0.2 ml 30% H_2O_2, and dissolved in 0.5 ml 0.1 M HCl and 0.035 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 Crémière et al. (2016). U-Th age calculations were performed using in-house Microsoft Excel spreadsheets using the ^{230}Th and ^{234}U decay constants of Cheng et al. (2013).

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