

# IMPROVED AMS $^{14}\text{C}$ DATING OF SHELL CARBONATES USING HIGH-PRECISION X-RAY DIFFRACTION AND A NOVEL DENSITY SEPARATION PROTOCOL (CarDS)

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**ABSTRACT.** One critical variable in the successful application of radiocarbon dating is the effective removal of carbonaceous contaminants. In the case of marine carbonates, contamination appears usually in the form of secondary low-magnesium calcite, the stable polymorph of calcium carbonate and byproduct of the post-mortem recrystallization or replacement of the autochthonous phase, originally in the form of high-magnesium calcite or aragonite. Depending on the nature of the depositional environment, the secondary phase may be contemporary in age with the original shell carbonate and may have even been derived from it by dissolution-recrystallization processes, or can be an exogenous contaminant of younger or older age. The limited ability of current pretreatment protocols to detect and remove the secondary mineralogical phases prior to dating carbonates has been one of the reasons marine shell and coral  $^{14}\text{C}$  determinations are often difficult to validate in terms of their reliability. We have developed a new pretreatment protocol designed to achieve greater reliability and accuracy in the dating of this material. The method entails 2 steps. The first one involves the improved detection and quantification of secondary calcite in aragonite using X-ray diffraction, at a precision of  $\sim 0.1\%$  and  $\sim 0.8\%$ , respectively. Next, where this is required, a novel density separation step using non-toxic heavy liquids (CarDS) is applied to the diagenetic sample. This enables the clear separation of calcite and aragonite, with only the latter kept for dating. We have applied the new steps, screening and separation, on standard and archaeological examples and our initial results suggest that it is successful and reproducible. In this paper, we describe the method and initial results.

## INTRODUCTION

Carbonates are an attractive material for radiocarbon dating as they are widely distributed throughout the Earth's lithosphere, hydrosphere, and biosphere in various forms, such as geological formations (e.g. speleothems) or as part of living organisms (e.g. molluscan shells). The remains of the latter are often found in archaeological sites, either as food refuse, shell beads, or tools, sometimes even forming the site itself, as in the case of shell middens.

A number of variables influence the reliable  $^{14}\text{C}$  dating of marine shell. Certain common forms of carbonates are unstable and chemically more active than other materials often employed in  $^{14}\text{C}$  dating (wood, charcoal, or bone). For this reason, there is a greater source of error associated with them. Post-mortem diagenesis of the carbonate shell skeletons implies replacement of the original crystal structure and often involves carbonate dissolution, recrystallization, and carbon exchange with the burial environment. Uncertainties linked with the marine reservoir effect, or in the case of shellfish growing in riverine or lacustrine systems linked with hard-water effects, add to the difficulties associated with the reliable dating of this material.

## BACKGROUND

### Shell Diagenesis

Marine molluscan skeletons are mainly comprised of low-magnesium calcite (LMC, 0–4%  $\text{MgCO}_3$ ), high-magnesium calcite (HMC,  $>4\%$   $\text{MgCO}_3$ ), and aragonite (the allochem of preference for most molluscan taxa), precipitated within an organic, proteinaceous matrix (Lowenstam and Weiner 1989;

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Addadi et al. 2006). The 3 polymorphs have almost identical compositions but quite different crystal structures and thermodynamic equilibria. Due to preferential incorporation of various cations among their unit cells, such as Mg and Sr, the specific gravity of calcite and aragonite also differs. The theoretical density of aragonite is 2.94 g/cm<sup>3</sup> and that of calcite is 2.71 g/cm<sup>3</sup> (Gussone et al. 2005).

After death and burial of the organism, physical, chemical, and biological factors may cause alteration to the carbonate skeleton. Diagenesis involves several reactions such as carbonate dissolution, recrystallization, and replacement, often requiring the presence of aqueous solutions in order to evolve. All of these processes are often embraced under the term neomorphism (Tucker 2001). It is expected that the metastable polymorphs, HMC and aragonite, will in time recrystallize to the more stable LMC (Schmalz 1967; Bathurst 1971; Chappell and Polach 1972; Folk and Assereto 1976; Allan and Matthews 1982; Morse and Mackenzie 1990; Morse et al. 1997; Magnani et al. 2007). This process is greatly influenced by the diagenetic fluid chemistry, such as Mg:Ca ratio (Folk 1974); pH; concentration of phosphates and sulfates (Walter 1986); the precipitation rate (Given and Wilkinson 1985); and other kinetic, biological, and hydrologic controls.

Very rare and notable exceptions to this situation, which involve isomineralogic diagenetic changes, have been reported in the literature (Enmar et al. 2000; Webb et al. 2007). In these cases, however, very specific environmental conditions and aqueous geochemistry were identified as the most possible reasons for the “aragonite to aragonite” overgrowth.

A chalky appearance is usually associated with aragonite dissolution and precipitation of single-crystal calcite, in microregions where the dissolution rate is higher than that of precipitation (McGregor and Gagan 2003). In some cases, calcite cement appears in the form of spars with an inward direction and in others it precipitates within the biological voids and in areas left void due to protein degradation. Regardless of its form, the identification of secondary calcite in shells that were originally formed as aragonite evidences diagenesis. The overall process may have progressed in a closed chemical system, in an open system freely exchanging with the ambient environment, or both—during different diagenetic events. Therefore, carbonate samples manifesting diagenesis ought to be treated with caution when they are <sup>14</sup>C dated.

### **Previous Pretreatment Protocols**

It is often assumed that the products of neomorphism are confined largely the surface of carbonate specimens and may be effectively removed by abrasion or sand-blasting. A second method, that of the controlled chemical etching, is often applied by <sup>14</sup>C laboratories and involves a 30–80% removal of shell or coral samples prior to <sup>14</sup>C dating (Burr et al. 1992; Bard et al. 1993; Edwards et al. 1993; Yokoyama et al. 2000). This pretreatment targets surface contaminants such as attached sediment, loose secondary carbonates or absorbed modern carbon (Chiu et al. 2005). Several selective dissolution experiments on coral material have demonstrated that partial, stepwise dissolution leads to older <sup>14</sup>C ages (Bard et al. 1990; Burr et al. 1992; Yokoyama et al. 2000). It ought to be noted, however, that aragonite is more soluble than calcite (Chave et al. 1962; Wolf and Günther 2001), which means that chemical etching could preferentially increase the proportion of diagenetic calcite in the sample. Vita-Finzi and Roberts (1984) and Chiu et al. (2005) both demonstrated that the acid-etching method concentrated the recent secondary products (calcite) because they were more resistant to acid than the original, more soluble aragonite phase. However, more data of coral and shell dissolution experiments using acids at various concentrations (dilute and very concentrated) need to be generated to support the effect of preferential solubility of aragonite over calcite during the acid-etching preparation of this material.

In this study, we took an alternative step and examined the possibility of effectively separating the 2 calcium carbonate polymorphs (original aragonite and secondary calcite) present in the same sample, without attempting to dissolve the diagenetic phase.

### **Carbonate Density Separation (CarDS): A New Approach**

Density separation of solid particles has been traditionally performed in the fields of geology, paleontology, and palynology (e.g. Green 2001; Vandergoes and Prior 2003). A variety of organic liquids such as dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), diiodomethane ( $\text{CH}_2\text{I}_2$ ), carbon tetrachloride ( $\text{CCl}_4$ ), -tetrabromide ( $\text{CBr}_4$ ), -disulfide ( $\text{CS}_2$ ), trichloroethylene ( $\text{C}_2\text{HCl}_3$ ), tetrabromoethane ( $\text{C}_2\text{H}_2\text{Br}_4$ ), chloroform ( $\text{CHCl}_3$ ), and bromoform ( $\text{CHBr}_3$ ) have been used widely in the past. Most of these, however, are considered toxic and their supply and disposal have become subject to very stringent requirements since they pose danger to personal health and the environment.

Over the last 2 decades, a new generation of non-toxic heavy liquids based on polytungstates, such as sodium polytungstate (SPT) and lithium heteropolytungstate (LST), were introduced. These have several advantages over the toxic alternatives, which include easy preparation, fast separation, lower viscosity at high concentrations, recyclability, therefore low cost per sample and longer “bench” duration, wide ranges of densities (1.0–3.1  $\text{g}/\text{cm}^3$ ), and do not require preparation under fumehoods (Callahan 1987; Krukowski 1988; Munsterman and Kerstholt 1996).

The difference in the relative densities of calcite and aragonite was considered able to be utilized in attempts at physical separation of the 2 phases by density fractionation. The basis of heavy-liquid flotation is that solid particles of different specific gravities dispersed into liquids of intermediate density will separate as distinct fractions within the separation column. The particles with a density less than that of the fluid will float, while those with a greater density will sink.

The density fractionation method has been applied in bone carbonates and requires that biogenic minerals of different density exist together as discrete units (Richelle 1964). In the case of shells that have undergone post-mortem diagenesis, the newly formed LMC will theoretically exist next to the original phase, related but not entirely cross-linked to it. This renders the separation of the 2 minerals a feasible task. In some instances, however, aragonite structures will be enclosed by diagenetic calcite, in which case the phases will be very difficult to disconnect unless the material is thoroughly ground-up to particle liberation size so that the average grain size is lower than the size of the diagenetic aggregates.

The density separation of marine carbonates was first described by Takenaka et al. (1999) who applied it to the separation of calcite and aragonite from bimodal species (containing both aragonite and calcite) as a preparation step for the determination of the chemical forms of Na and Cl ions in marine shell structures. Later, Henderson et al. (2000, 2001) used it for the separation of carbonate minerals of marine origin during U-series dating of beach slopes and platforms. In all 3 cases, the separation was reported as complete and gave satisfactory results. Despite their success, these publications appear to have been overlooked by the  $^{14}\text{C}$  community and their potential application for diagenetic shell carbonate separations of diagenetic shell carbonates was not investigated.

In the present paper, we describe the development of a novel separation protocol to precede the  $^{14}\text{C}$  dating of diagenetic carbonates. We term the protocol “CarDS” (carbonate density separation), which refers to the use of heavy liquids, in this case polytungstates, in the separation of LMC from aragonite (or in some cases, LMC from HMC).

## MATERIALS

Three types of materials were used in the present study: reference geological and biogenic material, modern molluscan shells, and archaeological specimens. The reference samples consisted of Icelandic spar, chalk, mineral aragonite, and modern cuttlefish bone, which were used in the production of a calcite quantification curve, based on X-ray diffraction (XRD) data.

We experimented with modern marine shells of various species (*Glycymeris glycymeris*, *Nassarius mutabilis*, *Columbella rustica*, *Dentalium* sp.) in order to test the effect of grinding procedures to the mineralogy of aragonite samples.

For the development of the CarDS protocol, we used: (A) mixtures of calcite (Icelandic spar) and aragonite (geological “Sputnik”); and (B) archaeological shells and 1 coral. For Group A, 21 binary mixtures of various calcite concentrations (0–80%) were prepared. Group B included 4 Late Pleistocene and Holocene shells and a coral sample, all with evidence for recrystallization. In detail, these were the following:

### *Fiji-1*

This sample is part of a coral (*Porites* sp.) collected from an emerged coral microatoll in the Avea region, Vanuabalavu Island (Fiji). It had previously been submitted to the Waikato Radiocarbon Laboratory where it was conventionally  $^{14}\text{C}$  dated and also underwent several accelerator mass spectrometry (AMS) determinations as part of an internal laboratory testing.

In 2007, the coral was obtained by the Oxford Radiocarbon Accelerator Unit (ORAU) to be included in the current investigation. The sample retained most of its structural features, but its chalky appearance and filling of the skeletal voids strongly implied some diagenetic alteration.

The external surface of Fiji-1 was removed by sand-blasting and a fragment of ~200 mg obtained from within the coral body was crushed manually. A small fraction was  $^{14}\text{C}$  dated according to the ORAU routine pretreatment protocol (Brock et al. 2010). Following this, 100 mg underwent twice the new CarDS protocol.

### *Ana-1*

An archaeological bivalve shell (*Anadara* sp.) from the Mort Creek Site Complex, Australia, was also analyzed. Ana-1 was retrieved from a natural shell deposit (chenier) underlying the cultural deposit at the site (Ulm 2006). The specimen, of original aragonite composition, was poorly preserved and its surface was extremely brittle and chalky.

### *KA-50, and KA-51*

A *Glycymeris* sp. valve, KA-50, and a *Nassarius gibbosulus* shell, KA-51, were selected from the malacological collection of the Naturalis Natural History Museum (the Netherlands). KA-50 and KA-51 come from levels XXII and XXIII, respectively, of the Paleolithic site of Ksar Akil (Lebanon). Level XXII was recently dated in Oxford at ~37 ka  $^{14}\text{C}$  BP; thus, the 2 shells were expected to be of similar age.

### *Bomb-16*

Bomb-16 is a *Nassarius incrassatus* shell from the Aurignacian levels (A1 stratigraphic unit) of Riparo Bombrini, a Paleolithic rockshelter in Balzi Rossi (N Italy).

## METHODS

### X-ray Diffraction (XRD)

XRD analysis is a major mineralogical tool used extensively in the identification, characterization, and quantification of phases in mineral clusters (for reviews see: Milliman 1974; Klug and Alexander 1974; Bish and Post 1993). Quantitative analysis using this method requires meticulous calibration of the instrument, carefully prepared standards, and many repetitive steps to establish the optimal setup.

Standard carbonate mixtures were prepared in triplicate; these were combinations of (a) calcite from Icelandic spar mixed with geological aragonite; (b) Oxford chalk (pure calcite) mixed with cuttlefish bone (*Sepia officinalis*, aragonite); (c) Icelandic spar mixed with cuttlefish bone. XRD analysis was used both for the reference mixtures and the archaeological samples before and after the application of the CarDS protocol.

A small portion (8–10 mg) of sample powder was prepared using the methods of Chiu et al. (2005). Powder XRD analysis was performed at the Department of Materials (University of Oxford) with a Philips PW 1820 diffractometer operating at 35 kV and 50 mA, using Cu K $\alpha$  radiation. During configuration of the instrument, various combinations of the defining parameters (step size, step time) were investigated in order to optimize the analytical conditions and obtain the highest calcite and aragonite peak resolution in optimal time. Of all combinations, a step size of 0.02° with 2.5 s per step from 25–50° 2 $\theta$  on the Bragg scale, demonstrated the best results in 52 min. For treatment and conversion of the results to readable formats, we used the X'Pert HighScore (PANalytical) software.

### Mechanical Cleaning, Grinding, and Organics Removal

Mechanical cleaning of sample surfaces is an effective way of removing surficial contamination. The mechanical cleaning of all shell samples in this study was performed using an air-abrasive system with aluminum oxide of 29  $\mu$ m diameter. Abrasion was undertaken until the shell skeleton surface was removed and its internal, usually opaque, layers were exposed.

Both archaeological samples and laboratory reference mixtures were sampled by removing a small fragment of the carbonate using a handheld rotary saw, wet-crushing it in an agate mortar and pestle for 3 min, and sieving the powder through a 200-mesh sieve (grain size:  $\leq 73 \mu$ m). We considered this particle size range sufficient for the separation; therefore, we did not try to define or reach the “liberation size” of carbonate particles. Since secondary calcite grains are not of uniform size, it was not possible to calculate a “liberation size” as in Shin (2007).

The effect of our preparation method to the mineralogy of the shells was checked routinely by applying the same procedures to several species of modern aragonite specimens. In addition to the sawing and grinding of a shell fragment, we also experimented with the extraction of powder sample from the same specimens using a dentist's rotary drill at a fixed speed, for about 3 min. The generated powder was checked with XRD for possible aragonite to calcite phase transformation, introduced by the sawing, grinding, or milling procedures.

In theory, when dealing with biominerals, the presence of organics in their crystal structure ( $\sim 1 \text{ g/cm}^3$ ) lowers the overall density of the shell, rendering the separation of calcite and aragonite difficult. Several methods exist for the removal of organics prior to isotopic analyses (e.g. plasma oxidation, bleaching, heating). In our efforts to do so, we attempted thermal protein degradation *in vacuo* at 250 °C and 350 °C of modern shell samples (the same specimens used in the aforementioned grinding and drilling experiments).

### The CarDS Protocol

For the CarDS method, we use LST (Fastfloat). LST liquid was used either unaltered at the manufacturer's density (2.83 g/mL) or was adjusted to the required density by diluting it with Milli-Q™ water or by concentrating it through heat-induced water evaporation. Since LST is acidic, we performed repeated experiments to investigate on the possible dissolution of the carbonate samples when immersed in it. Known-weight chalk fragments were placed into the liquid for 10–30–50–120 min and were sealed in vacuo. In addition, we systematically surveyed the LST solution for carbon traces using Chromosorb™ (carbon-free inert silica), which we burned in an elemental analyzer as a proxy for real sample handling.

For the CarDS protocol, around 100 mg of powder was combined with 4–5 mL of LST solution ( $\rho = 2.75 \text{ g/cm}^3$ ) in 12-mL glass tubes. The mixture was vortex mixed for 30 s and ultrasonicated for 10 min. We did this in order to break up macro- and micro-aggregates formed as result of the surface tension exhibited on the particles by the surrounding medium (Arnarson and Keil 2001). The solution then underwent centrifugation for 20 min at 3500 rpm, which increased the settling velocities and prevented further agglomeration of the mineral particles (Ijlst 1973). The lighter, supernatant fraction (calcite) was carefully pipetted off and the walls of the glass tube were cleaned with a glass spatula to remove any attached powder. The higher-density fraction was subjected to a further separation step of resuspension in slightly heavier liquid ( $d = 2.83 \text{ g/cm}^3$ ), 20 min centrifugation, and removal of the floating particles by pipetting.

Instead of removing the supernatant fraction by pipetting, another approach included the freezing of the mixture in the glass tube using liquid N<sub>2</sub>. This immobilizes all particles and preserves the density stratification of the separated sample unaltered (Basford and Coscio 1973). The upper phase was removed by slowly warming the surface of the frozen mixture in the tube with Milli-Q water. The liquefied solution was then transferred to a separate tube and cleaned as described below. This procedure reduces sample handling and allows more control over the transferring and dispensing processes.

Any remaining polytungstate was rinsed off the separated phases by adding Milli-Q water, centrifuging for 10 min and decanting the solution 3–4 times, after which the carbonate residue was frozen for 12 hr and freeze-dried for 24 hr. This last step was applied to avoid the adherence of the remaining powder to the glass vessels, which often happens during water evaporation and which may decrease the final carbonate yield.

When the separation was shown by XRD as not final or the calcite removal was below the desired levels, and given that enough material was present (>50 mg), a second application of the CarDS protocol was performed.

### AMS <sup>14</sup>C Dating

Approximately 25 mg of sample was reacted with 5 mL of 80% phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) for 12 hr at 60 °C, under vacuum. The CO<sub>2</sub> evolved via this process was extracted through a manifold, was cryogenically purified, and transferred into a glass ampoule. The ampoule was cracked, and the gas run through an automated elemental analyzer connected to a continuous flow isotope-ratio-monitoring mass spectrometer. The purified CO<sub>2</sub> was then reduced to graphite using H<sub>2</sub> at 560 °C for 6 hr, in the presence of 2 mg of an Fe catalyst. The graphite was pressed into a target holder prior to AMS. All <sup>14</sup>C dates in this study were produced at the Oxford Radiocarbon Accelerator Unit (ORAU), University of Oxford.

## RESULTS

### XRD Analysis

Despite the great overlap of the aragonite and calcite XRD peaks, certain reflections are diagnostic of the 2 minerals and can be used in their identification and quantification in a binary mixture. In this study, we used the characteristic calcite peak at the 104 reflection ( $\sim 29.4^\circ 2\theta$ ) and the aragonite peak at the 012 reflection ( $\sim 33^\circ 2\theta$ ).

All reference mixtures and both end-members were scanned at least 3 times per sample to account for possible distortions caused by sample preparation (for example, preferred orientation of the grains or uneven crystal distribution on the slide surface).

Based on peak heights of the 2 peaks ( $\sim 29.4^\circ$  and  $\sim 33^\circ 2\theta$ ), we generated a calibration curve by plotting the weight percentage of calcite versus the peak height ratio of  $(H_{\text{calcite}})/(H_{\text{calcite}}+H_{\text{aragonite}})$  after correcting for background noise (Figure 1). The calibration curve generated using peak area ratios was not very different either. The results of this exercise will be reported separately, but the achieved detection and quantification limits are 0.1% and 0.8–1.0%, respectively, values very similar to the ones recently reported by Sepulcre et al. (2009).

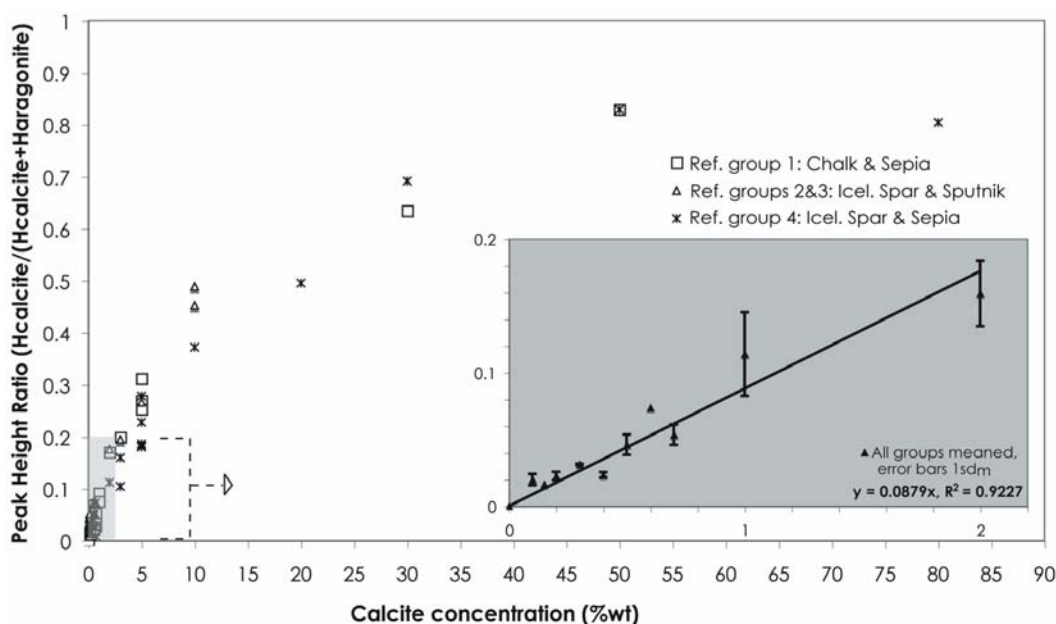


Figure 1 XRD calibration curves based on peak height ratios of known-concentration binary mixtures of calcite and aragonite. Detail of the mixtures with 1–2% calcite concentration is shown in the lower right corner.

### Effects of Sample Preparation

Manual grinding did not induce phase transformation of the shell mineral, but interestingly enough, partial conversion of aragonite to calcite was always observed when we used microdrilling to extract carbonate powder from the modern shells. XRD analyses showed these, previously solely aragonite, samples to contain calcite at various concentrations, from 5 to 20%. These results support the notion that the use of drilling and milling techniques to extract aragonite aliquots leads to phase transfor-

mation of the metastable polymorph due to the shear stress applied by the drill bit and the friction that causes local heating (Foster et al. 2008). This preparation method was abandoned and only sawing and manual grinding were performed in this study.

With regards to the protein degradation experiment, evolution of gas pressure in the vacuum chamber suggested partial decomposition of organics. However, the XRD scans of the heated samples also showed that aragonite to calcite phase transformation occurred readily above 250 °C. This agrees with previous studies (Gaffey et al. 1991; Lécuyer 1996; Balmain et al. 1999); therefore, this method should be used with caution, if at all. The majority of archaeological samples used in this study were all Holocene or Late Pleistocene specimens from arid depositional environments. Their organic content was considered to be low; thus, we did not apply any technique for shell protein removal prior to the separation protocol.

It is unclear whether the calcite formed after the heating or drilling of aragonite undergoes C isotopic fractionation or exchanges with atmospheric CO<sub>2</sub> or with the remaining organic component of the biogenic aragonite. This would have an effect on the <sup>14</sup>C result. Whatever the case, the formation of calcite during the early stages of pretreatment undermines the results of the subsequent XRD analysis, which aims to assess the preservation condition of the shell sample based on the presence or not of secondary, diagenetically formed calcite.

#### **CarDS - AMS <sup>14</sup>C Dating**

LST manufacturers specify a pH of 4 ± 1 for the solution, which is in accordance to our lab measurement of pH 3.5. The acidic nature of the product, however, did not affect the carbonate samples and the experiments with known-weight chalk chunks showed minimum dissolution after various lengths of time they remained immersed in the liquid. Furthermore, almost no carbon traces (<600 ppm C) were detected in the LST solution after the investigation with Chromosorb<sup>TM</sup> intentionally “contaminated” with the polytungstate. The Chromosorb background ranged from 300–600 ppm C; hence, it proved impossible to differentiate the “contaminated” Chromosorb from the background values (Figure 2).

As mentioned previously, the new protocol was applied to 2 groups of samples. For Group A, the success of CarDS was checked by XRD analysis. Samples from Group B, were screened by XRD and were also <sup>14</sup>C dated before and after the CarDS pretreatment.

#### *Group A: Reference Material*

After pretreating with CarDS, the separation of the 2 polymorphs in the known-concentration mixtures was 100% successful in 12 out of the 21 mixtures (~60%). For the rest, the concentration of residual calcite ranged between 0.1–0.5% (in 6 of them), whereas in the 3 remaining mixtures (of original calcite concentrations 2, 5, and 80%) the residual calcite content was slightly higher (0.7%, 4%, and 2%, respectively). The reason for this may have been recontamination during the pipetting and rinsing processes during which—unless done very carefully—the light fraction, either attached to the vessel walls or the pipette tip, may not be removed along with the heavy liquid, but it returns back to the bottom of the tube where it mixes with the heavy fraction.

Overall, the results showed, with very few exceptions, very low remaining quantities of calcite in the separated mixtures (Figure 3) after only 1 application of the CarDS protocol.



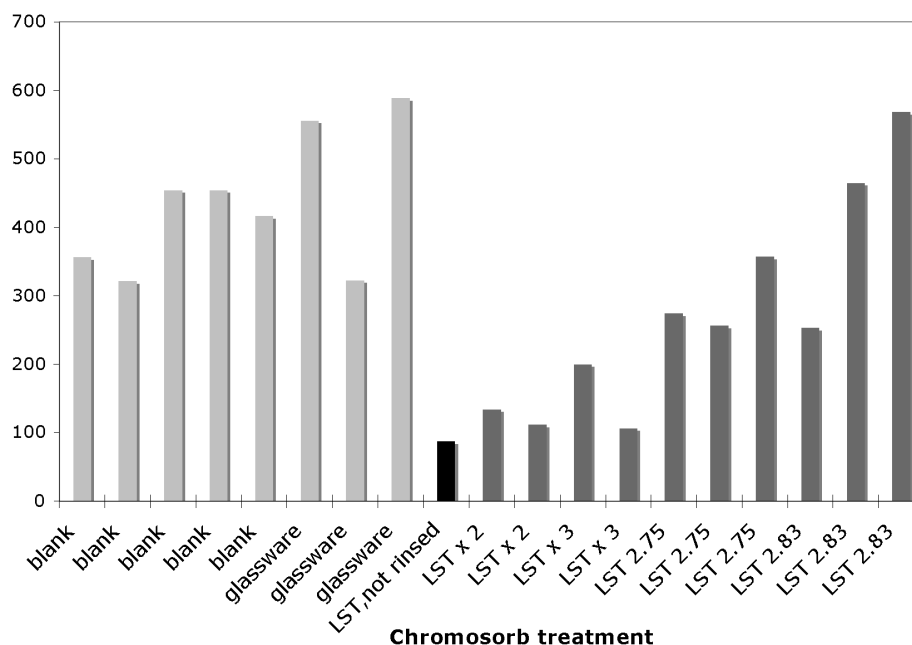


Figure 2 Diagram showing the concentration of C (in ppm) during the CarDS protocol. Chromosorb (inert silica) was used as a proxy for real sample handling and ~10 mg of mixture were combusted in an elemental analyzer. The first 5 samples are “blanks,” i.e. Chromosorb as supplied by the manufacturer; the next 3 labeled as “glassware” refer to Chromosorb that has been through glass tubes to test for possible cross-contamination during glassware cleaning; “LST not rinsed” (dark bar) refers to Chromosorb mixed with a few mL of LST in a tin capsule, without any rinsing steps involved; and all “LST”-labeled samples refer to Chromosorb that has undergone the CarDS protocol with 2 or 3 LST steps, or once using single density solutions, followed by 3 rinsing steps.

### Group B: Archaeological Samples

The fossil shells and the coral of this group were diagnosed as containing traces of secondary calcite in their mineralogy and were selected as candidates for the CarDS protocol. Untreated samples and 1 or 2 post-separation, CarDS residual samples were  $^{14}\text{C}$  dated to ascertain the effects of the protocol on  $^{14}\text{C}$  age.

#### Fiji-1

XRD screening corroborated the macroscopic observation of the coral’s brittle preservation state and confirmed the presence of calcite in a concentration of ~7% (Figure 4). This sample was previously conventionally dated in the Waikato Radiocarbon Laboratory to  $4110 \pm 60$  BP (Wk-7589) (Nunn and Peltier 2001), and more recently using AMS with a range of dates, spanning from  $4357 \pm 26$  to  $4472 \pm 38$  BP (F Petchey, personal communication). In ORAU, it was dated 3 times; once using the routine preparation method as described by Brock et al. (2010) and twice following the CarDS protocol.

After the first application of the CarDS protocol, XRD analysis showed that the separation was incomplete (~1% calcite was still present); thus, the procedure was repeated, after which the XRD scan revealed an almost calcite-free residue (<0.3% calcite) (Figure 4). Residue material from both separations was  $^{14}\text{C}$  dated.

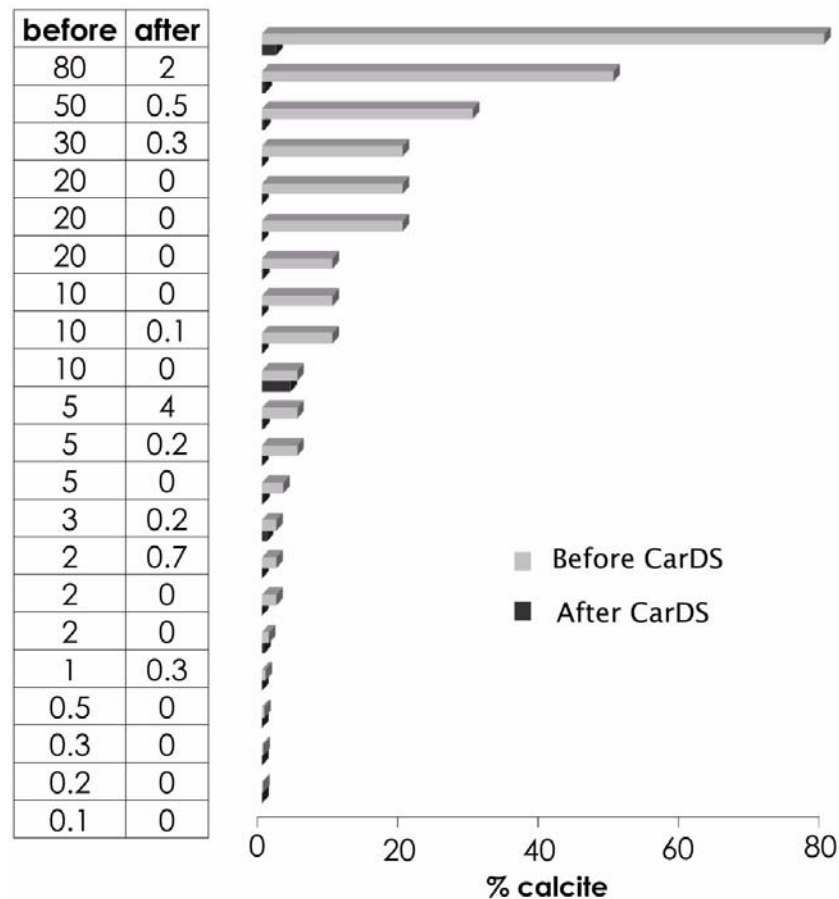


Figure 3 Results after the CarDS separation of laboratory-prepared mixtures of geological calcite and aragonite (Group A). The results show the removal of calcite in the vast majority of the examples, after the first application of CarDS.

The  $^{14}\text{C}$  results produced from all 3 phases (OxA-19284:  $4499 \pm 29$ , untreated; OxA-X-2281-21:  $4498 \pm 27$ , treated once/“CarDS-1”; OxA-X-2281-22:  $4450 \pm 28$ , treated twice/“CarDS-2”) were identical ( $T = 2.00$ , compared with  $\chi^2_{2;0.05} = 5.99$ ) (Table 1), which suggests that recrystallization of the aragonite took place in a closed system without any traceable carbon isotopic exchange, or shortly after the coral’s death. The difference between our dates and the Waikato conventional date is difficult to explain. It may reflect surface contamination since both laboratories dated different parts of the coral.

#### Ana-1

XRD analysis confirmed the presence of secondary calcite (~30%) in the valve. The sample underwent 2 sets of separation with progressive calcite removal, after which no calcite was present (Figure 4). Three  $^{14}\text{C}$  dates were obtained (OxA-19283:  $5174 \pm 30$ , untreated; OxA-X-2281-18:  $5136 \pm 30$ , CarDS-1; OxA-X-2282-19:  $5144 \pm 30$ , CarDS-2) but, again, no differences were observed in the ages or the isotopic compositions of the 3 fractions ( $T = 0.89$ , compared with  $\chi^2_{2;0.05} = 5.99$ ) (Table 1).

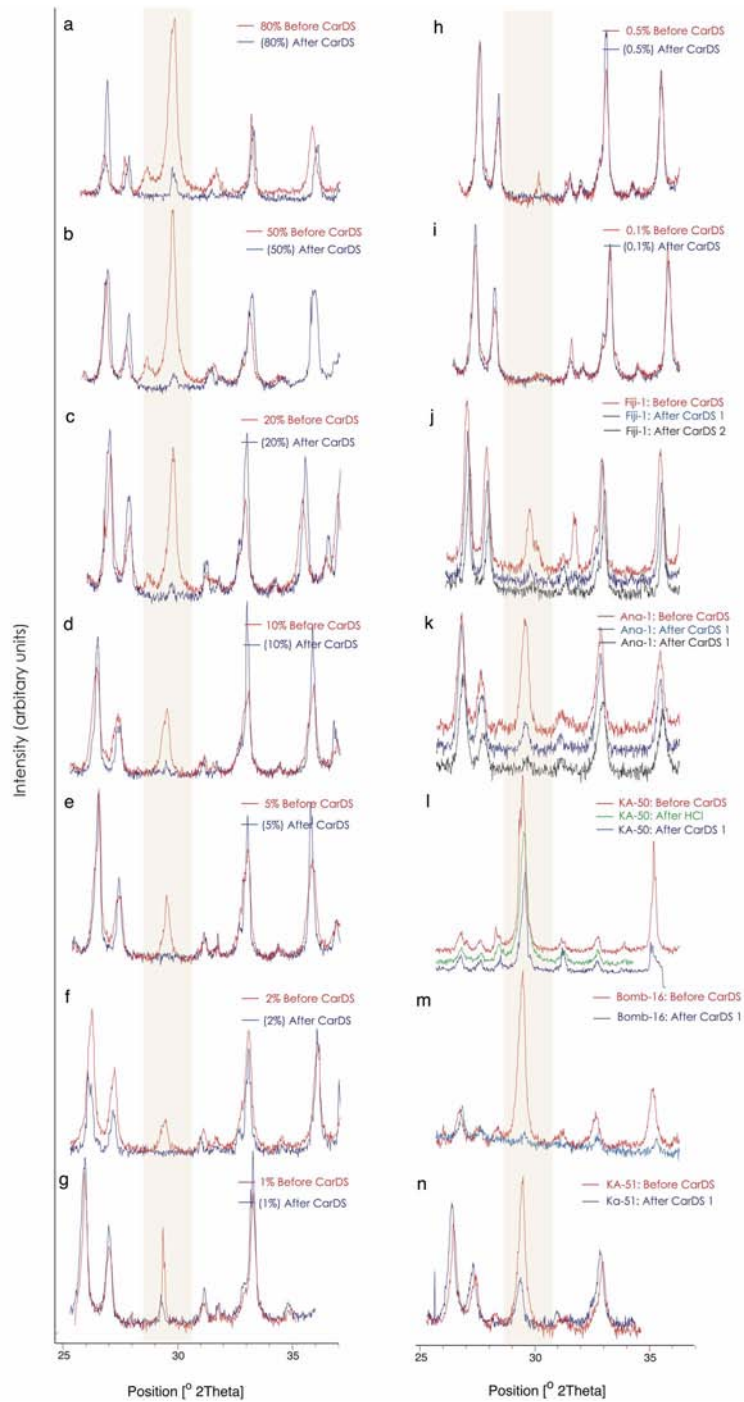


Figure 4 XRD scans of reference material (Group A, a–i) and of archaeological samples (Group B, j–n) before and after separation. Fiji-1 and Ana-1 (j–k) were separated twice. For KA-50 (l), the XRD scan after an HCl step is also included. Note the changes on the highlighted 104 reflection at 29.4° 2θ (calcite) and the 012 reflection at 33° 2θ (aragonite).

Table 1 Five archaeological samples (Group B) were diagnosed with secondary calcite. They were dated using the routine acid hydrolysis method with and without CarDS step (see text for details). The calcite concentration was calculated based on reference standards and the agreement of the dates (before and after CarDS) on  $\chi^2$  test.

Sample ID	Species	Preparation	Calcite %	OxA-	Date BP	$\pm 1 \sigma$	Agreement
Fiji-1	<i>Porites</i> sp.	Normal	7	19284	4499	29	$T = 2.00, \chi^2_{2;0.05} = 5.99$
Fiji-1	<i>Porites</i> sp.	CarDS 1	1	X-2281-21	4498	27	
Fiji-1	<i>Porites</i> sp.	CarDS 2	~0.3	X-2281-22	4450	28	
Ana-1	<i>Anadara</i> sp.	Normal	30	19283	5174	30	$T = 0.89, \chi^2_{2;0.05} = 5.99$
Ana-1	<i>Anadara</i> sp.	CarDS 1	2	X-2281-18	5136	30	
Ana-1	<i>Anadara</i> sp.	CarDS 2	0.9	X-2281-19	5144	30	
KA-50	<i>Glycymeris</i> sp.	Normal	80	X-2290-53	7328	35	$T = 437.8, \chi^2_{1;0.05} = 3.84$
KA-50	<i>Glycymeris</i> sp.	CarDS 1 <sup>a</sup>	60	X-2296-17	8409	38	context ~37 ka BP
Bomb-16	<i>Nassarius incrassatus</i>	Normal	80	19616	32,890	170	$T = 10.83, \chi^2_{1;0.05} = 3.84$
Bomb-16	<i>N. incrassatus</i>	CarDS 1	10	19795	31,840	270	
KA-51	<i>N. gibbosulus</i>	Normal	80	20489	36,790	270	$T = 2.34, \chi^2_{1;0.05} = 3.84$
KA-51	<i>N. gibbosulus</i>	CarDS 1	7	20490	37,430	320	

<sup>a</sup>More separations of KA-50 are underway.

#### KA-50

KA-50 displayed evidence of extreme recrystallization in the form of distinct secondary calcite crystals present within its structure also covering a large portion of its surface (Figure 5). The initial XRD scan showed exceptionally high peaks of calcite (>80%). We attempted to separate the original aragonite from the diagenetic calcite using the CarDS protocol, but only a small improvement was achieved with the calcite phase being reduced to around ~60%. We tried to further decrease the calcite content by acid-etching the shell with mild HCl, which led to 60% mass loss. The XRD scan of this fraction, however, showed no calcite reduction, and the scans before and after HCl etching are identical (Figure 4).

The untreated fraction gave a date of  $7328 \pm 35$  BP (OxA-X-2290-53). The phase that underwent the CarDS protocol dated 1000 yr older, at  $8409 \pm 38$  BP (OxA-X-2296-17, CarDS-1), still substantially younger than the context from which it comes. Further work is underway on this particular specimen.

#### KA-51

Despite a rather good appearance, this sample was identified as containing an extremely large portion (>80%) of calcite. The XRD peak sitting on the  $29.4^\circ$   $2\theta$  angle on the Bragg's scale was broad and of great intensity, typical of recrystallization caused by heating.

A small fragment of the shell was divided in 2 portions: one was directly  $^{14}\text{C}$  dated (OxA-20489:  $36,790 \pm 270$  BP) and the other underwent the CarDS protocol resulting in a reduction of the calcite content from 80% to ~7%. This last fraction was subsequently  $^{14}\text{C}$  dated and gave a statistically identical age to the first (OxA-20490:  $37,430 \pm 320$ ) ( $T = 2.34$ , compared with  $\chi^2_{1;0.05} = 3.84$ ) (Table 1).

#### Bomb-16

Using XRD, this sample was also diagnosed with high levels of diagenetic calcite (~80%) despite a relatively shiny surface. The distinct calcite peak at  $29.4^\circ$   $2\theta$  was extremely broad (Figure 4), as above. A shell fragment of ~200 mg was crushed and 20 mg of powder was dated following the rou-

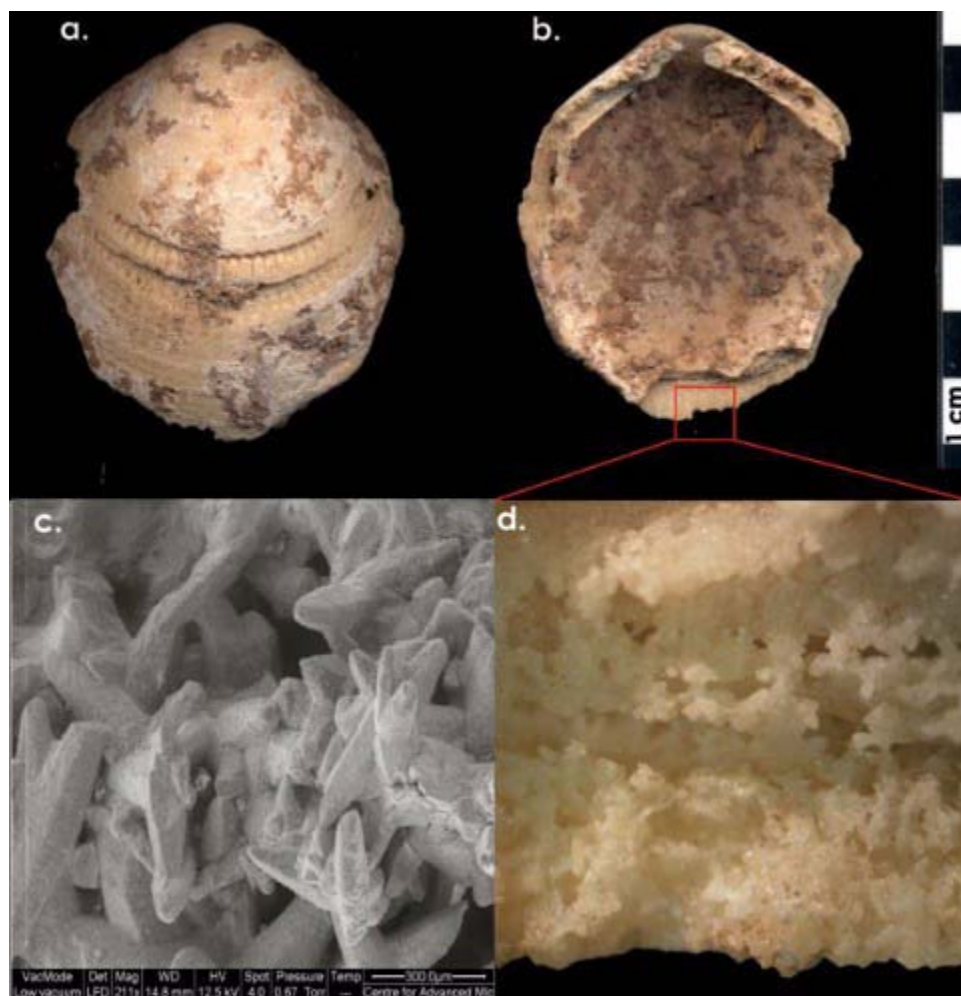


Figure 5 External (a) and internal (b) views of the poorly preserved bivalve shell KA-50; (c) ESEM pictograph of (d) detail of the ventral margin with distinct secondary formed material in the form of single rhombohedral calcite crystals.

tine preparation method for carbonates (Brock et al. 2010) and gave a  $^{14}\text{C}$  age of  $32,890 \pm 170$  BP (OxA-19616). The rest of the material underwent the CarDS protocol, which led to a reduction in calcite concentration from  $\sim 80\%$  to  $<10\%$  and a younger age of  $31,840 \pm 270$  BP (OxA-19795). This is statistically different from the routinely produced one ( $T = 10.83$ , compared with  $\chi^2_{1;0.05} = 3.84$ ) (Table 1). Due to sample size, a second application of the CarDS protocol for further calcite reduction was not possible.

## DISCUSSION

Many early researchers have reviewed the reliability of shell  $^{14}\text{C}$  dates (e.g. Thommeret and Thommeret 1965; Chappell and Polach 1972; Grant-Taylor 1972; Vita-Finzi 1980) and agreed that post-mortem processes are of great importance and require further understanding. Since most of the variables involved in the evolution of these processes (such as geochemistry of diagenetic fluids, pH conditions, or saturation levels) are usually unknown or very difficult to estimate, any theoretical assessment to the effect of post-mortem diagenesis on the  $^{14}\text{C}$  age is rather precarious.

$^{14}\text{C}$  dates for the routinely, non-CarDS pretreated fractions of Fiji-1 and Ana-1 were indistinguishable from the dates of the CarDS-treated fractions despite the initial presence of secondary calcite in both specimens. This leads us to suggest that diagenesis must have occurred at a very early stage of their post-mortem history and/or it took place within a closed system so that the original isotopic signature was not affected. Changes in carbonate mineralogical composition may not be accompanied by isotopic exchange, especially when these occurred in a closed system. In addition, the infilling and replacement processes can be very rapid, even <50 yr (Allison and Pye 1994). If isotopic exchange has occurred so soon after death this will be practically undetectable by  $^{14}\text{C}$  dating.

In cases of extreme recrystallization, such as with sample KA-50, retrieval of the original mineralogical phase is very difficult due to the extensive replacement of aragonite structures and the firm encasement of these relic phases among neomorphic calcite. From our experience with Late Pleistocene-aged material, such cases tend to be rare in the archaeological record and are easy to detect. Although appearance is by no means indicative of the preservation state of a molluscan shell, in extreme situations like that of sample KA-50, specimens with observable overgrowths should be avoided.

The 2 gastropod samples (Bomb-16 and KA-51) yielded very large proportions of calcite, which was rather surprising since both samples appeared well preserved. We suggest that the calcite in these specimens may be derived from a firing event (over 200 °C) rather than a diagenetic process. As mentioned earlier, it is well known that heating over certain temperatures (200–250 °C) causes phase conversions, and we have attested this in the experiments with modern aragonite shells we reported above. The  $29.4^\circ 2\theta$  calcite peaks of the 2 gastropods are very wide at their base, resulting in an unusually large area under the peak (Figure 4: m & n). Since this is not due to sample preparation as the same procedure was followed for all samples, the broadening of the XRD peak, often called “diffuse scattering” (Welberry 2004), must reflect crystal lattice distortions in a relatively poorly ordered calcite. This is a feature typical of crystal growth developed unrestricted by organic matrices, either in diagenetic fronts or during high-temperature/pressure conditions (Gross 1965; Northwood and Lewis 1970; Bell et al. 1998; Foster et al. 2008). It is difficult to establish whether exogenous carbon is incorporated within the calcite structure during heat-induced phase transformation, but we assume that heating degrades any remaining organic material and leaves the carbonate matrix prone to the incorporation of secondary minerals. This is, however, not explicitly attested in our study as only the Bomb-16 CarDS-treated sample gave a younger and statistically different age than the routinely processed one.

Overall, as far as our protocol is concerned, its effect on diagenetic carbonates was checked with XRD and  $^{14}\text{C}$  analysis and the results are encouraging. The method has great potential as a safe and effective way of removing secondary calcite from affected specimens. Application of CarDS to samples that have undergone meteoric diagenesis, such as coral used in the compilation of marine  $^{14}\text{C}$  calibration curves, should add further confidence in the results. According to Reimer et al. (2006), despite the very careful preparation, coral samples normally contain some degree of calcite especially when coming from pre-LGM periods. These authors write: “Fairbanks et al. (2005) and Chiu et al. (2005) insist that a protocol of ‘no detectable calcite’ be adopted as the new standard [by the IntCal group]. This may well be good advice, but doing so would exclude nearly all of the coral data presently available.” The application of CarDS, corroborated by high-precision XRD as routinely used by the IntCal group, may substantially improve the future dating of coral samples and lead to the inclusion of such data sets in future IntCal calibration curves.

## CONCLUSIONS

CarDS is a novel pretreatment protocol enabling the removal of secondary calcite from diagenetically altered corals and molluscan shells prior to AMS  $^{14}\text{C}$  dating. We have demonstrated the successful removal of calcite phases from laboratory-prepared mixtures and from 5 archaeological samples. When coupled with high-precision XRD, CarDS is a powerful tool that ought to improve the dating of carbonate samples, free of the diagenetic contaminants that have plagued this material since the inception of the  $^{14}\text{C}$  method.

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