

## SELECTIVE LEACHING OF SHELLS FOR $^{14}\text{C}$ DATING

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**ABSTRACT.** Although acid leaching of shell carbonates prior to  $^{14}\text{C}$  assay is usually desirable, under some circumstances it can worsen contamination by preferentially dissolving unaltered shell and thus increasing the proportion of secondary carbonate. The risk can be eliminated by monitoring the progress of leaching with the help of microscopy and x-ray diffraction.

Interest in the late Quaternary evolution of marine and lake shorelines continues to grow among palaeoclimatologists, archaeologists, and students of recent crustal deformation. As mollusk shells are the commonest organic material found in strandline deposits their suitability for  $^{14}\text{C}$  dating is an important issue.

Granted that contamination by modern carbon is not always readily detected, careful sample selection and pretreatment can at least minimize the area of doubt by confining the material used for dating to carbonate which gives no indication of secondary contamination. A judicious combination of mechanical cleaning and acid leaching is, in our experience, often successful in removing secondary carbonate and recrystallized shell (Vita-Finzi, 1980). This note draws attention to the need for monitoring the progress of leaching. Samples are often leached until a certain proportion by weight has been removed, on the assumption that contamination is concentrated in the outer parts of the shell and leaching will consequently deal with it. The assumption is not always justified and leaching can make things worse than they originally were.

The commonest sources of shell contamination by younger carbonate stem from replacement of the original shell material by carbonate (usually calcite) and deposition of secondary carbonate coatings or infillings. Its recognition is, of course, not always easy. An existing cavity (such as a tubule) in an aragonitic shell may thus be filled by micritic aragonite and, as Chappell and Polach (1972) have shown, recrystallization can operate in a closed system mode and need not incorporate extraneous carbon. This paper is concerned only with secondary carbonate because it is generally easy to identify by a variety of techniques.

The first stage in the screening of shell samples for  $^{14}\text{C}$  analysis is usually to inspect representative specimens under the light microscope. When the offending cement is on the outside of the unaltered material, the effects of leaching are readily traced by taking peels or thin-sections before and after abrasion and leaching (Vita-Finzi, 1980). Difficulties arise when the section does not intersect all the voids in which secondary carbonate is present, a distinct possibility in the case of lenticular chambers present in some oyster shells (Moore, 1971), as the acid is unlikely to reach the contaminant and the observer is none the wiser. Even if the crack is exposed it is essential to ensure that leaching has removed the infilling rather than the shell (pl 1).

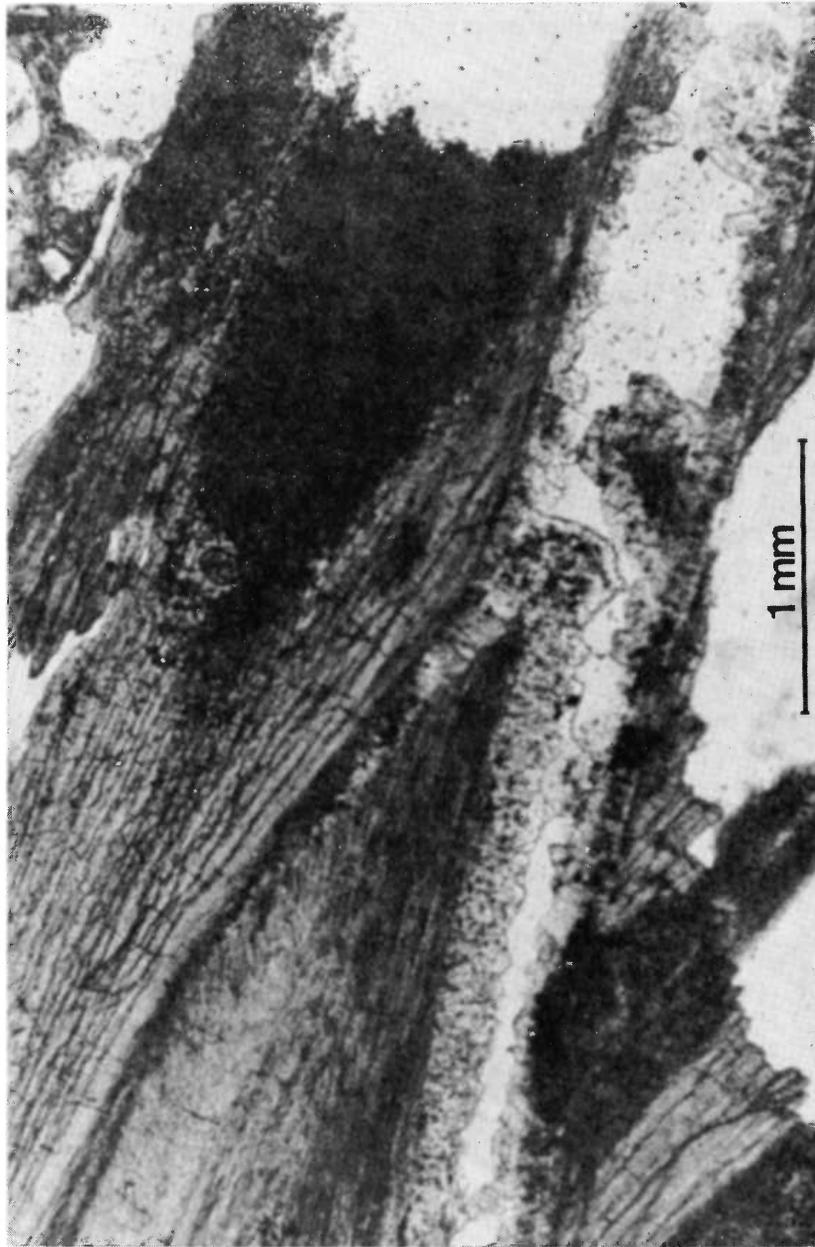
Where the contact between the secondary carbonate and the unaltered shell is not well defined, the success of any pretreatment may need to be checked by scanning electron microscopy, as neither thin sections nor peels lend themselves to high-power inspection in ordinary light. Walker (1979; see also Vita-Finzi, 1980) has illustrated in a specimen of *Oliva* a sharp boundary between neomorphic calcite enclosing relic aragonite lamellae and a zone where the aragonite crossed-lamellar structure has only undergone etching. Plate 2 shows how the SEM can be used to establish the extent of contamination. In the example illustrated the secondary carbonate is confined to the surface and can thus be removed by abrasion and leaching.

X-ray diffraction permits the amount of contaminant to be assessed with ease in the case of shells originally composed of aragonite if (as is usually the case) the cement is calcitic. As only a few mg of samples are required for each analysis, and as the assay is performed easily and quickly, the progress of leaching can be monitored by repeated determinations on the critical part of the shell section (Vita-Finzi, 1980) or on homogenized subsamples representative of the shell as a whole. The latter approach is illustrated in the experiment discussed below.

The material in question comprised bivalve shells of *Dreissena* sp (ca 2cm long) from shoreline sediments of palaeo-lake Konya in south-central Turkey  $^{14}\text{C}$ -dated to ca 20,000 yr BP (for details, see Roberts, 1983). Some of these shells were coated with a secondary calcite cement which had been laid down within and between the shells by percolating meteoric water. If dated along with the shells, the calcite cement would thus have reduced the  $^{14}\text{C}$  age of the sample. Because the unaltered shells consisted of aragonite, it was possible to distinguish them from the secondary (calcite) carbonate by XRD and hence to measure contamination for shell samples subject to different degrees of acid leaching.

Contaminated *Dreissena* shells were broken into fragments 0.5 to 2mm in diameter, homogenized, and divided into subsamples, each weighing 0.4gm. Apart from a few which were left unleached, subsamples were leached in 2 to 10% HCl, the resulting weight loss ranging between 14.8% and 86.6%. After washing, drying, and re-weighing, they were ground to a powder for ca 2 minutes in a mortar and pestle. The ground subsamples were each analyzed by XRD, using  $\text{Cu-K}\alpha$  radiation over  $2\theta$  angles between  $20^\circ$  and  $31^\circ$ . This range incorporates the first-order peaks of both aragonite ( $26.24^\circ$ ) and calcite ( $29.49^\circ$ ). From the resulting chart traces, the heights of the aragonite and calcite peaks were calculated, duplicate traces being obtained whenever possible. The peak heights provide values for the proportion of calcite in each subsample, and therefore also for the percentage of secondary contamination. In the ratio used ( $R_1$  of Milliman, 1974), a value of 1.0 indicates 100% aragonite and zero contamination, and lower values represent increasing per cent of calcite and of contamination, 0.0 indicating 100% calcite. The maximum accuracy of peak intensity analysis is ca  $\pm 1\%$ .

## PLATE 1



Calcite crystals partially filling cavity in *Ostrea* sp (sample CBIU). Note how leaching has removed foliated shell in lower right but spared the infill. Scale bar measures 1mm.

PLATE 2



Scanning electron micrograph of cross-lamellar aragonite in *Spondylus gaederopus* (sample G82/601). Secondary carbonate is absent from the tubule (lower right) and confined to the surface (eg. lower center). Scale bar measures 10 $\mu\text{m}$ .

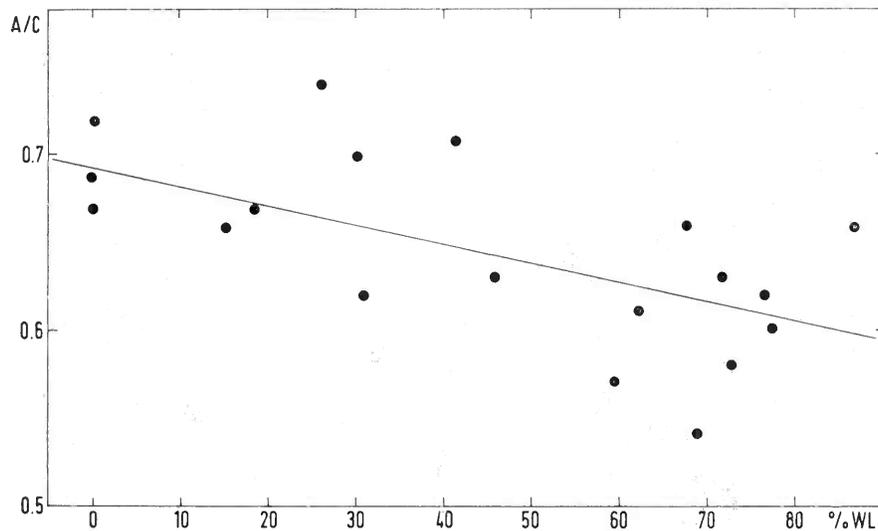


Fig 1. Relationship between % of weight loss by leaching (WL) and aragonite/calcite ratio by the peak intensity method (A/C).  $r = -0.63$ ,  $n = 19$ .

As leaching is designed to reduce contamination, it should be positively correlated with the aragonite/calcite ratio. The *Dreissena* shells analyzed gave a weak negative correlation of  $-0.63$  between per cent weight loss by acid leaching and this ratio (fig 1). Unleached samples had  $R_1$  values ca 0.7, and these fell to 0.6 at ca 80% leach. In other words, the secondary calcite cement was more resistant to acid than the original shells, and leaching increased the proportion of contamination. For samples such as these, pretreatment should consist of mechanical cleaning and leaching of individual shells after hand sorting. The operation is tedious but is rewarded by confidence in the  $^{14}\text{C}$  date.

#### ACKNOWLEDGMENT

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