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## Organic protection of aragonite in Recent dune sands

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The carbonate-rich sands of north Cornwall are well known. Sand from the Camel estuary was exploited for manure at the rate of 100,000 tons per annum in the 1830s (de la Beche 1839). Storms as recent as that in 1869 (Salmon 1973) have provided substantial carbonate debris for dune deposits in addition to that supplied by daily sedimentation. In the construction industry, the high content of skeletal debris restricts the use of dune sand to mortar work. However, mixed with seaweed it has proved effective as an agricultural conditioner in acid soils (Goode and Taylor 1988). Dune sands from the St Minver district and at Upton Towans were examined to establish the carbonate mineralogy and geochemistry as well as the implications of physico-chemical weathering in a vegetated, stable dune environment.

Molluscs dominate the skeletal component of dune sands of south-west England, and similarly, the shore and estuarine sands from which the dunes are derived. Layers of organic

matrix between the crystalline layers of molluscs are known to give the shells greater flexibility during impact (Wainwright 1969). Generally, the crystalline layers are composed of either low-Mg calcite (LMC), aragonite, or both carbonate types. Cirriped tests contribute LMC; bryozoan, echinoderm, sponge spicules, decapods and algal remains, high-Mg calcite (HMC) to the sediments. Foraminifera also occur.

This association is characteristic of temperate-water carbonates (Lees and Buller 1972). Most particles (87%) of dune sand from this study passed through a 500 $\mu$ m sieve. The fine sand fraction (250-125 $\mu$ m) from the St Minver area proves most abundant at 53% of the total sand deposit. 66% of the fine sand is carbonate. Coastal dune sand from Upton Towans proves coarser than at St Minver. Although 97% passed through a 500 $\mu$ m sieve, the medium sand fraction (500-250 $\mu$ m) is the most abundant at 59%, of which 78% is carbonate (Fig. 1).

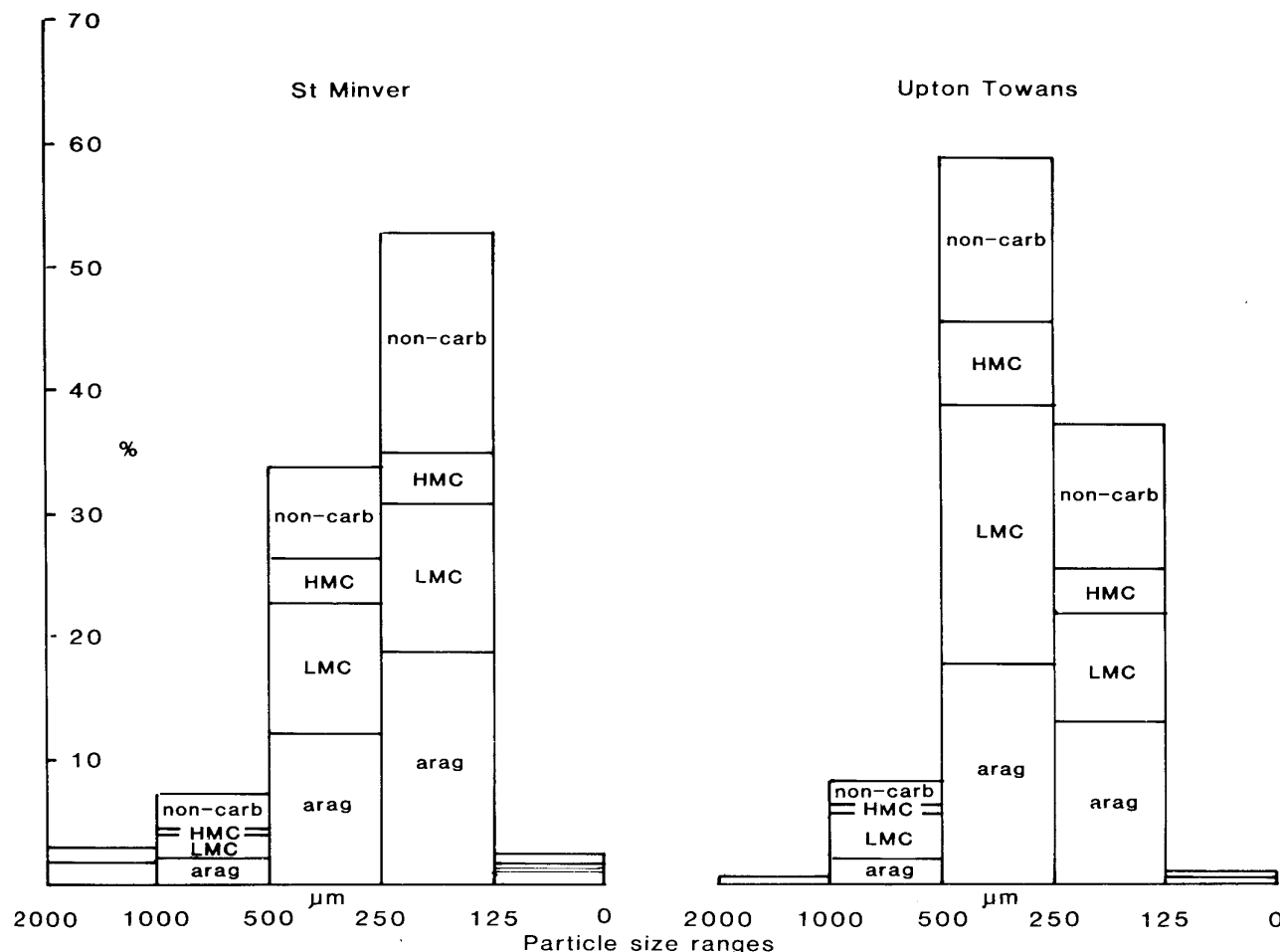


Figure 1. Carbonate mineralogy and particle size distribution in dune sands from St Minver and Upton Towans. In both examples the aragonite increases relative to low-Mg and high-Mg calcite as particle size decreases.

Table 1. Comparison of carbonate mineralogy from dune, estuary and coastal sands of north Cornwall.

	total carb.	aragonite	LMC	HMC
St Minver dunes	46-66	41-57	35-44	6-15
Camel estuary	30-62	44-64	28-38	9-18
coastal	65-79	41-48	37-41	15-18
Upton Towans	66-73	43-51	34-42	12-18

Total carb. is expressed as % of <500 $\mu$ m fraction. Carbonate mineralogy is given as % of carbonate component.

Total carbonate levels were determined gravimetrically by difference after 1M acetic acid attack. The total carbonate range from St Minver sands is from 46-66% with a mean of 56%. The carbonate range at Upton Towans is 66-73% with a mean of 71%. Samples ground in a ball mill were pelleted and analysed for carbonate minerals by X-ray diffraction (XRD). Standardisation was against mixtures of biogenic calcite/aragonite. Aragonite values from St Minver range from 41-57%, LMC 35-44%, and HMC 6-15% (Table 1). The aragonite range at Upton Towans is 43-51%, LMC 34-42% and HMC 12-18%. Estuarine sands from the Camel give a similar range of 44-64% aragonite, 28-38% LMC and 9-18% HMC (Merefield 1982). Intertidal shore sands from Constantine and Watergate Bays (NGR SW855746 and SW838650) have reported aragonite levels of 41.48%, LMC 37-41% and HMC 15-18% (Merefield 1984). Notably, aragonite values in the dune sands increase landwards away from the estuary and source area. The HMC concentrations decrease landwards in contrast.

Mg, Sr and Na were determined by flame emission on the acetic acid leachate. Mg concentrations from 2895-5699ppm Mg, compute to a range of 5616-8661ppm Mg on a 100% carbonate basis. They prove lower than values from intertidal estuarine sands of the Camel estuary with similar HMC, and a range of 9050-11,100ppm Mg. Sr

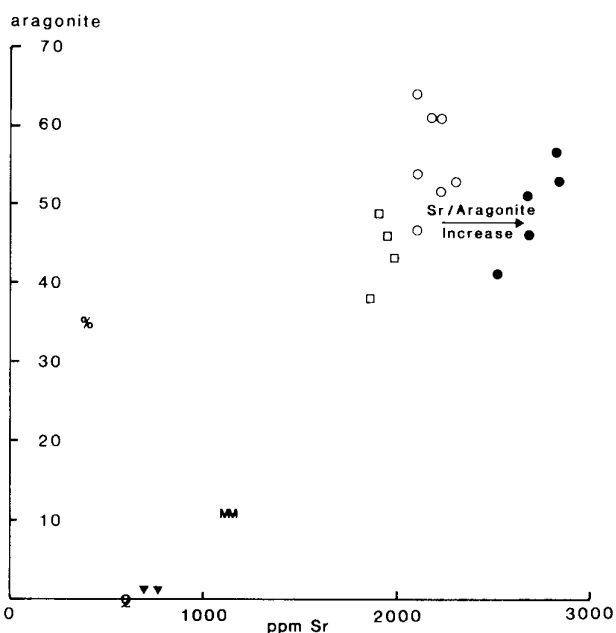


Figure 2. Aragonite/Sr relationship in dune (black dots), estuarine (open circles) and coastal beach sands (open squares). Raised beach deposits (black triangles) and analyses of *Mytilus edulis* (M) and *Ostrea* (Q), are also plotted to show the relationship at low and zero aragonite levels. The increase in Sr results from humic acid attack on bivalve debris.

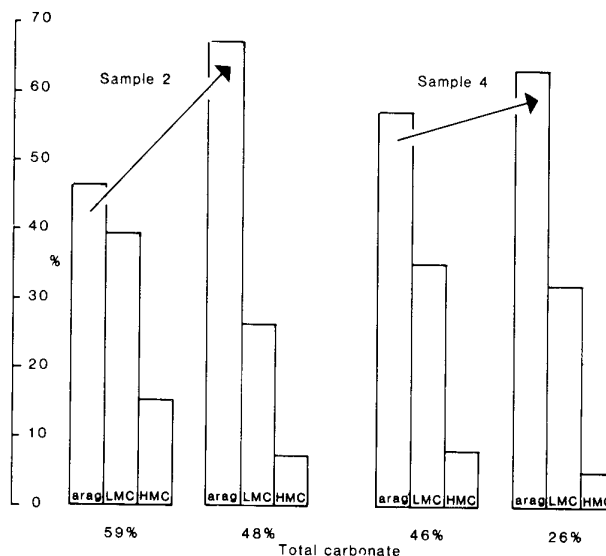


Figure 3. Results of 1M acetic acid attack on two samples of sands 0.3km (2) and 1.5km (4) from the shoreline of the Camel estuary. In each case aragonite increases relative to calcite (LMC and HMC). The rate of increase is less in sample 4 as humic acids have already destroyed some calcite in the dune-soil environment.

concentrations of the dune sands range from 1300-1680ppm Sr and compute to a range of 2553-2802ppm Sr on a 100% carbonate basis. When plotted against aragonite values they prove higher than Camel estuary data with similar aragonite concentrations (Fig. 2). Sodium levels from St Minver decrease from the shore of the Camel estuary landwards from 0.7% to 0.5% Na.

Samples of dune sand from two sites at St Minver were attacked with 1M acetic acid for 15 hours. They were then washed, ground and pelleted for XRD analysis. In both cases aragonite increased at the expense of LMC and HMC (Fig. 3). Significantly, the rate of increase proved more from sampling point 2, about 0.3km from the present shoreline of the Camel estuary, than from sampling point 4, about 1.5km from the shoreline.

Samples of inorganic calcite and aragonite were crushed and sieved to provide material for an "artificial" or non-biogenic carbonate sand. This sand was split into two sub-samples. One was ground and pelleted for XRD, the other was acid-treated before grinding and pelleting. The 1M acetic acid treated sample lost one third by weight of carbonate. In contrast to the biogenic carbonate experiments, however, this acid-treated sample retained an identical calcite/aragonite ratio (peak heights cps) of 7.4 to the untreated split.

Increasing values of aragonite and Sr concentration landwards in the dune sands from the St Minver area suggest that aragonite is protected in the humus-rich zone. It has long been known that Sr substitutes for Ca in aragonite (Noll 1934), and that when aragonite converts to calcite there is less lattice space for the large Sr ion (radius 1.12 $\text{\AA}$ ) which is lost. This is demonstrated where Pleistocene raised beach material at Trebetherick Point, Cornwall (NGR SW926781), formerly similar to present-day beach sands, now contains a low-Mg calcite (West 1973) and shows a two-thirds loss of Sr (Merefield 1984). Mineralogical and geochemical components are not uniform throughout the shell layers. For example, Hallam and Price (1968) showed the inner layer of *Cardium edule* to contain about two-thirds (0.21%) the Sr of the outer layer (0.32%). However, in skeletal debris inner and outer layers of former shells are exposed equally to environmental effects. Humic acids in these vegetated areas are potential agents for dissolution. The laboratory experiments show that aragonite increases with acid attack on the sand grains. This implies that either the aragonite

structure or inter-layer organic matter is protecting the carbonate. Acid treatment of inorganic mixtures, showing no change in calcite/aragonite ratios, supports the view that the structural differences do not play a role.

Dune sands of south-west England have a similar carbonate mineralogy and geochemistry to local shore and estuarine sands. Where soils have developed there is evidence of preferential aragonite protection. Laboratory experiments show that the aragonite of the skeletal assemblages survives acid attack better than HMC and LMC. The importance of organic layers in the protection of aragonite (present in the natural sand grains but not in the inorganic mixtures of laboratory experiments) is emphasised. This suggests that biogenic aragonite is able to withstand weathering better than calcite in vegetated dunes as a result of organic protection.

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