Brown Pelican Eggshells: X-Ray Diffraction Studies

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There is considerable current interest concerning the effect of the metabolites of DDT (1, 1, 1 - trichloro - 2, 2 - bis (p - chlorophenyl) ethane) upon the eggshells of certain raptorial and fish-eating birds. Much has been written on the cause and effect relationships between DDT and the thinning of eggshells of these vertebrates which, like man, are at the top of the food chain (1-12). No attempt will be made here to summarize this work except to indicate that the evidence appears conclusive that small doses of persistent pesticides, such as chlorinated hydrocarbons, have had significant effects. The Brown Pelican (Pelecanus occidentalis) has shown dramatic population declines in North America, particularly in the States of California, Texas, Louisiana and more recently, South Carolina. In California for example, the Brown Pelican is no longer considered a breeding species.

Much of the problem manifests itself in the thinning of the pelican eggshell. Thinning and breakage of the eggshell is believed to be the result of inhibition of carbonic anhydrase by DDT and its metabolites. During the last decade most investigators have characterized these eggshells by the criteria of weight loss and decrease in shell thickness. Recently, McFarland, Garrett and Nowell (2) have made a scanning electron microscopy study of normal and thinned eggshells, but to my knowledge, no x-ray diffraction comparisons have yet been made. In this report, I will describe some recent x-ray diffraction results which have been obtained from thick and thin pelican eggshells.

Eggshells from Anacapa Island, California, several locations in South Carolina, and Florida are compared in this study. Samples of eggshells were separated from the membrane and ground by hand in an alundum mortar to a particle size of approximately 200 mesh. Grinding was done carefully for a period of 1-2 minutes to avoid phase transformation problems (13,14). It was shown* that no changes in relative phase concentration occurred as a result of the grinding. The sample powder was then

* A Florida Brown Pelican eggshell was ground for periods of 2, 4, 6 and 8 minutes. The measured x-ray diffraction patterns showed no appreciable differences in the calcite, aragonite and vaterite line intensities.

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coated on a glass slide with collodion and amyl acetate and examined in a Norelco diffractometer using nickel filtered copper kα radiation, a scintillation detector and pulse height selection (15,19). Samples of unground Florida and Anacapa Island eggshells were also examined using a pinhole diffraction technique to observe any gross differences in the grain size of the crystalline eggshell material. The diffracted intensities from the powders were measured from a strip chart recorder and the eggshells were found to contain several polymorphs of calcium carbonate, namely: calcite, hexagonal (rhombohedral), a = 4.98Å, c = 17.062Å, ρ = 2.711 (16), aragonite, orthorhombic, a = 4.9598Å, c = 5.7379Å, ρ = 2.93 (17) and vaterite, hexagonal, a = 7.135Å, c = 8.524Å, ρ = 2.56 (18). The initial x-ray diffraction comparison between the Florida Brown Pelican eggshell (thickness 0.495 mm) and a very thin Brown Pelican eggshell (0.150 mm) obtained from Anacapa Island (March, 1969) indicated several distinct differences. The Florida eggshell contained calcite, aragonite and vaterite present in amounts not exceeding 3 to 5% each. The Anacapa Island egg, on the other hand, contained only calcite and aragonite (3-5%). In addition, it was shown by observing the line profile broadening of the ($11\bar{2}3$) calcite line that the Florida egg had a coherently diffracting domain size (D_{eff}) of 1480Å compared to 835Å for the California egg. These domain sizes were measured with a simple Scherrer (19) analysis technique. Fourier analysis of the line profiles is currently in progress in order to make a more detailed study of this line shape change. The pinhole diffraction patterns made from pieces of the unground eggshells showed that grain size of the California eggs was larger than the grain size of it's Florida counterpart although no quantitative differences have been established at this time. Additional studies were made on a series of Brown Pelican eggs obtained from both South Carolina and Florida locations (8). These results are summarized in Table 1 where the calcite, aragonite and vaterite absolute intensities are indicated as well as the ratios calcite/aragonite, calcite/vaterite and aragonite/vaterite. Note that the thickness measured includes shell plus membrane.

It is suggestive from Table 1 that differences do exist in the mineral composition of eggshells obtained from different locations. To date, it is only suggestive that presence of vaterite is associated with relatively unaffected eggshells and that an increase in the calcite to vaterite line ration might be indicative of a potential problem in eggshell breakage.

(Table 1 is on following page.)

TABLE 1

X-RAY DIFFRACTION LINE INTENSITIES AND INTENSITY RATIOS FOR POLYMORPHS OF CALCITE FOUND IN BROWN PELICAN EGGSHELLS

Sample Identity	Diffracted Intensities*			Intensity Ratios			
	Calcite d=3.88Å	Aragonite d=3.386Å	Vaterite d=3.318Å	Calcite / Aragonite	Calcite / Vaterite	Aragonite / Vaterite	Thickness of Shell (mm)
Cocoa Bch., Fla.	49	26	26	1.88	1.88	1.0	.495
Anacapa, Calif.	44	21	NONE	2.10	∞	∞	.150
Pelican Isl., Fla.	53	28	15	1.89	3.53	1.8	.47
Cape Romain, S. C.	47	23	9	2.04	5.23	2.56	.37
	44	16	NONE	2.75	∞	∞	.45
	42	16	10	2.62	4.20	1.6	.41
Cedar Key, Fla.	52	23	15	2.26	3.46	1.53	.58
Matlacha, Fla.	58	20	20	2.90	2.90	1.0	.59
Buchanan Key, Fla.	34	15	3	2.27	11.3	5.0	.55
Deveaux Bank, S. C.	44	20	13	2.20	3.39	1.54	.45
	39	18	6	2.16	6.50	3.0	.46

* Peak minus background in chart units.

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Summary

X-ray diffraction studies of Brown Pelican eggshells from various localities in North America have shown that the crystalline shell material consists of three calcium carbonate polymorphs, calcite, aragonite and vaterite. The data suggest that thin eggshells show a high calcite to vaterite ratio compared with thicker Florida shells.

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