

High-Purity Calcium Carbonate in Freshwater Clam Shell

Abstract. *The calcium carbonate in freshwater clam shells is similar in purity to that designated reagent grade. A simple reprecipitation of the shell extract results in a product having less Sr and Mg than reagent grade CaCO₃. Clams are harvested commercially, and discarded shells are a high-quality raw material for the production of CaCO₃.*

Biogeochemical prospecting is a generally accepted technique based on an anomalous distribution in the environment of chemical elements created by organisms. Most investigations have been concerned with abnormal chemical concentrations in plants or plant parts (1). Utilization of knowledge of biogeochemical relationships among plants and their environment has obvious economic implications in locating subsurface ore deposits. Another facet of biogeochemistry that may be of economic importance is the metabolic discrimination against trace elements in biogenic calcareous materials. The biogenic materials, such as clam shell, are a renewable natural resource rather than an exhaustible one, such as ore bodies. The purpose of this paper is to compare trace element concentrations in commercially available reagent grade CaCO₃ with those deposited in freshwater clam shell and to suggest clam shell as a possible commercial source of CaCO₃.

The distribution of stable Sr in clam shells was studied in connection with the behavior of ⁹⁰Sr in the Clinch and Tennessee rivers (2). Because of the low Sr concentration in freshwater clam shell, a new analytical technique was developed to measure accurately Sr concentrations in calcareous material (3). When Sr concentrations in unpurified clam shell and reagent grade CaCO₃ were compared, it was apparent that CaCO₃ from clam shell was of equal or better purity.

The clam shells were ashed in a muffle furnace at 800°C for 2 hours. A portion (1 to 5 g) of the ash was transferred to a 250-ml beaker and dissolved in 2M HCl. The solution was transferred to a 100-ml volumetric flask and diluted with water to calibrated volume. Portions were taken from this solution and element concentrations were determined by flame emission spectrophotometry (Table 1). All data were confirmed by an emission spectrographic method (4).

Table 1. Flame conditions for the determination of trace elements. Instrument: Jarrel-Ash flame spectrophotometer and modified ORNL 1887A power supply. Multiplier phototube: RCA, 1P28 for all elements except potassium; ITT-FW-118 for potassium. Fuel gases: oxy-hydrogen. Aspirating media indicated by italics.

Element	Wave Length (mμ)	Concentration (μg/ml)	Ref.
<i>0.001M HCl</i>			
Li	670.8	0.1-0.5	(13)
Na	589.0	0.1-0.5	(13)
K	766.5	0.1-0.5	(13)
<i>10 percent glycerol; 0.1M HClO₄</i>			
Mg*	285.2	0.5-2.0	(13)
Ca	422.7	1-5	(14)
Sr	460.7	0.1-0.5	(3)
<i>50 percent acetone; 10 percent glycerol; 0.1M HClO₄</i>			
Mn	403.1	0.1-0.5	(13)
<i>60 percent acetone; 10 percent glycerol; 0.1M HClO₄</i>			
Ba	553.6	0.4-2.0	(15)

* Concentrations less than 0.5 were determined by atomic absorption spectrophotometry.

The CaCO₃ (clam shells) was purified by neutralization of the solution (pH 7 to 8) with ammonia gas or ammonium hydroxide and then filtered if any precipitate was formed. Solid ammonium carbonate was added to the solution to precipitate the Ca as CaCO₃. The precipitate (CaCO₃) was washed with a saturated solution of ammonium carbonate and dried at 130°C for 2 hours. The product was white, finely powdered CaCO₃.

Table 2. Trace element concentrations in clam shells, reagent grade calcium carbonate and river water.

Sample	Sr	Mg	Ba	Mn	Li	Na	K	Ca
<i>Micrograms per gram</i>								
Lot 1*	229	30	84	262	<0.2	1700	11	
Lot 3†	147	21	71	486	<0.2	1900	5	
Lot 3A‡	110	<10	36	<5	<0.2	560	4	
Reagent grade CaCO ₃ §	174-1500	55-1500	7-40	<5	<0.2	130-700	2-5	
<i>Micrograms per milliliter</i>								
River water TRM 591.8	0.063±0.014	5.5±2.8				9.5±3.7	1.3±0.4	21±5
River water CRM 14.4 ¶	0.069±0.009	7.7±1.0	0.027±	0.004±		2.4±0.5	1.3±0.2	21±2

* *Elliptio crassidens*, collection site, Tennessee River mile (TRM) 521. (River miles are measured from the mouth of the river.) † *Quadrula pustulosa*, collection site, Clinch River mile (CRM) 16. ‡ Purified *Quadrula pustulosa*. § Range of results obtained on eight lots of CaCO₃ from three manufacturers. || Weekly samples for 28 months (16). ¶ Weekly samples for 58 weeks (16). # Average of two analyses.

Table 3. Biological fractionation ratio of the element to calcium in the shell divided by that in the environment, of trace elements in shell deposition.

Clam	Sr	Mg	Ba	Mn	Na	K
<i>Quadrula pustulosa</i>	0.112	0.000143	0.138	6.38	0.0416	0.0202
<i>Elliptio crassidens</i>	.191	.000286			.939	.0444

Strontium concentrations in eight different lots of reagent grade CaCO₃ were variable (Table 2) and Sr concentrations in the better commercial products were similar to clam shell. Magnesium concentrations in clam shell were lower than in the prepared chemicals. Otherwise, the ashed clam shell contained slightly greater quantities of Ba and K and much higher concentrations of Mn and Na. In all instances Li concentrations were below the limits of detection by either flame spectrophotometry or emission spectrography.

The purified clam shell (lot 3A) was equal to or better than reagent grade chemicals in all respects. The simple purification procedure was particularly effective in reducing the Mn and Na concentrations to those in reagent chemicals. The CaCO₃ deposited by clams has less Mg than any of the reagents tested, and the precipitation procedure resulted in a considerably better product. Clam shells were used as a raw material for the preparation of a reagent standard CaCO₃ having < 2 μg of Sr per gram. Also, the shell material was used in emission spectrography for standards having low Mg concentrations.

An element having biogeochemical significance either must be required for the metabolic activities of the organism or must occur in the organism in greater concentrations than in the environment (5). With all elements a higher concentration exists in the shell than

in the river environment (Table 2), and classically all elements in the shells would have biogeochemical significance. Ashed clam shell is essentially pure CaCO_3 and contains 40 percent Ca or 1.9×10^4 times the Ca concentration in water from the Clinch and Tennessee rivers. However, of greater interest is the discrimination during concentration against several elements with respect to Ca.

Discrimination in deposition results in a biological fractionation of the elements relative to Ca between the environment and the shell (Table 3). Biological fractionation of the several elements is a reflection of physiological processes related to shell deposition. Each element shows a similar distribution between the shell and the environment for both species although the factors are somewhat smaller for *Quadrala pustulosa*. The fractionation factors for Sr and Na are similar to those for contemporary marine mollusk shells (6). Comparatively, about one-tenth as much Ba occurs in the freshwater mollusks as in the marine forms. Manganese, having a concentration factor of 1.2×10^5 , is the only element with a greater concentration in the shell relative to Ca.

Biological fractionation results in a calcareous material that is quite pure initially. A simple chemical precipitation results in a CaCO_3 that compares favorably with available commercial products. The analytical data from clams (Table 2) are from composite sample^c of eight *Elliptio crassidens* and 12 *Q. pustulosa* shells. Previously, over 200 individual clams of 16

species from the Clinch and Tennessee rivers were analyzed for Sr (7). *Anodonta corpulenta* specimens contained the highest Sr concentrations, *Q. pustulosa* the lowest, and *E. crassidens* was typical of the remainder. While some variation in chemical composition within individuals of a species was observed, these variations were generally small (8). Strontium concentrations were related directly to growth rate in some species and with *A. corpulenta* the Sr concentrations were higher in the older individuals. The CaCO_3 in all unionid clams that have been examined is aragonite (9); consequently mineralogy is not a factor in the observed differences in chemical composition.

The freshwater clam fauna is restricted primarily to rubble-gravel-sand bottoms (10). Most species are found together in the suitable habitats and are harvested indiscriminately by crowfoot brails dragged across the river bottom. The harvested shells are considered essential to the cultured pearl industry (11). Annual yields of high quality shells have ranged from 5,000 to 10,000 tons, but recently yields decreased because of overfishing, pollution, or siltation of the habitats.

Large quantities of shells are harvested and discarded because they have undesirable color or structural characteristics for the pearl industry. The discarded shells have desirable chemical qualities, *E. crassidens* being an example. The suggestion of using a biogenic calcareous substance as a raw material in manufacturing is not unusual (12), although production of a high quality chemical reagent from these shells would be unique. Current research

(11) on the life histories and management of this valuable, renewable natural resource is indeed opportune.

D. J. NELSON

Health Physics Division, Oak Ridge National Laboratory,
Oak Ridge, Tennessee

T. C. RAINS*

J. A. NORRIS†

Analytical Chemistry Division,
Oak Ridge National Laboratory,
Oak Ridge, Tennessee

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- * Present address: National Bureau of Standards, Washington, D.C.
† Baird-Atomic, Inc., Cambridge, Mass.

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