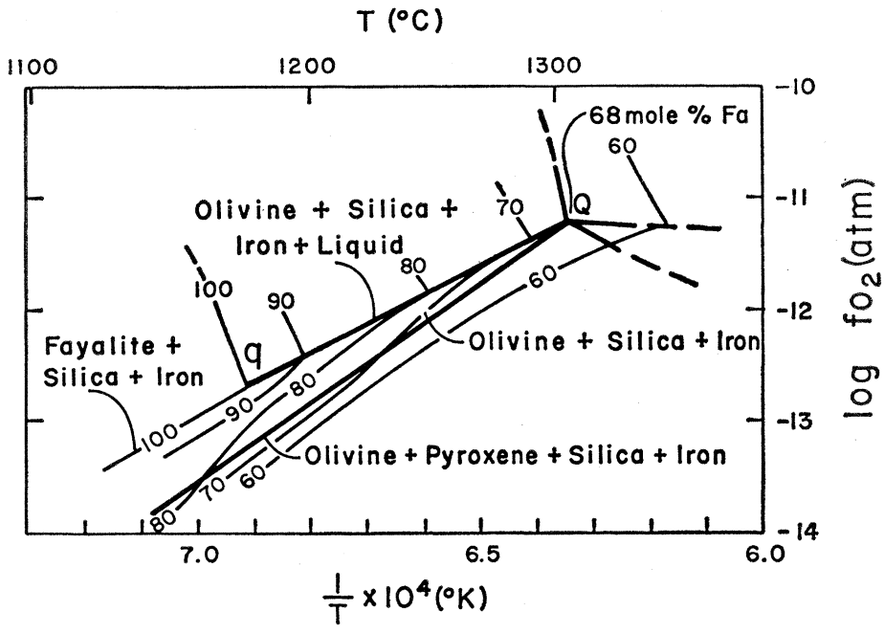

Fig. 2. Composition of olivine (mole percent of fayalite) in portions of the T-fO_2 projection for the various assemblages in Fig. 1. Unlabeled boundary curves and other information are defined in Fig. 1.

the oxidation of metallic iron to Fe^{++} per gram-atom of oxygen is 63 kcal (*4*). Thus, the addition of less than 2 gram-atoms of oxygen, changing the bulk composition, provides enough heat of oxidation to exceed the heat of fusion for the new bulk composition.

This phenomenon will exist up to the pressure for the stability of ferrosilite in the assemblage fayalite + silica + iron + liquid, determined to be at 17.5 kbar total pressure (*5*) and represented for comparison with the relations at 1 atm total pressure by the point q' in Fig. 1. The points Q and q move towards q', which is an invariant point in the limiting ternary Fe-Si-O, with increasing pressure as the amount of Fe^{++} in the pyroxene phase increases to $FeSiO_3$. The spatial relations of the assemblage olivine + silica + iron + pyroxene to olivine + silica + iron + liquid are expected to remain similar, that is, a portion of the stability field olivine + silica + iron remains on the high-temperature side of the curve Q-q. The stability field of olivine + silica + iron disappears under pressures greater than 17.5 kbar.

The phenomenon described could be expected to be present in a two-metal–oxide–silicate system, where the oxidation of the metal is exothermic, if at least one of the metals present has a variable oxidation state and the composition of the silicate phase becomes enriched in that metal with cooling. Metals such as Ni, Co, and Mn could be expected to show similar behavior. This type of process and the energies involved should be considered in any discussion of reactions where metallic iron or possible Fe-Ni-Co-Mn alloys coexist with ferromagnesium silicates. An immediate suggestion is that the apparent localized melting in meteorites with little or no obvious sources of radioactive heat might possibly be caused by this process.

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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 $CaCO_3$. Clams are harvested commercially, and discarded shells are a high-quality raw material for the production of $CaCO_3$.*

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 $CaCO_3$ with those deposited in freshwater clam shell and to suggest clam shell as a possible commercial source of $CaCO_3$.

The distribution of stable Sr in clam shells was studied in connection with the behavior of ^{90}Sr 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 $CaCO_3$ were compared, it was apparent that $CaCO_3$ 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 2*M* 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*).

The $CaCO_3$ (clam shells) was purified by neutralization of the solution (*p*H 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 $CaCO_3$. The precipitate ($CaCO_3$) was washed with a saturated solution of ammonium carbonate and dried at 130°C for 2 hours. The product was white, finely powdered $CaCO_3$.

Strontium concentrations in eight different lots of reagent grade $CaCO_3$ 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 $CaCO_3$ 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 $CaCO_3$ having $< 2\ \mu g$ 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).

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: oxyhydrogen. Aspirating media indicated by italics.

Element	Wave length ($m\mu$)	Concentration (μg/ml)	Ref.
	0.001M HCl		
Li	670.8	0.1–0.5	(*13*)
Na	589.0	0.1–0.5	(*13*)
K	766.5	0.1–0.5	(*13*)
	10 percent glycerol; 0.1M $HClO_4$		
Mg *	285.2	0.5–2.0	(*13*)
Ca	422.7	1–5	(*14*)
Sr	460.7	0.1–0.5	(*3*)
	50 percent acetone; 10 percent glycerol; 0.1M $HClO_4$		
Mn	403.1	0.1–0.5	(*13*)
	60 percent acetone; 10 percent glycerol; 0.1M $HClO_4$		
Ba	553.6	0.4–2.0	(*15*)

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

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 *Quadrula 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 samples 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 to-

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

Sample	Sr	Mg	Ba	Mn	Li	Na	K	Ca
				Micrograms per gram				
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	
				Micrograms per milliliter				
River water TRM 591.8 ‖	0.063±.014	5.5±2.8				9.5±3.7	1.3±0.4	21±5
River water CRM 14.4 ¶	0.069±.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 $CaCO_3$ 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
Quadrula pustulosa	0.112	0.000143	0.138	6.38	0.0416	0.0202
Elliptio crassidens	.191	.000286			.939	.0444

gether 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.

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Epinephrine: Cascade Reactions and Glycogenolytic Effect

Abstract. *The concept of a cascade reaction may serve to indicate the underlying chemical similarity between several biological amplification processes, and as a basis for the formulation of units that emphasize amplification phenomena in reaction kinetics. This approach is discussed in relation to the glycogenolytic effect of epinephrine.*

Blood coagulation has been represented by Macfarlane (*1*) as a cascade reaction that can provide a series of amplifications of a weak initial stimulus; by Davie and Ratnoff (*2*), as a waterfall sequence. Wald (*3*) has drawn an analogy between blood coagulation and visual excitation and has suggested that amplification systems of this type may occur elsewhere in living systems.

Elevation of blood glucose by epinephrine is now known to be associated with a rather complex chain of events that connects the hormone and the glycogenolytic enzyme phosphorylase (*4*). The events divide into at least five stages, in four of which a chemical agent acts by influencing the rate of a reaction whose product is an agent that influences the stage immediately following. There is some justification for classification of these events as a cascade amplification system and for their arrangement in the form of Fig. 1. First, the same physiological necessity for amplifying a weak signal exists here as in blood coagulation or vision; and second, three of the individual stages are similar to the conversions of proenzyme to enzyme that occur in blood coagulation.

However, in the phosphorylase system there are additional complications: First, various agents, such as 5′-adenosine monophosphate (5′AMP), glucose-6-phosphate, and adenosine triphosphate (ATP), that are not produced specifically in response to the original hormonal stimulus also act by influencing one or more of the enzymic stages; they appear to act for control systems that are distinct from or complementary to the hormones. At the phosphorylase stage, for instance, 5′AMP acts by stimulating the activity of phosphorylase *b* (*5*), thus producing the same effect as epinephrine but at the same time decreasing the amplification of a hormonal signal to the extent that it may have no effect on the production of glucose from glycogen; calcium and a kinase-activating factor act similarly at the kinase stage (*4*). Second, 3′5′AMP appears to act as a 'second messenger' for various hormones other than epinephrine, as an agent to accomplish either the same end (as with glucagon and the elevation of blood sugar) or different ends [as with vasopressin (*6*)]. However, if we consider the glycogenolytic response to epinephrine as an isolated (and well documented) system, it appears that the cascade manner of arrangement may be acceptable as an indication of the chemical similarity between this and several other biological amplification systems.

The question then arises of an appropriate unit to be used in describing amplification at each stage. The number of molecules of product obtained in unit time, in response to one molecule of the agent influencing the enzymic reaction, appears to be one way of expressing the information required. Although enzyme kinetics has been concerned with the rate of change of substrate or product under various conditions, this particular quantitative relation has received little attention. At present, amplifications can be expressed in this way only in terms of epinephrine, 3′5′AMP, and glucose-1-phosphate, each of which has a well-determined molecular weight. The range of numerical values for this expression, obtained with the individual stages in the postulated chain of events and compared with the values obtained for the overall response, in terms of micromoles of final product per micromole of hormone, may provide evidence on the validity of the theoretical scheme.

Although reported experiments were not designed for this type of approach, they yield some relevant data. Numerical values for this expression would be expected to vary somewhat with the ratio of quantity of agent to quantity of enzyme; this variation has been demonstrated with particulate preparations of adenyl cyclase from dog myocardium by Murad *et al.* (*7*). From their figures one may calculate that with $4 \times 10^{-3}M$ ATP and $1 \times 10^{-5}M$ epinephrine about 1/10 molecule of extra 3′5′AMP was formed in 12 minutes at 30°C in response to 1 molecule of epinephrine. At the lowest concentration of epinephrine shown on their graph (about $6 \times 10^{-7}M$) about ⅓ molecule of 3′5′AMP was formed in 12 minutes in response to 1 molecule of epinephrine. In view of other, more general requirements of the tissues for ATP, it may be physiologically significant that only a small proportion of