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MAGNESIUM, STRONTIUM, AND BARIUM CONCENTRATIONS AND CALCITE-ARAGONITE RATIOS OF SOME RECENT MOLLUSCAN SHELLS

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ABSTRACT

Approximately 100 recent molluscan shells have been analyzed spectrographically for Mg, Sr and Ba; their calcite-aragonite ratios were determined by X-ray diffraction. The methods are described in detail. The most important parameter controlling the concentration of these trace elements in calcium carbonate shells appears to be generic association rather than water temperature or calcite-aragonite ratio of the shell. As a group, snails are higher in Mg and lower in Sr and Ba than clams. The "fractionation ratio" of the trace alkaline-earths [e.g., $f = (\text{Sr/Ca})_{\text{shell}}/(\text{Sr/Ca})_{\text{sea}}$] increases from 0.00041 for Mg to 0.18 for Sr to 1.6 for Ba, indicating other than a simple ionic size control in trace element incorporation into the shells.

INTRODUCTION

The relationship of chemical composition and crystal structure of calcareous tests to environment and phylogeny of an organism has been a subject of recent study, particularly by geologists seeking a possible additional clue to the nature of ancient environments [see Chave (3, 4), Lowenstam (9, 10); Turekian (14); Turekian and Waagé (16); Odum (11)].

It is evident from these studies that the trace element composition of a calcium carbonate shell will be a function, to a greater or lesser degree, of: (a) trace element content relative to calcium in the environment from which the shell is deposited; (b) temperature of the water in which the animal lives; (c) a "species" effect perhaps related to the microenvironment of the living organism, its feeding habits, and mode of shell construction; (d) the particular polymorph or ratio of polymorphs of calcium carbonate deposited, *viz.*, calcite and aragonite; and (e) salinity.

A fossil shell incorporated in a sediment-water matrix is also subject to the vicissitudes of the subsequent local diagenetic history

of that region, hence it may not bear an exact chemical record of the original environment.

In this paper the general spectrographic techniques used in determining the concentration of Mg, Sr and Ba in calcium carbonate materials and the X-ray techniques used to determine the calcite-aragonite ratios are described and applied to a cursory study of some contemporary marine molluscan tests. We will report later on other modern marine fauna as well as fossil materials.

EXPERIMENTAL

Magnesium, strontium, and barium (trace alkaline-earths) were determined by using a Jarrell-Ash 3.4 m Ebert mount plane grating spectrograph and a DC arc source. For high values of Sr encountered in modern shells, a flame photometric or X-ray fluorescence technique might be more convenient. On the other hand, the low Ba and Mg values are probably ascertained better with the emission spectrograph. The alternate chemical methods appear to require a larger amount of time than the emission spectrographic procedure, with an additional disadvantage of doubtful accuracy at the levels of concentration encountered in this work.

The calcite-aragonite ratios have been determined with a Norelco Diffractometer, using radiation from a copper target. Our X-ray diffraction method has given results similar to those obtained by Lowenstam (9) and others.

Spectrographic Procedure for Magnesium. Each sample was mixed with two parts of spectrographically pure graphite (National Carbon SP-2 grade). Five mg of this mixture were weighed to 3% in a Roller-Smith torsion balance and placed in a $\frac{3}{32}$ " deep, necked, $\frac{3}{16}$ " diameter electrode (National Carbon Co. L4006) and arced to completion at 10 amp (DC arc). Kodak SA-2 plates were used and processed in D-19 developer at 20°C for 3 minutes with continuous agitation.

There is option in the choice of Mg lines that can be used for analysis. At low concentrations a set of five lines around 2800 Å is satisfactory. In this study we have used the Mg 2779.834; this line is usable when the Mn concentration is low, as is the case for modern molluscan shells (7); otherwise the less sensitive neighboring Mg 2781.417 is preferred because no interferences from Mn are present.

The Mn content of modern gastropods, about 5 ppm, will not be a significant error in our present work.

Ca 3009.21 was used as an internal standard.

Fig. 1 is a working curve constructed from standards listed in Table II. The coefficient of variation is approximately 12% so that duplicate analyses will give an error at the 95% confidence level of $\pm 17\%$ of the average value reported.

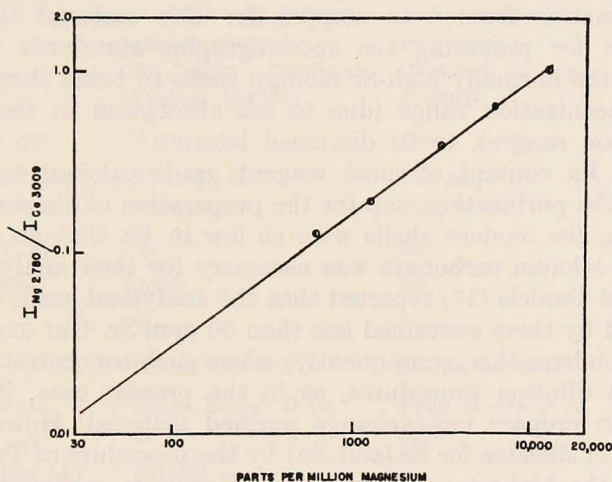


Figure 1. Working curve for magnesium.

The range of values for which the Mg 2780 line is useful is from 10 ppm to at least 13,000 ppm (our highest standard). For higher values of Mg, as may be encountered in nonmolluscan tests such as those of echinoderms, corals, some foraminifera, algae or in magnesium-rich limestones, the Mg 3329.93 line may be used. This line is also compared to the Ca 3009 line as the internal standard, and background correction is essential. Since the Kodak SA-2 emulsion has a constant gamma over the range of wavelengths used, only a single film calibration curve is necessary.

Spectrographic Procedure for Strontium and Barium. A procedure previously developed for Sr in carbonate rocks and fossils (Kulp, *et al.*, 8) was improved for modern shells and was modified to include simultaneous determination of Ba.

For standards and dilution purposes it was necessary to obtain calcium carbonate with low concentrations of Sr and Ba. At first this was obtained by purifying the best analytical grade calcium carbonate (Mallinkrodt "Primary Standard" calcium carbonate which contained about 400 ppm Sr and less than 10 ppm Ba) by an ion-exchange procedure described previously (Turekian, *et al.*, 15). Depending on the method employed in ion-exchange separation, it was usually possible to obtain purified calcium carbonate ranging in contamination from 5 to 50 ppm Sr. This material then was useful both for preparing the spectrographic standards and for dilution of the normally high-Sr modern shells to bring them in the correct concentration range (due to self-absorption in the higher concentration ranges), to be discussed later.

The low Ba content of most reagent grade calcium carbonate eliminates the purification step for the preparation of Ba standards. In addition, the modern shells were so low in Ba that no dilution by Ba-free calcium carbonate was necessary for their analysis.

Wray and Daniels (17) reported that the analytical grade calcium nitrate used by them contained less than 50 ppm Sr. Our experience generally confirms this; consequently, where such concentrations are tolerable in dilution procedures, as in the present case, it is not necessary to prepare ion-exchange purified material. However, in an analysis of silicates for Sr (and Ba) by the procedure of Turekian, *et al.* (15), the highest possible purity of calcium carbonate is required for accurate determinations.

Sr standards were prepared by mixing known amounts of strontium carbonate with ion-exchange purified calcium carbonate. Ba standards were made by mixing known amounts of barium carbonate with analytical grade calcium carbonate.

Concentrations of Sr and Ba in the calcium carbonate bases used in preparing standards were determined by a common correction procedure described by Ahrens (1:142).

The spectrographic parameters in determining Sr and Ba are listed in Table I. Since Ca is the dominant component, no difficulty with regard to a matrix effect was anticipated (15). The Ca 4579 line was used as an internal standard for both Sr and Ba; the lines used for these elements are Sr 4607 and Ba 4554. For the Kodak SA-1 emulsion these wavelengths are in the region of a rapidly changing gamma, but the three utilized lines of Sr, Ca, and Ba are close enough to allow the use of a common film calibration curve.

TABLE I. SPECTROGRAPHIC PARAMETERS*

	<i>Magnesium</i>	<i>Strontium</i>	<i>Barium</i>
Special Sample preparation	1:2 with graphite	1:4 with purified (50 ppm Sr) calcium carbonate for modern shells	None for modern shells
Electrodes	5 mg sample-graphite mixture in $\frac{3}{32}$ " deep, necked electrodes ($\frac{3}{16}$ " diam.) (National Carbon #4006)	5 mg in $\frac{3}{16}$ " deep, necked electrode ($\frac{3}{16}$ " diam.) (National Carbon #4000)	Same as Sr
Electrode gap	4 mm	4 mm	4 mm
Arcing (D.C. arc Anode excitation)	10 amps to completion	16.5 amps to completion	16.5 amps to completion
Slit width (μ)	10	50	50
Transmission	100%	3%	3%
Filter	None	Glass	Glass
Emulsion	Kodak SA #2	Kodak SA #1	Kodak SA #1
Development	3 min. Kodak D-19, 20°C	3 min. Kodak D-19, 20°C	3 min. Kodak D-19, 20°C
Analysis line (Å)	2779.83 or 2781.42 or 3329.93	4607.33	4554.04
Comparison calcium line (Å)	3009.21	4578.56	4578.56

* Spectrograph: Jarrell-Ash 15,000 lines/inch grating, 3.4 meter Ebert mount, 5 Å/mm dispersion.
Microphotometer: Jarrell-Ash Model 2100.

The Sr 4607 line in a step sector image was used for construction of this calibration curve.

Use of a glass filter is desirable to eliminate any important interfering second order lines, but this was not done in the work of Kulp, *et al.* (8). The importance of such a precaution becomes evident for samples high in iron (15). In the case of most calcareous materials this may not be a fundamental difficulty. However, the second order background may affect the accuracy, since background correction is

important in determining the true relative intensities of lines in this region of the spectrum.

Data for Sr standards are given in Table II and are used for the working curve in Fig. 2. From these and previous results (8), an estimate of error can be made. This corresponds to a coefficient of variation of about 9%, hence the figures are valid for single determinations on the 95% probability level, to $\pm 18\%$; for duplicate

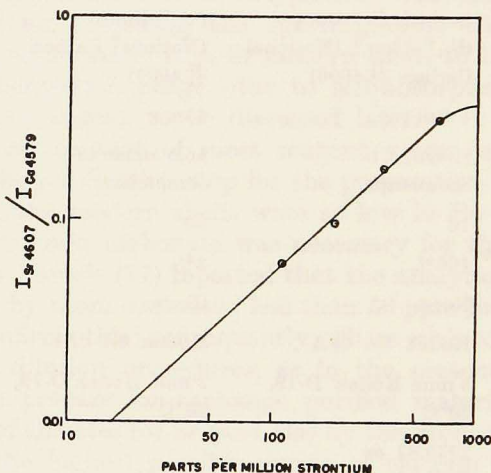


Figure 2. Working curve for strontium.

determinations the precision is $\pm 13\%$ of the value listed. Most of the values for Sr are single analyses.

Note in Fig. 2 that self-absorption becomes prominent for the Sr 4607 line when the concentration of Sr exceeds about 650 ppm. Since most modern shells fall above this value it was necessary to dilute each shell sample in a ratio of 4 to 1 with the purified calcium carbonate containing 50 ppm Sr in order to get proper results.

Data for the Ba standards and the working curve are presented in Table II and Fig. 3. The coefficient of variation is about 15%, so that at the 95% confidence level a duplicate analysis will have an error of about $\pm 20\%$. The Ba content of modern shells is so low that no dilution was necessary. However, in some fossil shells high Ba concentrations were encountered (16); in such a case

TABLE II. REPLICATE DETERMINATIONS OF INTENSITY RATIOS USED IN THE CONSTRUCTION OF WORKING CURVES FOR MAGNESIUM, STRONTIUM, AND BARIUM (PPM IN STANDARD)

MAGNESIUM						
	Run	680	1330	3280	6530	13000
I_{Mg} 2780	1	0.128	0.219	0.384	0.726	0.818
I_{Ca} 3009	2	0.136	0.242	0.405	0.523	1.094
	3	0.108	0.159	0.388	0.658	1.000
	4	0.138	0.162	0.379	0.741	1.084
	5	0.135	0.184	0.412	0.601	1.145
	Av.	0.129	0.193	0.394	0.650	1.028
Coeff. of Var. (%)		9.6	18.8	3.6	13.9	12.5
STRONTIUM						
	Run	110	199	347	644	1237
I_{Sr} 4607	1	0.066	0.088	0.193	0.300	0.376
I_{Ca} 4579	2	0.056	0.088	0.163	0.327	0.392
	3	0.058	0.094	0.164	0.298	0.388
	4	0.063	0.113	0.198	0.316	0.378
	5		0.101	0.182	0.362	0.362
	Av.	0.061	0.097	0.180	0.315	0.379
Coeff. of Var. (%)		9.1	10.8	8.8	8.5	2.6
BARIUM						
	Run	12	40	75	183	
I_{Ba} 4554	1	.095	.240	.555	1.10	
I_{Ca} 4579	2	.155	.320	.495	0.99	
	3	.110	.258		1.18	
	Av.	.120	.273	.525	1.09	
Coeff. of Var. (%)		26	15.3		8.7	

dilution may be necessary. The Ba 4554 line becomes too dark for use, with the exposure conditions employed, before self-absorption is noticed.

Procedure for Determination of Calcite-aragonite Ratios. To determine shell mineralogy, a quantitative X-ray analysis was employed. This method is simple, reasonably precise, and can be applied to a powdered specimen of almost any size down to a few milligrams; moreover, it is nondestructive as well as noncontaminative. The same powdered shell which was used for the spectrographic analyses was used for X-ray analysis without further preparation.

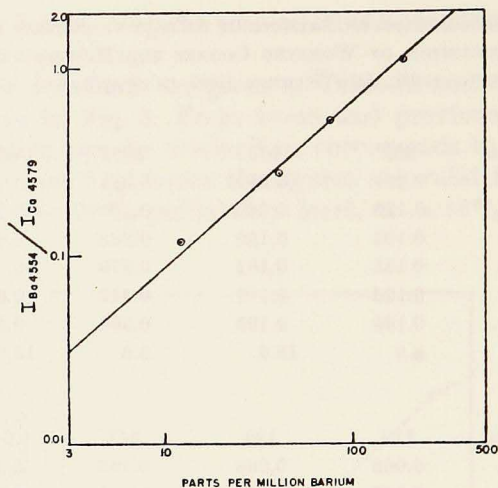


Figure 3. Working curve for barium.

Two methods were used for mounting samples, the choice of method depending on the quantity of material available. No systematic deviation between the two types of mounts could be detected. If the sample was of sufficient size it was poured into brass holders with a circular central depression approximately 1 mm deep and 22 mm in diameter. The top of the loosely packed sample was gently flattened with a spatula to the top level of the holder. Jiggling and tapping of the holder and excessive packing or scraping with the spatula was avoided. No special attempt was made to insure that the sample evenly filled the depression in the holder, since only the central portion was exposed to the X-ray beam. So long as the central portion was reasonably flat and gently packed, no excessive deviations due to preferred orientation were found. It is necessary that the sample be finely ground in order to obtain good reproducibility.

For samples which were too small for the brass holders, circular cover glasses were used. The sample was thinly spread out in the center of the glass disk and flattened gently with a spatula. Samples of as little as 5 mg could be satisfactorily prepared in this manner. If the spinning sample in the goniometer head occasionally broke apart and shifted the edges of the glass disk during peak measurements, then the sample had to be remounted and rerun.

The apparatus was a North American Philips Company X-ray diffraction unit on which was mounted a goniometer spectrometer equipped with a geiger counter. Working conditions were: copper radiation, source operated at 30 kv and 20 ma, nickel filter, 1 degree diverging and .006 inch receiving slits, multiplier setting 1, time constant 8 sec, scale factor variable, scanning manual. The $\{111\}$ aragonite peak at $\sim 26.2^\circ 2\theta$ and the $\{104\}$ calcite peak at $\sim 29.4^\circ 2\theta$ were used for analysis. Maximum peak intensities were read from the ratemeter dial, using manual scanning. A background measurement was made between 28.5° and $29^\circ 2\theta$.

After correction for background, peak intensities were converted to a function:

$$R = \frac{\text{Intensity of Calcite Peak}}{\text{Intensity of Calcite Peak} + \text{Intensity of Aragonite Peak}}$$

The calcite percentage corresponding to the resulting ratio was read from the standard curve shown in Fig. 4.

Two types of standards were used in preparing the curve. Specimens of pure calcite and aragonite crystals were ground and mixed in various proportions. Using these standards, an original curve was prepared. Comparison with the curve published by Lowenstam (9) showed a moderate discrepancy, so new standards were prepared

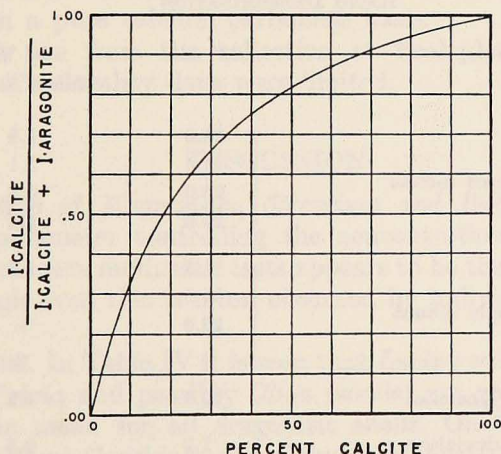


Figure 4. Working curve for calcite-aragonite ratio.

with shell calcite from *Ostrea lurida* and aragonite from *Strombus gigas*. In addition some of the original standards were reground and fresh mineral standards were prepared. Careful measurement with the new standards established the curve shown in Fig. 4. The mineral and shell standards gave identical results which have been fitted to the theoretical curve drawn from $\alpha X / [\alpha X + (1 - X)] = R$, where X = the mole fraction calcite, α = intensity ratio, and I-calcite/I-aragonite for a 1:1 mixture. Our α value for the standard curve is 4.5, which is slightly larger than the α of Lowenstam's curve (about 4.1). Thus calcite percentages determined from the two curves will differ by a maximum of 2%; usually the difference will be less, since only values near the center of the curve are greatly affected.

Runs of several shell samples and standards were repeated under varying conditions at different times in order to obtain an estimate of the precision of the method (see Table III). It is apparent that the coefficient of variation is a function of the calcite content of the sample. For intermediate concentrations (20 to 60% calcite), the coefficient of variation is approximately 5%, decreasing at higher concentrations and increasing with lower concentrations. A standard containing 1.1% calcite in aragonite showed a coefficient of variation of 38%.

TABLE III. PRECISION TEST OF CALCITE-ARAGONITE
RATIO DETERMINATION

Sample	AF 128	1.1% Calcite Stand.
Brass sample mount	24.0	1.9
	21.5	1.1
	23.0	0.5
	22.5	1.3
Glass sample mount	21.5	1.5
	24.5	-
	23.0	-
	-	-
Average (% calcite)	22.9	1.3
Standard deviation	1.2	0.5
Coefficient of Variation (%)	5.2	38

In the region of low calcite concentrations there is an added uncertainty because of variations in background intensity. Thus pure aragonite may appear at times to have 0.5% calcite when compared to the theoretical curve constructed with an $\alpha = 4.5$. Consequently, where values of 0.5% calcite were encountered during the routine gathering of data, these were assumed to be pure aragonite.

RESULTS

Results obtained on approximately 100 modern marine molluscan shells are presented in Table IV. The Ba and Mg figures are an average of two determinations while most of the Sr numbers are from single determinations; exceptions are the *Macoma* series (AF-34 to AF-43) which were run in duplicate. The appropriate error estimate for each element is given under the description of analytical procedures.

Since concentrations were determined from working curves in which parts per million of the element sought was plotted as a function of the intensity ratio of the analysis line to the appropriate calcium standard line, the values are to be interpreted on the basis of a pure calcium carbonate base. The ratios of the trace alkaline-earths to calcium can be determined by normalization based on this assumption. Modern shells contain about 3% organic matter (13), but this will not seriously affect our results even though they are presented on a pure calcium carbonate basis.

The shells are from the collection at Peabody Museum, Yale University. The locality data were limited.

DISCUSSION

Concentration of Magnesium, Strontium and Barium. The most important parameter controlling the concentration of these trace elements in modern molluscan tests appears to be the generic association, although even this is often obscured by individual differences.

MAGNESIUM. In Table IV it is seen that *Lucina* and *Chione* (clams) as well as *Trivia* and possibly *Oliva* (snails) are generally lower in Mg than the mean for all aragonitic shells. On the other hand, *Glycymeris* (clam) *Cerithium* and *Columbella* (snails) generally show higher Mg than this mean.

TABLE IV. COMPOSITION AND CALCITE-ARAGONITE RATIOS OF RECENT MOLLUSCAN SHELLS, IN PPM.

PELECYPODA (clams)

Number	Species	General Location	% Calc.	Mg	Sr	Ba
<i>Macoma</i>						
AF 34	<i>M. balthica</i>	L.I. Sound, Conn., U.S.A.	0	155	1700	33
AF 35	<i>M. balthica</i>	Halifax, N.S., Canada	0	280	1400	27
AF 36	<i>M. sabulosa</i>	Gulf of Maine, U.S.A.	0	150	1700	17
AF 37	<i>M. balthica</i>	Gulf of Maine, U.S.A.	0	125	1400	9
AF 38	<i>M. fragilis</i>	L.I. Sound, Conn., U.S.A.	0	185	1600	7
AF 39	<i>M. fragilis</i>	Labrador, Newfoundland	0	185	1600	11
AF 40	<i>M. constricta</i> Brug	Sanibel, Fla., U.S.A.	0	135	1800	15
AF 41	<i>M. balthica</i>	Wood's Hole, Mass., U.S.A.	0	320	1700	11
AF 42	<i>M. constricta</i>	Jamaica, B.W.I.	0	210	1500	7
AF 43	<i>M. sabulosa</i>	off Martha's Vineyard, Mass., U.S.A.	0	175	1700	16
<i>Cardium</i>						
AF 44	<i>C. costatum</i>	Zanzibar	0	190	1600	9
AF 45	<i>C. vathelute</i>	Suez	0	130	1200	10
AF 46	<i>C. negosum</i>	Ceylon	0	90	1500	10
AF 47	<i>C. edule</i>	England	0	110	1800	12
AF 48	<i>C. aculeatum</i>	Mediterranean	0	88	1300	7
<i>Hemicardium, Laeicardium</i>						
AF 49	<i>H. unedo</i>	Philippines	0	140	1000	10
AF 50	<i>H. obvalis</i>	Bay of Panama	0	130	1400	12
AF 51	<i>L. lyratum</i>	Philippines	0	120	1100	25
AF 52	<i>L. elenese</i>	Gulf of California	0	220	1500	9
<i>Chione</i>						
AF 53	<i>C. gnidia</i>	Guaymas, Gulf of Calif.	0	89	1100	9
AF 54	<i>C. histrionica</i>	Perlas Islands, Panama	0	95	1400	8
AF 55	<i>C. fluctifraga</i>	California, U.S.A.	0	98	1400	18
AF 56	<i>C. amathusia</i>	Zanitos, Peru	0	81	1600	18
AF 57	<i>C. lamarcki</i>	China	0	65	1100	15
AF 58	<i>C. stutchburi</i>	Aukland, New Zealand	0	72	1300	12
<i>Lucina</i>						
AF 59	<i>L. borealis</i>	Bantry, Great Britain	0	53	1500	7
AF 60	<i>L. nutthalli</i>	San Diego, Calif., U.S.A.	0	89	1300	6
AF 61	<i>L. filosa</i>	Martha's Vineyard, Mass., U.S.A.	0	58	1000	

(cont.)

TABLE IV. (cont.)

Number	Species	General Location	% Calc.	Mg	Sr	Ba
<i>Tellina</i>						
AF 62	<i>T. venulosa</i>	Philippines	0	120	2100	14
AF 63	<i>T. crucigera</i>	Japan	0	100	2200	7
AF 64	<i>T. modesta</i>	California, U.S.A.	0	59	—	17
AF 65	<i>T. staurella</i>	Fiji Islands	0	180	2000	8
AF 66	<i>T. cumingi</i>	Gulf of California	0	99	1600	6
AF 67	<i>T. incarinata</i>	Mediterranean	0	100	2300	7
AF 68	<i>T. dispar</i>	Vaneole Bay, Oahu, Hawaii	0	160	> 5000	9
AF 69	<i>T. elizabethae</i>	Guam	0	140	2100	6
<i>Arca</i>						
AF 70	<i>A. senelis</i>	W. Africa	0	69	1300	8
AF 71	<i>A. granosa</i>	East Indies	0	69	1200	6
AF 72	<i>A. kraussi</i>	Shantung, China	0	99	2500	41
AF 74	<i>A. ovalis</i>	New Haven, Conn., U.S.A.	0	140	1300	8
<i>Glycymeris</i>						
AF 75	<i>G. diomedea</i>	Hawaii	0	220	1800	29
AF 76	<i>G. gigans</i>	Gulf of Mexico	0	140	1600	17
AF 77	<i>G. scriptus</i>	W. Africa	0	190	1900	6
<i>Codakia</i>						
AF 78	<i>C. nigifera</i>	Fiji Islands	0	105	1300	4
AF 79	<i>C. thaanumi</i>	Hawaii	0	200	1500	7
<i>Pecten</i>						
AF 80	<i>P. ventricosa</i>	Guaymas, Gulf of Calif.	100	1400	860	8
AF 81	<i>P. magellicanus</i>	Eastport, Maine, U.S.A.	100	440	1100	6
AF 82	<i>P. hericius</i>	Puget Sound, Wash., U.S.A.	95	610	—	—
AF 83	<i>P. albolineatus</i>	Oahu, Hawaii	80	3400	660	12
AF 84	<i>P. celator</i>	Stewart Island, New Zealand	95	1400	1100	7
AF 85	<i>P. pallium</i>	New Caledonia	100	4700	1200	9
GASTROPODA (snails)						
<i>Tectarius</i>						
AF 86	<i>T. Echivella cumingi</i>	India	0	99	1500	14
AF 87	<i>T. pagodus</i>	Australia	0	310	1300	8
<i>Tonna, Malea</i>						
AF 88	<i>T. maculata</i>	Philippines	0	81	1400	7
AF 89	<i>M. pomum</i>	Indian Ocean	0	130	1000	5

(cont.)

TABLE IV. (cont.)

Number	Species	General Location	% Calc.	Mg	Sr	Ba
<i>Conus</i>						
AF 90	<i>C. eburneus</i>	Ceylon	0	120	2100	6
AF 91	<i>C. princeps</i>	Gulf of California	0	76	1100	7
AF 92	<i>C. pulicarius</i>	Tutuila, Samoa	0	220	1100	5
AF 93	<i>C. dactyloeus</i>	New Zealand	0	430	1000	8
AF 94	<i>C. hebraeus</i>	Hawaii	0	120	1000	7
AF 95	<i>C. papilionacens</i>	W. Africa	0	51	1100	15
AF 96	<i>C. marmoreus</i>	Moluccas	0	84	1300	6
AF 97	<i>C. striatus</i>	Red Sea	0	75	1000	6
<i>Littorina</i>						
AF 98	<i>L. tenebrosa</i>	France	75	1400	1500	7
AF 99	<i>L. scabra</i>	Philippines	0	180	1700	9
AF 100	<i>L. melanostoma</i>	Ceylon	0	800	1800	6
AF 101	<i>L. pulchra</i>	Panama	0	180	1600	8
AF 102	<i>L. fasciata</i>	Panama	0	170	1600	-
AF 103	<i>L. basteroti</i>	Dalmatia	0	1450	1100	7
<i>Astraea</i>						
AF 104	<i>A. sulcata</i>	Australia	33	1900	1700	12
AF 105	<i>A. petrosum</i>	Fiji Islands	0	1200	1900	8
AF 106	<i>A. calcer</i>	New Caledonia	2	1600	2500	12
<i>Cerithium</i>						
AF 107	<i>C. ruprestre</i>	Mediterranean	0	510	1100	8
AF 108	<i>C. vertagus</i>	East Indies	0	490	1300	7
AF 109	<i>C. stercus muscarum</i>	Panama	0	170	1100	5
AF 110	<i>C. columna</i>	Hawaii	1	430	860	6
AF 111	<i>C. morus</i>	Ceylon	0	290	1100	7
<i>Oliva</i>						
AF 112	<i>O. guttata</i>	Society Islands	0	150	1800	5
AF 113	<i>O. elegans</i>	New Guinea	0	72	1400	6
AF 114	<i>O. erythrostoma</i>	Philippines	0	99	1800	5
AF 115	<i>O. peruvana</i>	Peru	0	58	1300	6
AF 116	<i>O. venulata</i>	Gulf of California	0	64	1200	8
<i>Trivia</i>						
AF 117	<i>T. europaea</i>	Guernsey	0	84	1300	6
AF 118	<i>T. sanguinea</i>	Panama	0	72	1700	7
AF 119	<i>T. solandri</i>	Peru	0	38	1400	4

(cont.)

TABLE IV. (cont.)

Number	Species	General Location	% Calc.	Mg	Sr	Ba
<i>Columbella</i>						
AF 120	<i>C. pardalina</i>	Bay of Yeddo, Japan	0	460	1200	9
AF 121	<i>C. flavida</i>	Ceylon	0	73	1500	5
AF 122	<i>C. major</i>	Panama	0	480	1400	5
AF 123	<i>C. ovulata</i>	Philippines	0	1100	2700	7
<i>Fissurella, Diodora</i>						
AF 124	<i>F. volcano</i>	California, U.S.A.	37	270	900	5
AF 125	<i>F. lineata</i>	Australia	1	480	1100	9
AF 126	<i>D. aspersa</i>	California, U.S.A.	38	140	1000	8
<i>Nerita</i>						
AF 127	<i>N. fuviculatum</i>	Ceylon	27	3000	1200	7
AF 128	<i>N. scrabricosta</i>	Panama	22	3000	1100	—
AF 129	<i>N. polita</i>	Philippines	52	4300	1200	5
AF 130	<i>N. costata</i>	Nicobar	26	3400	1700	7
AF 131	<i>N. albicella</i>	Red Sea	44	3800	1200	7
AF 132	<i>N. plicata</i>	Micronesia	3	460	1500	7

Those genera which have species with some calcite in the shell structure are generally high in Mg, and this obtains even when a species of such a genus has no calcite in it at all. Compare, for example, *Littorina tenebrosa* (75% calcite, 1400 ppm Mg) with *L. melanostoma* (0% calcite, 800 ppm Mg), or *Astraea sulcata* (33% calcite, 1900 ppm Mg) with *A. petrosum* (0% calcite, 1200 ppm Mg). Note that the snail genus *Nerita*, whose species show ranges from 3–52% calcite, has a mean value of 3200 ppm Mg, while the clam genus *Pecten*, with 80–100% calcite, has an average of only 2000 ppm. This elicits the fundamental importance of generic control of the Mg content of the organism rather than the aragonite-calcite ratio, as suggested by Chave (3).

In our sampling, the snails as a group are higher in Mg than the clams (Table IV). For Chave's smaller sampling (11 clams, 7 snails) the reverse appears to be the case; his average of individual shells analyzed for Mg is different from the values he determined from separated calcareous sediments (4). The following are his values in ppm Mg for the molluscan fraction of carbonate sediments: Caesar Creek, Florida – 580; Angelfish Key, Florida – 580; Great Isaac Bank, B.W.I. – 12,000; average of separate molluscan shells – 2,700. His two Florida samples agree well with our average for individual

molluscan shells (533 ppm), but on the basis of either of our sets of analyses his Great Isaac Bank sample seems to have some constituent other than a molluscan component.

STRONTIUM. A similar story can be told for this element, although the range of variation is not as great as that for Mg. The aragonitic clam genus *Tellina* is fundamentally high in its Sr concentration relative to other molluscan genera, as was shown also by Thompson and Chow (13) and Odum (11). At the other end, the aragonitic snail genera *Conus*, *Cerithium*, and the mixed *Fissurella* and *Diodora* contain only half as much Sr as *Tellina*. The other aragonitic forms and mixed aragonite-calcite forms (excepting *Pecten*) show about the same mean value, with some variation within genera. The mainly calcitic *Pecten* species are low in Sr, but not much more so than the totally aragonitic *Conus* and *Cerithium*. Hence we see again the importance of generic control on the trace-element concentration of molluscan tests.

Clams as a group are higher in Sr than snails (Table V), as concluded previously by Thompson and Chow (13) from their large sampling. Our values for clams and snails show remarkably good agreement considering the fact that we used different techniques and a different sampling of shells.

TABLE V. AVERAGE Mg, Sr AND Ba CONCENTRATIONS IN MOLLUSCAN SHELLS OBTAINED IN THIS STUDY, INCLUDING COMPARISON OF Mg AND Sr WITH DATA FROM CHAVE (3) AND THOMPSON AND CHOW (13) RESPECTIVELY

	Magnesium				Strontium				Barium	
	T. and A.		Chave		T. and A.		T. and C.		T. and A.	
	No.	Mg	No.	Mg	No.	Sr	No.	Sr	No.	Ba
	obs.	(ppm)	obs.	(ppm)	obs.	(ppm)	obs.	(ppm)	obs.	(ppm)
Clams	51	354	11	3080	49	1570	44	1620	49	12
Snails	47	727	7	2160	47	1390	46	1470	45	7
Clams and snails	98	533	18	2700	96	1480	90	1540	94	10

BARIUM. The low amount of Ba in contemporary molluscan shells is a consequence of the low Ba concentration in the ocean. However, of the three elements here considered, the greatest variability in concentration was observed for this trace alkaline-earth. Clams on the whole have a higher Ba concentration than snails; this may be

explained in terms of the environment in which these two groups are most often associated. Snails to a large extent are epifauna while clams have a large component of infauna. The low content of Ba in the sea contrasted with its high content in marine muds and shales may provide the difference in environment of shell growth of clams and snails which leads to our results.

We have noted not only a marked enrichment in the Ba content of relatively recent (<10,000 years old) fossil clam shells but also a much greater increase in older fossil shells with original shell structure (16). Presently we are studying the problem of its incorporation in shells before and after burial.

MOLLUSCAN SHELL COMPOSITION RELATIVE TO SEA WATER COMPOSITION. Table VI lists the ratio of each trace alkaline-earth to Ca for both molluscan shells and sea water; it also gives the degree of fractionation of these three elements during shell growth. The Sr and Mg values for sea water are from the compilation of Richards (12) and the Ba value is from Bowen (2).

TABLE VI. SHELL COMPOSITION COMPARED TO SEA WATER

	(% Mg/% Ca) × 10 ³	(% Sr/% Ca) × 10 ³	(% Ba/% Ca) × 10 ³
(A) Molluscan shells	1.33	3.70	0.025
(B) Sea water	3180.0	20.2	0.0155
"fractionation" A/B	0.00041	0.18	1.6

Note that Ba is slightly enriched in shells relative to Ca when compared to sea water. On the other hand, Mg is markedly discriminated against by molluscan shells. Sr is also discriminated against, but not as much as Mg.

The observed relationship suggests that the adsorption properties of ions on the surface of the growing shell front or during complexing in the blood of the organism has a strong effect on the ultimate trace element content of a molluscan test. If it were a matter of simple substitution in the lattice, then Goldschmidt's (5) commonly quoted rules would be operative and Ba should be excluded relative to both Ca and Sr because of its much larger ionic radius. However, if adsorption and complexing are important controls, one might expect a greater enrichment of Ba than Sr in a growing shell.

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