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## REVISED CARBONATE-WATER ISOTOPIC TEMPERATURE SCALE

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## REVISED CARBONATE-WATER ISOTOPIC TEMPERATURE SCALE

BY S. EPSTEIN, R. BUCHSBAUM, H. A. LOWENSTAM, AND H. C. UREY

## ABSTRACT

The relationship between temperature and  $O^{18}$  content relative to that for a Cretaceous belemnite of the Pee Dee formation previously reported (Epstein, Buchsbaum, Lowenstam, and Urey, 1951) has been re-determined using modified procedures for removing organic matter from shells, and is found to be

$$t(^{\circ}C) = 16.5 - 4.3\delta + 0.14\delta^2,$$

where  $\delta$  is the difference in per mil of the  $O^{18}$  to  $O^{16}$  ratio between the sample and reference gas. The new relationship agrees with that determined by McCrea (1950) for inorganically precipitated calcium carbonate. Carbonate-carbon dioxide exchange experiments were done to determine the direct and indirect effects of organic matter in the shell on the mass spectrometer analyses.

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## INTRODUCTION

Recently the writers (Epstein, Buchsbaum, Lowenstam, and Urey, 1951) reported on the determination of a temperature scale for measuring the temperature at which a marine shell-bearing animal grows its shell by determining the  $O^{18}/O^{16}$  ratio in the calcium carbonate of the shell. Although the method reported was fundamentally correct, extraneous oxygen was introduced into the calcium carbonate during one of the stages of the processing of the shell which introduced an error in the temperature scale. The complete problem was re-ex-

amined, and a modified method for preparing samples of carbon dioxide from the calcium carbonate of the shell is here described.

## ACKNOWLEDGMENTS

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La Jolla, California, is gratefully acknowledged. A great deal of the laboratory work was done by Mrs. Toshiko Mayeda, and her efforts are appreciated.

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#### PURIFICATION OF THE CALCIUM CARBONATE OF MARINE SHELLS

##### *General Discussion*

The previously described purification of the calcareous shell consisted of heating 50 mgs of the powdered sample in a slow stream of helium at 470°C. The helium, which was purified from organic compounds by passing it over cupric oxide heated to 700°C and through a liquid nitrogen cooled trap, became contaminated with oxygen gas originating from the cupric oxide and from back diffusion through the furnace opening. The oxygen oxidized the organic material of the powdered shell to form CO<sub>2</sub> which in turn exchanged with the calcium carbonate of the shell. Since carbon dioxide formed with atmospheric oxygen analyzes approximately -20‰ relative to carbon dioxide extracted from calcium carbonate of a normal marine shell, the isotopic exchange lowered the O<sup>18</sup>/O<sup>16</sup> ratio of the oxygen of the calcium carbonate of the shells. The samples used for the temperature scale were treated in the same manner with the result that a near constant error was obtained. This approximate duplication masked the detection of the error, resulting in what was thought to be a valid temperature scale. Further work which showed a large discrepancy between the O<sup>18</sup>/O<sup>16</sup> analyses of the calcium carbonate in the prismatic and pearly layers taken from the same fragment of a shell led to the discovery of the error. An example of the discrepancies in the analyses is shown in Table 1.

$$\delta = (R_{\text{sample}} / R_{\text{standard}} - 1) 1000$$

where  $R_{\text{sample}}$  and  $R_{\text{standard}}$  are ratios of CO<sup>16</sup>O<sup>18</sup> to CO<sub>2</sub> for the sample and standard reference gas respectively, and  $\delta$  is essentially the difference between the O<sup>18</sup> content of the sample and that of the reference gas.

TABLE 1.—O<sup>18</sup> ANALYSES FOR CO<sub>2</sub> SAMPLES FROM DIFFERENT LAYERS OF A FRAGMENT FROM *Haliotis Rufescens* GROWN AT 21.0°C

Sample	$\delta$	T <sub>calc</sub> °C (old scale)
1. Inner pearly layer	-3.6 <sub>9</sub>	31.7
2. } Intermediate layers	-3.0 <sub>7</sub>	28.0
3. }	-2.0 <sub>2</sub>	21.8
4. }	-1.7 <sub>8</sub>	20.2
5. Outer prismatic layer	-1.8 <sub>9</sub>	21.0

All the analyses in Table 1 are erroneous. The differences in the above results we believe are due to a greater velocity of exchange of carbon dioxide with aragonite (pearly layer) as it is converted to calcite during heating. This is discussed further.

##### *Purification Process*

The process for the destruction of organic matter in the samples was modified. The apparatus is shown in Figure 1. Helium gas flowing at a rate of 0.4 cc per second passes through a copper-filled furnace kept at approximately 500°C, through an activated charcoal-filled trap cooled with liquid nitrogen, and into the roasting furnace. The continuous flow of helium sweeps the volatile decomposition products of the heated organic compounds away from the calcium carbonate and at the same time provides an inert atmosphere over the sample. The sample, in a platinum boat, is inserted into the furnace while the temperature of the furnace is low (less than 200°C) to permit sweeping out of all the air from the furnace before heating of the sample begins. The opening of the furnace is covered by a cap containing a capillary opening to prevent back diffusion of air. Sweeping with helium continues for 20 minutes before the heater of the furnace is turned on. This is sufficient to sweep out the furnace about six times. The sample roasts in the furnace at least 30 minutes after the temperature of the

furnace reaches 470°C. The resulting calcium carbonate, which is gray, is then reacted with phosphoric acid to release the carbon dioxide

the difference in  $O^{18}/O^{16}$  ratios between the waters in which the *Strombus* and the other specimens grew is 1.6‰, which is nearly suffi-

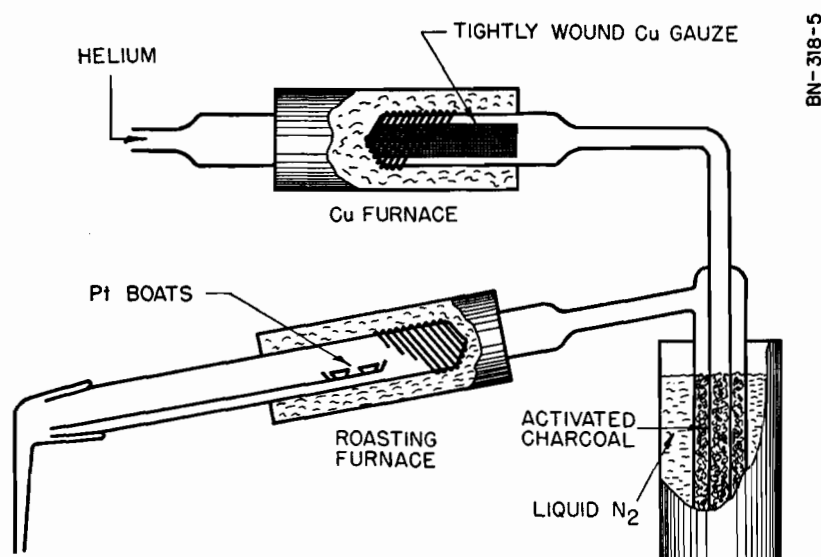


FIGURE 1.—PURIFICATION APPARATUS

for mass spectrometric analysis in the manner described in the previous publication. Under these conditions of purification the size of the sample, the length of time beyond 30 minutes of heating, and the difference in the type of layer in the abalone shell do not affect the results of the analyses, as shown in Table 2. The two fragments grew at different temperatures, and hence the analyses should be different.

The effect of heating by the modified procedure is to decrease the  $O^{18}/O^{16}$  ratio of the oxygen in the resulting calcium carbonate, but to a lesser degree than in the case of heating in an atmosphere of a mixture of helium and oxygen. The fact that roasting is still necessary is shown in Table 3.

The data show that heating affects the isotopic analysis of samples from different animals differently. Although the first three samples listed were grown simultaneously in the same tank, their respective mass spectrometer analyses check only after the heating procedure has been followed. The analysis for the *Strombus* checks those of the other specimen only because

TABLE 2.—EFFECT OF VARYING CONDITIONS OF HEATING ON THE  $O^{18}$  CONTENT OF  $CaCO_3$  FROM *Halotis* SAMPLES

Sample	Weight mgs	Time of heating at 470°C min.	$\delta$
Fragment I			
Pearly layer	10	30	-1.1 <sub>9</sub> , -1.4 <sub>4</sub>
	50	30	-1.3 <sub>2</sub> , -1.2 <sub>9</sub> , -1.0 <sub>0</sub>
Prismatic layer	50	30	-1.2 <sub>7</sub>
Fragment II			
Pearly layer	50	30	-0.8 <sub>8</sub>
	50	75	-0.8 <sub>6</sub>

cient to compensate for the difference in the temperature at which the specimen grew.

#### Isotopic Exchange Experiments

Although the heating of the samples in helium gas with rigorous exclusion of oxygen and other precautions outlined have given very consistent results, the investigation of the cause for the

previous errors is important if we are to be confident that the present consistency in results is not due to systematic errors. In the former

TABLE 3.—EFFECTS OF ROASTING ON ANALYSIS OF  $O^{18}/O^{16}$  RATIO OF  $CaCO_3$  FROM MARINE SHELLS

Sample	Growth Temp. °C	Fresh unheated sample $\delta$	Sample heated in He gas $\delta$	Change due to heating
Snail ( <i>Kelletia</i> )...	21.5	-0.3 <sub>3</sub>	-1.4 <sub>3</sub>	-1.1 <sub>0</sub>
<i>Haliotis</i> (prismatic layer).....	21.5	-0.9 <sub>8</sub>	-1.5 <sub>1</sub>	-0.5 <sub>3</sub>
Calcareous worms	21.5	-0.4 <sub>8</sub>	-1.3 <sub>6</sub>	-0.9 <sub>0</sub>
Snail ( <i>Strombus</i> )..	29.5	-1.3	-1.4 <sub>5</sub>	-0.1 <sub>5</sub>

produced from the decomposition of shell organic matter may exchange with the carbonate.

These possibilities could be investigated if the oxygen in the organic matter could be labeled and its contribution to the carbon dioxide extracted from the powdered shell detected. It was hoped that the oxygen in the organic matter could be preferentially enriched in  $O^{18}$  relative to the  $CaCO_3$  of the shell (and thus labeled) by heating the powder in an atmosphere of carbon dioxide enriched in  $O^{18}$  at temperatures high enough to facilitate exchange but low enough so that all the organic matter is not driven from the powder. Such preferential  $O^{18}$  enrichment of the organic material should be detected by comparing the

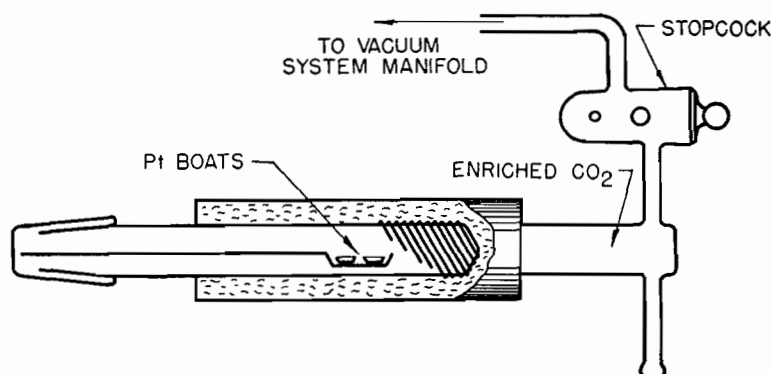


FIGURE 2.—FURNACE FOR EXCHANGE EXPERIMENTS

paper, it was concluded that the reaction of shells containing organic matter with phosphoric acid does not produce an impurity of masses 44 and 46 which interferes with the mass spectrometric analyses, and we know of no reason to change this view.

However, organic matter may affect the  $O^{18}$  content of the carbon dioxide extracted from shell in the following ways: (1) Its reaction with phosphoric acid may produce carbon dioxide different in isotopic composition from that produced from calcium carbonate of the shell; (2) Even in the absence of oxygen during the heating of shell sample in helium at 470°C, carbon dioxide or other oxygen compounds

mass spectrometer analyses for carbon dioxide samples extracted from the above powder with that extracted from powder which has been subjected to the above exchange after its organic matter is removed by heating at 470°C in an atmosphere of helium. The procedure used for these exchange experiments is described below.

A fragment of shell from a *Strombus gigas* which was 100 per cent aragonite and a fragment from an oyster shell were separately powdered, and a 30-milligram aliquot from each powder sample heated in a helium gas stream by the method described in the purification procedure. This procedure converted the aragonite to calcite in the former case and



destroyed the organic matter in both cases. Thirty milligrams, which will be designated as Sample I of the original unheated aragonite powdered shell, and an equal amount of the heated powder, designated as Sample II, were

ment in  $O^{18}$  was 0.42. Thus organic matter must directly or indirectly affect the isotopic composition of the carbon dioxide extracted from the shell. Since for Sample III the enrichment due to exchange at 320°C [comparison between

TABLE 4.—POWDERED SHELL- $CO_2$  EXCHANGE

Temp. of heating °C	Time of heating Mins.	Sample I (Crystal form after exchange) $\delta^0/_{\infty}$	Sample II Calcite $\delta^0/_{\infty}$
Not heated		(a) +0.1 <sub>9</sub> (100% aragonite)	(a) -0.2 <sub>1</sub>
320	30	(b) +1.3 <sub>0</sub> (100% aragonite)	(b) +0.0 <sub>5</sub>
320	60	(c) +1.9 <sub>8</sub> (100% aragonite)	(c) +0.2 <sub>1</sub>
420	60	(d) +14.5 <sub>5</sub> (80% calcite) Sample III Calcite	(d) +0.7 <sub>7</sub> Sample IV Calcite
Not heated		(a) -2.0 <sub>2</sub>	(a) -2.3 <sub>3</sub>
320	60	(b) -0.3 <sub>8</sub>	(b) -1.5 <sub>8</sub>
375	60	(c) +1.9 <sub>4</sub>	

placed simultaneously in separate boats in a furnace shown in Figure 2. The system was thoroughly evacuated, after which 85 cc of carbon dioxide which analyzed +100‰ higher in  $O^{18}$  relative to our standard was introduced into the furnace. The resulting pressure in the furnace was approximately half an atmosphere. The temperature of the furnace was raised to the desired value, and the samples allowed to exchange with the carbon dioxide for the desired length of time. The  $O^{18}$  enriched carbon dioxide was then removed, and 15 milligrams of each sample was reacted with phosphoric acid as previously described. The same procedure was repeated using the powdered oyster shell with the untreated sample designated as Sample III and the helium heated sample as Sample IV. The mass spectrometric analyses of the gas samples are given in Table 4. The crystalline form of the calcium carbonates was determined by x-ray analyses.

Comparison of the difference in analyses between Sample I(a) and Sample I(c) with the difference in analysis between Sample II(a) and Sample II(c) shows that in the case of Sample I, which contained organic matter, exchange with  $O^{18}$  enriched carbon dioxide resulted in an enrichment of the  $O^{18}$  of the carbon dioxide extracted from the shell of 1.7, while in the case of Sample II, from which organic matter was first removed before exchange with  $O^{18}$  enriched carbon dioxide was permitted to proceed, the resultant enrich-

TABLE 5.—EFFECT OF HEATING AT 475°C IN HELIUM ON  $O^{18}$  EXCHANGED SAMPLES

Sample (Exchange temp)	Before heating in Helium (from Table 4) $\delta$	After heating in Helium $\delta$	Change in $O^{18}$ content $\delta$
I(c) (320°C)	1.98	1.20	-0.78
III(b) (320°C)	-0.38	-1.0 <sub>9</sub>	-0.71
III(c) (375°C)	1.94	1.1 <sub>8</sub>	-0.76
IV(b) (375°C)	-1.58	-1.9 <sub>1</sub>	-0.33

III(a) and III(b)] is 1.64 and is similar to that for Sample I it appears that in this case aragonite and calcite powders behave similarly to exchange with carbon dioxide. The analyses for Sample I(d) show a very marked increase in  $O^{18}$  when aragonite transformed to calcite, whereas such an increase did not occur for the Sample II(d) which was treated similarly. Although further work is necessary to understand this effect, it is very likely that such transformation should weaken the bonds in the calcium carbonate and lower the activation energy necessary for exchange between calcium carbonate and carbon dioxide. This increase in exchange rate agrees with the results of Table 1—namely, the aragonite pearly layer of an abalone shell was more markedly affected by surrounding carbon dioxide than was the calcite prismatic layer when both were heated at 470°C.

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If the powdered samples of shell which were not first heated at 470°C and which were subjected to exchange with  $O^{18}$  enriched carbon

dioxide extracted from such heated samples. Accordingly, aliquots from Samples I(c), III(b), III(c), and IV(b) were heated at 470°C, and the carbon dioxide from these samples analyzed. The results are shown in Table 5.

Table 5 shows that the first three samples listed have lost  $O^{18}$  to a greater extent than did the last sample during the heating at 475°C. The first three samples contained organic matter while exchanging with  $O^{18}$  enriched carbon dioxide, while the last sample was purified of organic matter before it was allowed to exchange. It seems, then, that heating at 470°C in an atmosphere of helium eliminates some organic matter which would otherwise affect the analyses of the carbon dioxide extracted from a powdered shell. That no exchange has taken place during this 470°C heating is shown by the fact that Samples I(c) and III(b) have

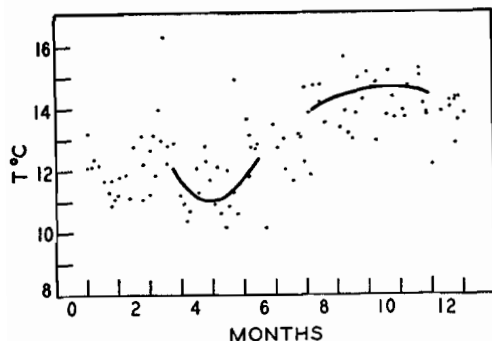


FIGURE 3.—SURFACE OCEAN TEMPERATURES AT PACIFIC GROVE, CALIFORNIA  
Average maximum 14.5°C, Average minimum 11.0°C.

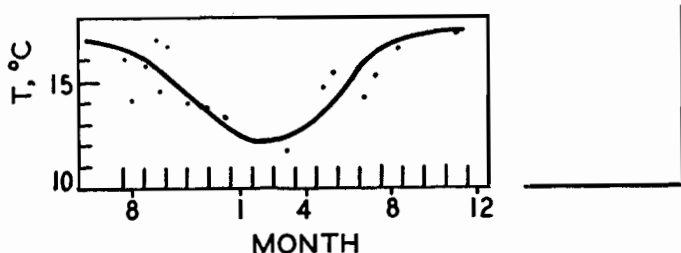


FIGURE 4.—SURFACE OCEAN TEMPERATURES AT SANTO TOMAS  
Average maximum 17°C, Average minimum 12°C.

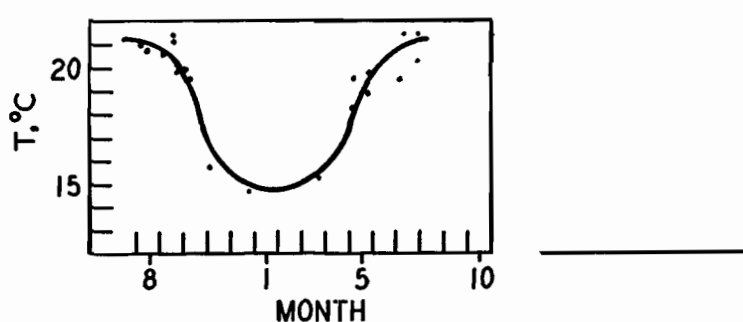


FIGURE 5.—SURFACE OCEAN TEMPERATURES AT POINT BETWEEN MORRO AND ENSENADA  
Average maximum 21°C, Average minimum 15°C.

dioxide contain preferentially  $O^{18}$  enriched organic compounds, then further heating of these samples in an atmosphere of helium at 470°C should destroy the organic matter, resulting in a lowering of the  $O^{18}$  content of the car-

bon dioxide extracted from such heated samples. Since the former sample was aragonite which converted to calcite at 470°C and the latter sample was originally calcite and thus suffered no crystallographic transformation during the

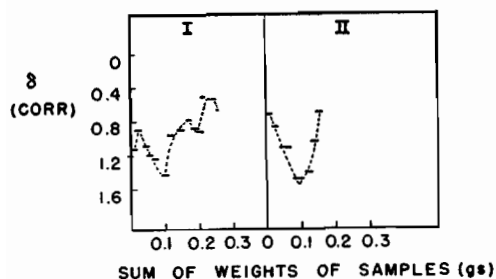


FIGURE 6.—PLOT OF  $O^{18}$  CONCENTRATION VS. GROWTH SEQUENCE OF LAYERS IN ABALONE SHELL

(*Haliotis*, Pacific Grove, Temperature 11–14.5°C)

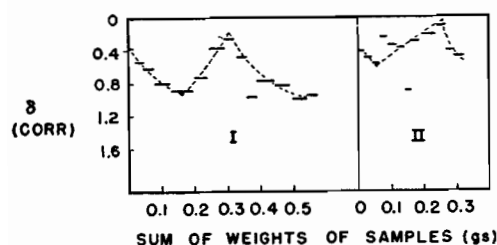


FIGURE 7.—PLOT OF  $O^{18}$  CONCENTRATION VS. GROWTH SEQUENCE OF LAYERS IN ABALONE SHELL

(*Haliotis*, St. Tomas, Temperature 12–17°C)

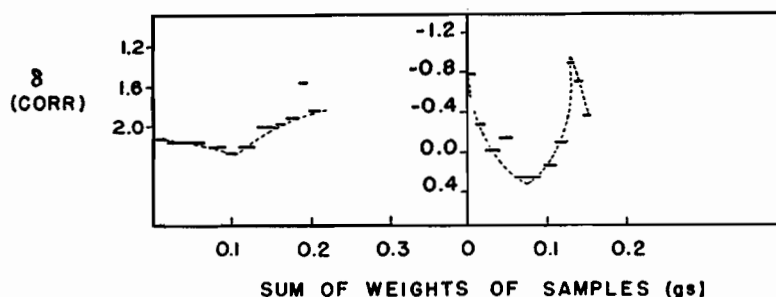


FIGURE 8.—PLOT OF  $O^{18}$  CONCENTRATION VS. GROWTH SEQUENCE OF LAYERS IN *Macoma* sp. (at left; Middle Channel, Temperature 7–9°C) AND IN ABALONE (at right, *Haliotis*; Point between Morro and Ensenada points, Temperature 15–21°C)

heating, then if exchange had taken place during the heating Sample I(c) would have been less depleted in  $O^{18}$  than Sample III(b).

The results in Column 3, when compared with the  $O^{18}$  analyses for the samples of oyster and *Strombus* which have merely been heated in helium at 470°C (IV(a) and II(a) respectively) show that there is a resultant enrichment in  $O^{18}$  in the calcium carbonate that occurred during the exchange experiment. The

enrichments are particularly large in the case of the sample that had organic matter during the exchange experiments. That calcium carbonate should exchange more readily when intimately mixed with decomposing organic matter is not surprising in the light of the work of Armstrong and Schubert (1947). They found that presence of water increases the rate of exchange between  $CO_2$  and carbonate. Possibly the less marked exchange that occurred in the case of the shell powder which had been previously purified of organic matter is due to water from its neighboring unpurified sample which had contaminated carbon dioxide in the furnace, and that the apparent loss of  $O^{18}$  by Sample IV(b) after being heated in helium at 470°C is due to loss of organic matter picked up by this sample from its neighboring Sample III(b) during the exchange experiment.

It has been noted that finely powdered Foraminifera which have been exposed to air for a few months will in some cases show a lower  $O^{18}$  content relative to that of freshly powdered shell. Fortunately this effect does not seem to exist for the samples used in the determination of the temperature scale since some of the

results reported here have been obtained over a period of a year. This effect should be guarded against in any further work on freshly gathered sea shells.

#### TEMPERATURE SCALE

With the development of a reliable process for destroying organic matter in organically precipitated calcium carbonate the work on the temperature scale was continued.



TABLE 6.—DESCRIPTION OF SHELL SAMPLE USED FOR DETERMINATION OF TEMPERATURE SCALE

Location	Specimen	Part of specimen used	Temp. °C	Water Analysis $\delta^{18}$
Thermostated tank at Hopkins Marine Station, Pacific Grove, Calif.	1. Black abalone, <i>Haliotis cracherodii</i>	Regenerated edge (mother of pearl)	19	-0.44
	2. Black abalone, <i>Haliotis cracherodii</i>	Regenerated holes of spec. 1 + spec. 2 (mother of pearl)		
	3. Black abalone, <i>Haliotis cracherodii</i>	Regenerated hole (mother of pearl)		
	4. Black abalone, <i>Haliotis cracherodii</i>	Regenerated notch in edge of shell		
	5. Black abalone, <i>Haliotis cracherodii</i>	Regenerated notch		
	6. Black abalone, <i>Haliotis cracherodii</i>	Regenerated notch		
	7. Black abalone, <i>Haliotis cracherodii</i>	Regenerated notch		
Thermostated tank at Scripps Institution of Oceanography, La Jolla, Calif.	8. Black abalone, <i>Haliotis cracherodii</i>	Regenerated hole	21.5	-0.45
	9 (a). Black abalone, <i>Haliotis cracherodii</i>	Pearly layer of regenerated notch		
	(b). Black abalone, <i>Haliotis cracherodii</i>	Prismatic layer of regenerated notch		
	10 (a). Black abalone, <i>Haliotis cracherodii</i>	Pearly layer of regenerated notch		
	(b). Black abalone, <i>Haliotis cracherodii</i>	Prismatic layer of the same		
	11 (a). Black abalone, <i>Haliotis cracherodii</i>	Pearly layer of regenerated notch		
	(b). Black abalone, <i>Haliotis cracherodii</i>	Prismatic layer of the same		
	12. Black abalone, <i>Haliotis cracherodii</i>	Average of regenerated notch		
	13 (a). Black abalone, <i>Haliotis cracherodii</i>	Pearly layer of regenerated notch		
	(b). Black abalone, <i>Haliotis cracherodii</i>	Prismatic layer of the same		
	14. Snail <i>Kellatia kellestii</i>	Average sample of regenerated edge		
	15. Oyster <i>Mytilus californianus</i>	Average sample of regenerated edge		
	16. Calcareous worm	Average sample		
Bermuda, tank in laboratory	17. <i>Strombus gigas</i>	Regenerated edge	29.5	+1.13
Hopkins Marine Station	18. <i>Haliotis cracherodii</i>	Fragment used in seasonal variation	Min. 11 Max. 14.5	-0.44

## TEMPERATURE SCALE

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TABLE 6—Continued

Location	Specimen	Part of specimen used	Temp. °C.	Water Analysis O <sup>18</sup>
Santo Tomas	19. <i>Haliotis cracherodii</i>	Fragment used in seasonal variation	Min. 12 Max. 17	-0.43
Point between Morro and Ensenada Points	20. <i>Haliotis rufescens</i>	Fragment used in seasonal variation	Min. 15 Max. 21	-0.29
Middle Channel, Puget Sound	21. <i>Macoma</i> sp.	Fragment used in seasonal variation	Min. 7.2 Max. 9.5	-0.63

To establish the relationship between O<sup>18</sup>/O<sup>16</sup> ratio of the oxygen in calcium carbonate precipitated by marine shells and the temperature at which they were precipitated, regenerated fragments of shell grown in temperature-controlled tanks as well as shells collected in their natural surroundings were used. One group of animals whose shells were notched or drilled and which then repaired their shells in a thermostated tank at 19°C was sent to us by Dr. Rolf Bolin from the Hopkins Marine Laboratory. A *Strombus gigas* which regenerated part of its shell at 29.5°C in a tank at Bermuda provided shell for a high-temperature calibration point. A third group of animals which regenerated their notched and drilled shells at 21.5°C was sent to us by Dr. Carl Hubbs. These three groups then provided three calibration points.

The other points on the curve were obtained by determining the variation of O<sup>18</sup>/O<sup>16</sup> ratio in calcium carbonate samples ground off from successive growth layers from a rectangular piece of shell. The marine shells grew in a location whose seasonal variation of temperature is known. The locations chosen were off the shores of Santo Tomas, a point between Morro and Ensenada points on the west coast of Lower California, and at Pacific Grove, California, and from Middle Channel in Friday Harbour, Puget Sound, Washington. The seasonal temperature variation of the first three locations is shown in Figures 3, 4, and 5. The data for the first two localities mentioned were sent to us by Dr. Carl L. Hubbs, and the data for the curve in Figure 5 are from Skagsberg and Phelps (1946). The samples from Middle

TABLE 7.—ISOTOPIC ANALYSES OF ORGANIC CALCIUM CARBONATE SAMPLES

Spec. No. (Table 6)	$\delta$ (obs.)	$\delta$ Average	$\delta$ Average corrected	Temp. °C
1	-1.03	-1.03	-0.59	19
2	-1.28	-1.28	-0.84	19
3	-1.20	-1.20	-0.76	19
4	-1.06	-1.06	-0.62	19
5	-1.06	-1.06	-0.62	19
6	-1.38, -1.10	-1.24	-0.80	19
7	-1.12, -0.88	-1.00	-0.56	19
8	-2.23, -1.80, -2.23	-2.09	-1.65	21.5
9(a)	-1.50, -1.50	-1.50	-1.05	21.5
(b)	-1.63, -1.30, -1.64, -1.52, -1.39			
10(a)	-1.57, -1.64	-1.47	-1.02	21.5
(b)	-1.22, -1.43			
11(a)	-1.46, -1.64, -1.64	-1.44	-0.99	21.5
(b)	-1.12			
12	-1.52	-1.52	-1.07	21.5
13(a)	-1.70, -1.78, -1.86, -1.60	-1.64	-1.19	21.5
(b)	-1.42, -1.50			
14(a)	-1.48, -1.43, -1.27	-1.46	-1.01	21.5
(b)	-1.53, -1.45, -1.62			
15	-1.44, -1.52	-1.48	-1.03	21.5
16	-1.29, -1.42	-1.36	-0.91	21.5
17(a)	-1.41, -1.40, -1.50	-1.46	-2.59	29.5
(b)	-1.51			

TABLE 7—*Continued*

Spec. No. (Table 6)	$\delta$ (obs.)	$\delta$ Average	$\delta$ Average corrected	Temp. °C
18(a)		1.02	1.46	11
(b)		0.06	0.50	14.5
19(a)		0.58	1.01	12
(b)		-0.35	0.08	17
20(a)		0.03	0.32	15
(b)		-1.20	-0.91	21
21(a)		1.64	2.27	7
(b)		1.20	1.83	9

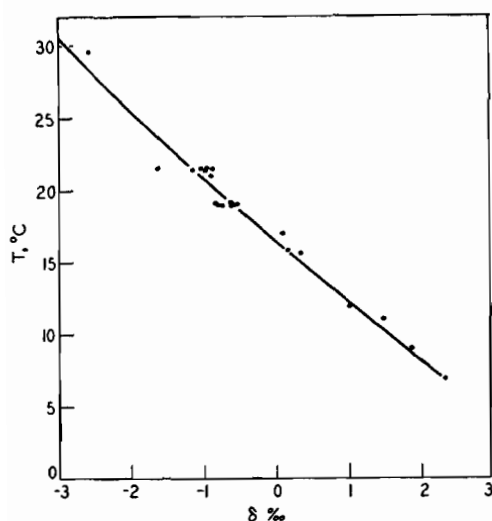


FIGURE 9.—ISOTOPIC TEMPERATURE SCALE

Channel locality lived at a depth of 145 meters, and the temperature ranges from about 9°C during July to about 7°C during December. The average maxima and minima of the temperatures of the localities were then estimated and matched with the maxima and minima in the respective curves resulting from the plot against the succession of layers in the shells shown in Figures 6, 7, and 8.

Table 6 lists the species and their location and temperatures of shell growth. The isotopic composition of the water in which these forms grew has been more carefully redetermined in conjunction with a complete program of determining the variation of isotopic composition

waters. From this study which will be reported elsewhere the analysis for the  $O^{18}/O^{16}$  ratio of carbon dioxide equilibrated with the average marine water was found to be 0.0‰ relative to our working standard gas. Therefore the correction, due to differences of  $O^{18}/O^{16}$  of water in which the marine animals grow, of the isotopic analysis of  $CaCO_3$  from the average isotopic composition of the oceans will be the negative value of the analyses for the water made in the same manner and is listed in the last column of Table 6. In Table 7 are listed the specimen numbers as specified in Table 6, the  $\delta$  analyses, and the  $\delta$  analyses corrected for the isotopic composition of the water. Figure 9 shows a plot of the results of the last two columns of Table 7.

Least squares calculations of the data in Table 7 gave the following equation:

$$t = 16.5 - 4.3\delta + 0.14\delta^2,$$

where  $t$  is the temperature in °C,  $\delta$  is the permil differences between the ratio of masses 46 and 44 of the sample and of the working gas. The intercept 16.5 is characteristic of the standard and the choice of the isotopic composition of the average marine waters. The standard deviation for  $t$  is equal to  $\pm 0.6^\circ\text{C}$ .

#### DISCUSSION AND CONCLUSIONS

There is one experimental point on the curve which deviates far beyond the experimental error from the calculated curve. This point was determined using mother of pearl shell which was regenerated at 21.5°C by the abalone in the process of covering a hole drilled in the shell. Similar points at 19°C deviate in the same direction, to a much lesser degree. Possibly such calcium carbonate may have been laid down by the abalone with sufficient rapidity to prevent complete isotopic equilibration between the solid calcium carbonate and surrounding water.

Least-squares calculations of data determined by McCrea (1950) for inorganically precipitated calcium carbonate in the range of 7–25°C give slopes of 5.2 and 4.1 and intercepts of 17.5 and 13.0 for series using Florida and

Cape Cod waters respectively. The value of the slopes is essentially in agreement with the present value of 4.3. Florida water of salinity 36.5 collected at Jacksonville analyzes  $+0.7\text{‰}$ , while the standard used by McCrea analyzes  $+0.4\text{‰}$  relative to our present working standard. The intercept obtained by McCrea where he used Florida water, when corrected for the differences in the  $\delta$  of the water and standards, becomes 16.0. The close agreement between the temperature scales based on inorganic and organic precipitation leads us to conclude that a valid isotopic temperature scale is here reported. The second equation from McCrea's data cannot be corrected since we do not have a sample of the water which he used.

## REFERENCES CITED

- ARMSTRONG, W. D., AND SCHUBERT, J., 1947, Exchange of carbon dioxide between barium carbonate and the atmosphere: *Science*, v. 106, p. 403.
- EPSTEIN, S., BUCHSBAUM, R., LOWENSTAM, H., AND UREY, H. C., 1951, Carbonate-water isotopic temperature scale: *Geol. Soc. America Bull.*, v. 62, p. 417-426.
- MCCREA, J. M., 1950, On the isotopic chemistry of carbonates and a paleotemperature scale: *Jour. Chem. Physics*, v. 18, p. 849-857.
- SKAGSBERG, T., AND PHELPS, A., 1946, Hydrography of Monterey Bay, California, Thermal conditions Part II (1934-1950): *Am. Philos. Soc., Proc.*, v. 90, p. 350-386.
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