moments. These conditions are required by classical statics. In Scholander's model the horizontal force components balance, but the vertical components clearly do not balance. If we suppose that the dolphin also develops a large downward force on its flippers in the region in front of the wave, so that the vertical force components balance, the moments clearly do not balance. The inescapable conclusion is that Scholander's model is not a possible one. In this light it is also clear that the experiment described by Scholander is not a pertinent one, because of the vertical reaction at the pivot of the support arm.

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 I am indebted to Scholander for sending me, through W. H. Munk, a copy of his article in advance of publication. The criticisms of the present note were submitted (again through Munk) to Scholander in private correspondence, but they were insufficient to induce him to withdraw his article from publication.
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- 13 May 1959

Eleven years ago Woodcock observed that a dolphin gets a free ride when in close proximity to the bow of a ship. In this situation the body of the dolphin rides in the horizontal water ahead of the bow-that is, it is not located within a wave. Only the tail fluke engages the disturbed water. This essential point was missed by both Woodcock and Hayes, who instead proceeded to explain an imaginary, unobserved situation where a dolphin supposedly gets a free ride in the front slope of a wind wave. With both dolphins and theories missing the boat, so to speak, it is no wonder that the observed bow-riding phenomenon remained unsolved.

Interesting, notwithstanding, is the thesis held by Hayes—namely, that a streamlined body of neutral bouyancy



Fig. 1. Towing a neutrally buoyant and balanced model in the front slope of a steep wave.

can be propelled within a wave at wave velocity. To most of my colleagues this seemed unrealistic, and with the authorities clearly split, the only way out was to test the idea experimentally. Standing on a dock one may easily observe that neutrally buoyant fish or pieces of seaweed in any orientation are not swept along with the waves passing by. The issue therefore narrows down to the question: Can the Hayes effect, if indeed it exists, maintain or assist a propulsion at wave velocity once such a propulsion has been started?

The following experiments were designed to test this. A skiff at the end of a rope 20 m long was towed from the tip of the transversely secured boom of one of the Scripps Institution research ships. By careful steering it was possible to maintain the skiff in a fixed relation to the waves coming off the side of the ship. Streamlined and neutrally balanced models were towed at four positions within these smooth and relatively very steep waves (Fig. 1). With the wave angle some 30° and the model weighing 650 gm, the Hayes effect would amount to some 300 gm. It can be seen from Fig. 2 that the drag merely reflected the relative velocity between the water and the model, being least in the crest, largest in the trough, and intermediary in the slopes. There is no indication whatever of a 300-gm push in the front slope (or of an added 300-gm drag in the back slope).

As pointed out in my original article, better data can certainly be obtained, but even now it seems clear that if Hayes, like myself, caters to the judgment of the multitude, he must come down to an experimental defense of his thesis. If through a more refined technique he can demonstrate that my relatively crude results are misleading, then I shall gracefully bow out, happy all the while to have contributed to a better understanding of what goes on in a wave. At present, however, Hayes' basic thesis is challenged by many and stands contradicted by experimental evidence (1).

Now, to return to the main issuenamely, the relationship between the dolphin's tail and the curvaceous bow of the ship. Hayes is eminently right when he echoes my concern that the situation, as outlined in his Fig. 1, theoretically is not a stable one; for in tending to topple over, the dolphin will slide back and out of position. So much for the theory, but in the actual fact he remains right there. We ourselves can beautifully handle unstable conditions, like standing upright, and no doubt the porpoise is equally proficient in similar control functions. If the dolphin in Hayes' diagram slides forward relative to the bow wave, the front edge of the tail fluke will soon catch horizon-



Fig. 2. Drag measurements in the trough, front, crest, and rear slope of a wave. Each point is a single reading. The short arrows in the wave profile indicate the direction of movement of the water particles. The large horizontal arrow indicates the direction of wave propagation.

tal water. This will depress the fluke against the rising water behind, with consequent propulsive effect. Perhaps some such scheme can be made to balance out. I shall confess, however, that my feeble attempts to show this experimentally have met with failure, so again we must bow to the dolphin. How, also, can a dolphin swim several times faster than predicted from drag and muscle power? This is another problem which has long amused physiologists but has rather worried students of theoretical fluid mechanics.

When playing around in the ocean, dolphins are pleasing to the eye no end, but let it only add to your thrill that these rascals are a graveyard to our wits. For is not finding out infinitely more exciting than knowing the answer?

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Note

1. For bibliography see the preceding report by Hayes.

4 September 1959

Carbon Isotope Fractionation in Bacterial Production of Methane

Abstract. Anaerobic bacteria from a Pacific Ocean mud cause unusually large carbon isotope fractionations during fermentation of methanol. The methane produced is about 8 percent enriched in C^{12} , relative to the original methanol. Fractionation factors determined at 30°C and 23°C were 1.081 and 1.094, respectively, which indicates that this process is dependent on temperature.

Bacterial fractionation of stable isotopes has been reported for sulfur (1)and hydrogen (2). Recent studies at this laboratory have revealed that an unusually large carbon isotope fractionation occurs during the bacterial production of methane. Because of the importance of bacteria to the carbon cycle, this process is being studied in some detail. The first reaction investigated was the anaerobic conversion of methanol to methane, which is believed to proceed as follows (3):

 $4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O_3$

The methane-producing culture used in this study was developed from a deep-sea mud cored in the northern Pacific Ocean (4). The culture was produced by enrichment with methanol and was grown in 16-by-125-mm screwcapped glass tubes at 23°C and at 30°C. Pure-culture study was not attempted, but a crude enrichment was achieved by serial transfer of the culture ten times at 2- to 4-day intervals before gas collections were made. Analyses were performed on gases produced by cultures growing in 600-ml Fenwal flasks completely filled with medium. The basal medium contained inorganic salts (5) dissolved in a mixture of three parts of synthetic sea water (6) to one part of distilled water. After sterilization of the medium at 122°C for 20 minutes, sufficient reagent-grade methanol was added to give a 0.10Mconcentration. To promote anaerobiosis, 0.03 percent of NA₂S·9H₂O was added before inoculation with 30 ml of an actively growing culture. The flasks were fitted with rubber stoppers through which the evolved gases were conducted via stainless-steel hypodermic fittings and polyethylene tubing to glass collection vessels filled with saturated NaCl solution.

Gas composition was determined with a Perkin-Elmer model 154 vapor fractometer. No attempt was made to recover or measure the carbon dioxide dissolved or precipitated in the culture medium during bacterial growth. The CH4 and CO2 fractions of the evolved gases were separated by condensing the CO₂ with liquid nitrogen. The CH₄ fraction was converted to CO2 by established combustion procedures (7). The carbon dioxide formed by combustion of CH4 and that produced during fermentation were analyzed separately in a modified Nier isotope ratio mass spectrometer (8) capable of measuring C^{13}/C^{12} ratios to a precision of ± 0.1 per mil (0.01 percent). These analyses are reported as permillage deviations (δ -values) of the C¹³/C¹² ratios of the samples from that of the CO₂ prepared from a special petroleum standard. The δ -value of this standard is -29.4 per mil relative to the Peedee belemnite standard used at the University of Chicago (9). The reported values have been cor-



Fig. 1. Changes in the carbon isotope ratio of methane produced by the bacterial fermentation of 0.10M methanol at 30°C.

Table 1. Volume yields and compositions of gases produced from 0.10M ($\delta C^{13}/C^{12}$ of original methanol is methanol -16.3 per mil) by bacterial fermentation at 30°C.

Time (day)	Methane		Carbon dioxide	
	Vol. (ml)	$\delta C^{13}/C^{12}$ (per mil)*	Vol. (ml)	$\delta C^{13}/C^{12}$ (per mil)*
4	183	-83.8	15	
8	146	-68.6	14	-1.2
12	182	-47.8	22	-3.8
15	162	-10.9	13	
21	142	+23.5	22	+11.1
25	63	+49.9	5	·

 $\delta C^{13}/C^{12}$ in permillage: C^{13}/C^{12} sample $-C^{13}/C^{12}$ standard

 $\overline{\mathbf{C}}^{13}/\mathbf{C}^{12}$ standard

 $\times 10^{3}$

rected for the O¹⁷ contribution to the mass-45 beam intensity (9).

Cultures grown at 30°C in a medium containing a 0.10M concentration of methanol produced 85 percent of the theoretical methane yield after 25 days. Chemical and isotopic analyses of the gases produced are shown in Table 1. Incomplete recovery of CO₂ is believed to have resulted from its retention in the medium by solution and by formation of calcium and magnesium carbonates (the medium contained 0.09 percent CaCl₂ and 0.37 percent MgCl₂). Compared with the original methanol, which has a C^{13}/C^{12} δ -value of -16.3per mil, the δ -values shown in Table 1 indicate that the methane produced by this fermentation is highly enriched in C^{12} . The extent of C^{12} enrichment is indicated by the plot (Fig. 1) of C^{13}/C^{12} δ -values against the volume of methane produced. As C12-enriched methane is produced during fermentation, residual undecomposed methanol necessarily becomes enriched in C13. The progressively increasing C^{13}/C^{12} ratio of the methane released reflects this enrichment. The C^{13}/C^{12} δ -values given in Table 1

were determined for finite gas volumes; they represent, therefore, the average isotope ratios of each volume of gas collected. Accordingly, in the graph shown in Fig. 1, isotope ratios are plotted against half of the volume of methane produced. Extrapolation of this curve to zero gas volume gives a δ -value of -90 per mil, from which we have computed a fractionation factor of 1.081 $(1\hat{0})$ for C¹² enrichment in CH₄ relative to the original methanol at the start of fermentation. The data indicate also a large isotopic disproportionation between the CH_4 and CO_2 produced; the CO₂ tends to be higher in C¹³ content than the CH4. A quantitative estimate of the carbon isotope distribution between these products was not possible because of incomplete recovery of CO₂ produced.

The experiment was repeated at the same temperature (30°C) with a higher concentration of methanol (0.25M) in the medium. Results obtained under these conditions were similar to those with 0.10M methanol, and a fractionation factor of 1.083 was computed from these data. The fractionation factor increased to 1.094 in another culture grown on 0.25M methanol at 23°C, indicating that this C¹² enrichment process is dependent on temperature.

These bacterial enrichments of light carbon (C^{12}) , which are of the order of 8 percent, represent the highest natural carbon isotope fractionations yet reported.

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- 10. The fractionation factor (k) for depletion of C¹³ (enrichment of C¹²) is determined from the expression:

 $\begin{array}{rl} \delta \mathbf{C}^{13}/\mathbf{C}^{12} \text{methane} & - & \delta \mathbf{C}^{18}/\mathbf{C}^{12} \text{ methanol} = \\ & (1-k) & (\delta \mathbf{C}^{13}/\mathbf{C}^{12} \text{methane} + 1000). \end{array}$

3 August 1959