21. V. Kohlschütter and C. Egg, *Helv. Chim. Acta* **8**, 470 (1925).
22. K. Krauss and W. Schriever, *Z. Anorg. Chem.* **188**, 259 (1930).
23. Four subsamples from two glendonites provided by E. Kemper (Hannover) gave the following $\delta^{13}C$ values: −20.53, −18.11, −20.67, and −21.96 per mil relative to PDB.
24. This work was supported by the Deutsche Forschungsgemeinschaft and the Office of Naval Research through grant N00014-79-C-0004, Project NR083-1026. We thank R.V. *Meteor*'s crew and captain for able support at sea, N. Mülhan (Kiel) and P. Holler (Kiel) for valuable shipboard assistance, R. Wittstock (Kiel) for unpublished oceanographic data, E. Kemper (Hannover) for the glendonite samples, and J. S. Killingley (La Jolla) for assistance with the micro mass spectrometer. Support was also provided through a travel grant by the Oregon State University Foundation. Joint Research Program SFB95, University of Kiel; Contribution No. 383.

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Stable-Carbon Isotope Ratios as a Measure of Marine Versus Terrestrial Protein in Ancient Diets

Abstract. *The stable-carbon isotope ratios for the flesh of marine and terrestrial animals from Canada's Pacific coast differ by 7.9 ± 0.4 per mil, reflecting the ~ 7 per mil difference between oceanic and atmospheric carbon. This difference is passed on to human consumers. The carbon isotopic values ($\delta^{13}C$) for human collagen thus yield direct information on the relative amounts of marine and terrestrial foods in prehistoric diets.*

In studies of the subsistence bases of prehistoric people, one may, by identifying faunal remains from archeological sites, determine the species of animals that were likely to have provided dietary protein. However, in those cases in which a population had access to two or more sources of protein, it is difficult to determine the relative amounts derived from each. It has been shown that stable-carbon isotope abundance ratios for human bone collagen can provide an estimate of the average fractions of the diet derived from C_3 and C_4 plants (C_3 plants fix carbon from ribulose diphosphate into a three-carbon acid, utilizing the enzyme ribulose-diphosphate carboxylase; in C_4 plants, CO_2 is first fixed into phosphoenolpyruvate to yield four-carbon acids, using the enzyme phosphoenolpyruvate carboxylase), because the C_3 and C_4 photosynthetic processes fractionate carbon by different amounts (*1*). In this report we show that a similar discrimination may be made between marine- and terrestrial-based diets on the coast of British Columbia and that this method can give a direct determination of the dietary adaptation of a population.

The purpose of this study was to determine whether the ~ 7 per mil difference observed between seawater bicarbonate and atmospheric CO_2 (*2*) is maintained through the various trophic levels, including human consumers, of the marine- and terrestrial-based food chains on the Pacific Coast. If such is the case, then a measurement of the $\delta^{13}C$ value,

$$\delta^{13}C = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000$$

where $R = {}^{13}C/{}^{12}C$, using the Pee Dee belemnite (PDB) standard for the bone collagen of a human consumer would give an estimate of the relative amounts of marine- and terrestrial-based carbon in the diet. The accuracy of this estimate will depend upon the variability in the $\delta^{13}C$ values for each food chain. If the variability introduced at each trophic level and in the collagen-forming process is large, it may obscure the difference between the two food chains.

Although the photosynthetic mechanisms may differ, marine phytoplankton fractionate carbon to approximately the same extent as terrestrial C_3 plants, that is, by about 19 per mil relative to their carbon source (*3*), thus maintaining the 7 per mil difference between air and ocean carbon at this trophic level. The plankton values do vary with ocean temperature but this variation is small (~ 0.35 per mil per degree celsius) (*4*), and we expect that for the study area considered here it will be negligible.

The fractionation between an animal's diet and the average $\delta^{13}C$ value for its whole body has been measured as 0.8 ± 1.0 per mil and is not species-specific (*5*). Therefore, the 7 per mil difference should persist between marine and terrestrial herbivores at this trophic level, without a great deal of variability being introduced. Furthermore, this small fractionation makes it possible to treat both plants and animals in a food chain as a single food source.

In this study the highest trophic level considered is man. For archeological studies, all isotope measurements should be made on bone collagen. This tissue reliably preserves its carbon isotope composition through time, as carbon replacement would result in the destruction of the protein. In living humans, bone collagen has a turnover of about 30 years (*6*), and so measurements will represent long-term average dietary intakes of individuals. This collagen is composed of amino acids which are derived from the food ingested. Dietary protein provides the essential amino acids, whereas the nonessential amino acids may be synthesized from carbohydrates or obtained from the protein. The diet on the Canadian Northwest Coast is reported (*7*) to have been very low in carbohydrate content, and so the human collagen would have been derived primarily from dietary protein. As this collagen results from the ingestion of a large number of animals and plants, it should therefore reflect the average $\delta^{13}C$ value for the food chain or chains upon which the diet is based. The $\delta^{13}C$ value for a consumer's collagen has been found to be ~ 5 per mil higher than that of its diet (*1*, *8*). The variability of this fractionation is not well known, but the limited available data suggest that it is ≤1 per mil (*1*, *8*).

Application of this technique will be

Table 1. Average $\delta^{13}C$ values relative to PDB for diet and consumer samples obtained from British Columbia and the Ottawa Valley, Quebec, and from the literature (*10*) (literature values are in parentheses). Variabilities are 1 standard deviation.

Description of samples	*N*	$\delta^{13}C$ (per mil)	Description of samples	*N*	$\delta^{13}C$ (per mil)
		Dietary materials			
Terrestrial mammals	27	−25.5 ± 1.5	Marine mammals	4	−17.5 ± 0.9
Terrestrial birds	15	−25.2 ± 1.5	Marine fish and shrimp	20	−17.5 ± 1.5
Freshwater fish	4	−28.8 ± 2.2	Littoral species	7	−18.7 ± 1.2
Population mean and error		−25.7 ± 0.3			−17.8 ± 0.3
		Human bone collagen			
(Northern European C_3 consumers	81	−19.6 ± 1.6)	(Greenland Eskimo	2	−12.8)
Ottawa Valley consumers	17	−19.6 ± 0.9	British Columbia consumers, coastal area	40	−13.4 ± 0.9
British Columbia consumers, interior area		(N = 5)	−15.4 ± 0.3		

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complicated when the diet includes both terrestrial C_3 and C_4 plants, since C_4 plants (such as maize) yield $\delta^{13}C$ values similar to those for marine species. However, this confusion does not arise in the British Columbia area. No agriculture was practiced, and the plants that would provide nutrition for either herbivores or humans are all C_3 species with the exception of a few (~ 6 percent) C_4 grass species in the southern and central interior portions of the province (*9*).

We compiled a list of animal species that would have provided the major portion of protein in the diet of local people by searching the archeological and ethnographic literature. Samples of muscle tissue from animals on the list were obtained for 19 marine species from British Columbia coastal waters and 19 terrestrial species from various areas of British Columbia.

Human archeological samples were obtained from the remains of 40 individuals from 11 coastal sites in British Columbia to represent people subsisting mainly upon marine protein. Since most prehistoric groups in British Columbia used at least some salmon, samples from purely terrestrial human consumers were not locally available. Therefore, consumers of terrestrial protein were represented by data from the literature (*10*) and by 17 samples from an Archaic population from the Ottawa Valley in Quebec. Five additional samples from humans recovered in the Lillooet area of interior British Columbia, where the diet included both terrestrial and marine species, were tested as an example of dietary mixing.

Muscle tissue samples were freeze-dried. Collagen samples were prepared by a version of Longin's method (*11*) as modified by Grootes (*12*). Two to four milligrams of each sample were combusted with CuO in evacuated Pyrex tubes, and the resulting CO_2 was analyzed in a Micromass 602D mass spectrometer. Measurements were made to a precision of 0.1 per mil (1 standard deviation) (*13*).

Table 1 presents the results of these measurements and data from the literature survey. The mean $\delta^{13}C$ value and error found for the flesh of the terrestrial animal population is -25.7 ± 0.3 per mil and for the marine animal population is -17.8 ± 0.3 per mil, giving a difference of 7.9 ± 0.4 per mil. The difference between oceanic and atmospheric carbon is thus preserved at this level in the food chains. The average human collagen value of -19.6 ± 1.6 per mil for a northern European population was identical to the value of -19.6 ± 0.9 per mil obtained in this study for the Ottawa Valley C_3 consumer population. [These values differ slightly from the value of -21.4 per mil found by Vogel and van der Merwe (*1*) for 31 humans from premaize levels of eastern North American sites. We do not know whether this represents a real difference, reflects different sample preparation techniques, or is perhaps a calibration difference.]

The difference between the European or Ottawa Valley C_3 consumer collagen value and the terrestrial food flesh average for British Columbia is 6.1 ± 0.4 per mil. This is close to the previously mentioned value of a ~ 5 per mil difference between diet and consumer collagen, although it is higher than the value of 3.9 per mil found by DeNiro and Epstein (*8*) in a control study with mice.

If we assume that human collagen is enriched by 5 per mil relative to the food protein, then the collagen of a purely marine consumer would be expected to have a value of -12.8 per mil. This value is in very good agreement with Tauber's measurements (*10*) on marine consumers from Greenland (Table 1).

Although we do not have data on human groups known to have been strictly marine or C_3 consumers, the human data (Table 1) and the data on food sources and collagen enrichment indicate that purely marine and purely terrestrial consumers from British Columbia should possess collagen with $\delta^{13}C$ values of about -13 and -20 per mil, respectively. Individuals who consumed a mixture of marine and terrestrial foods would have $\delta^{13}C$ values linearly scaled between these end points.

The uncertainty in estimating the marine/terrestrial carbon isotope ratio for an individual will depend upon the variability that exists within groups of consumers with identical diets. In the absence of control data for the purely marine or terrestrial consumers, we assume that the ± 0.9 per mil standard deviation found in this study for the British Columbia coastal population gives a maximum value for this variability. Then the marine/terrestrial dietary ratio for a mixed-diet consumer can be determined to an accuracy of ~ 20 percent at 1 standard deviation.

The British Columbia coastal population has an average collagen $\delta^{13}C$ value of -13.4 ± 0.9 per mil. This result suggests that, on average, these people consumed only 6 ± 20 percent terrestrial protein.

We also tested the technique by measuring five late prehistoric human samples from the Lillooet area of interior British Columbia. The average $\delta^{13}C$ result, -15.4 ± 0.3 per mil, indicates that these people obtained about 65 ± 20 percent of their protein from marine species.

We conclude that $\delta^{13}C$ measurements may be used to determine the relative proportions of marine- and terrestrial-based protein in aboriginal diets on the British Columbia coast. In view of the very close correspondence between our values and those obtained in other studies, it is highly likely that this technique can be applied in other geographic areas. In all such studies it will be necessary to examine carefully the local dietary options to determine any complications that could arise. The advantage of this technique is that the measurements may be easily and directly made on the target population.

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References and Notes

1. J. C. Vogel and N. J. van der Merwe, *Am. Antiq.* **42**, 238 (1977); N. J. van der Merwe and J. C. Vogel, *Nature (London)* **276**, 815 (1978).
2. H. Craig, *Geochim. Cosmochim. Acta* **3**, 53 (1953).
3. W. G. Deuser, E. T. Degens, R. R. L. Guillard, *ibid.* **32**, 657 (1968).
4. M. R. Fontugne and J.-C. Duplessy, *Oceanol. Acta* **4**, 85 (1981).
5. M. J. DeNiro and S. Epstein, *Geochim. Cosmochim. Acta* **42**, 495 (1978).
6. M. J. Stenhouse and M. S. Baxter, in *Radiocarbon Dating*, R. Berger and H. E. Suess, Eds. (Univ. of California Press, Berkeley, 1979), p. 324.
7. P. Drucker, *Indians of the Northwest Coast* (Natural History Press, Garden City, N.Y., 1955), chap. 2.
8. M. J. DeNiro and S. Epstein, *Geochim. Cosmochim. Acta* **45**, 341 (1981).
9. I. McT. Cowan and C. J. Guiguet, *B.C. Prov. Mus. Handb. 11* (1965); W. J. S. Downton, *Photosynthetica* **9**, 96 (1975); R. L. Taylor and B. MacBryde, *Vascular Plants of British Columbia* (Univ. of British Columbia Press, Vancouver, 1977); J. A. Teeri and L. G. Stowe, *Oecologia (Berlin)* **23**, 1 (1976); N. J. Turner, *B.C. Prov. Mus. Handb. 34* (1975).
10. Literature was collected from the following sources: data on the $\delta^{13}C$ values of Greenland Eskimo are from H. Tauber, in *Radiocarbon Dating*, R. Berger and H. E. Suess, Eds. (Univ. of California Press, Berkeley, 1979), p. 447; data on $\delta^{13}C$ values for northern Europeans were taken from various issues of *Radiocarbon*.
11. R. Longin, *Nature (London)* **230**, 241 (1971).
12. P. Grootes, personal communication.
13. Samples were combusted at 550°C. At this temperature, traces of graphite appear to remain in the Pyrex tubes. However, the yield of CO_2 from the combustion of meat and collagen is identical to that obtained at 900°C in Vycor tubing, which leaves no trace of graphite. The isotopic composition obtained by the two methods agrees to within the precision of the isotopic analysis, ±0.1 per mil.
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