Reports

Isotopic Paleoceanography of the Caribbean and East Pacific: Role of Panama Uplift in Late Neogene Time

Abstract. *Comparisons of carbon isotopic data on benthic foraminifera from Deep Sea Drilling Project sites 502 (western Caribbean) and 503 (eastern Pacific) indicate that the difference between the Atlantic and the Pacific in the per mil enrichment in carbon-13 of total dissolved carbon dioxide increased about 6 million years ago and again 3 million years ago, when the difference reached the modern level (1 per mil). Comparisons of planktonic foraminiferal oxygen isotopic data for the Caribbean and the Pacific suggest that the salinity of Caribbean surface waters began increasing 4 million years ago, possibly in response to shoaling of the Panama isthmus. These results suggest that modern circulation patterns in the Caribbean and eastern Pacific developed by 3 million years ago in concert with changing tectonic, climatic, and biogeographic patterns.*

The Atlantic and Pacific oceans are fundamentally different, in part because of a net export of deep waters from the Atlantic to the Pacific. This net flow, or "basin-basin fractionation" (*1*), has resulted in lime-rich, silica-poor sediments and oxygen-rich, nutrient-poor deep waters in the North Atlantic. In general, the North Pacific is the opposite, with silica-rich sediments and nutrient-rich, oxygen-poor deep waters. This pattern of deep-water circulation has led to a 1 per mil enrichment in ^{12}C in the deep Pacific relative to the deep Atlantic due to the oxidation of isotopically light organic matter (*2*). Surface waters also differ between the North Atlantic and North Pacific, with the North Atlantic being on average 2°C warmer and 1 per mil more saline at depths above 1000 m (*3*). These interoceanic contrasts have probably evolved through the Cenozoic due to changing geographic and climatic patterns (*4*). For example, climate in Neogene time cooled, as evidenced by growth of Antarctic ice cover in the middle Miocene (*5, 6*) and late Miocene (*7*) and growth of Northern Hemisphere ice cover in the middle Pliocene (*8*). Concurrent geographic changes include closing of the eastern Mediterranean (*9*) and initial shoaling of the Panama isthmus in the early Miocene (*10*), restriction of the western Mediterranean in the late Miocene (*11*), and final closing of the Panama isthmus in the Pliocene (*10, 12*).

To date, only one stable isotopic study has been conducted to trace the evolution of oceanographic contrasts between the Atlantic and the Pacific in Neogene time. Blanc *et al.* (*13*) investigated isotopes of carbon and oxygen in Neogene benthic foraminifera from Deep Sea Drilling Project (DSDP) site 116 in the northeast Atlantic and compared their results to findings from the southwest Pacific (*5*). The carbon isotopic patterns at both locations were similar until about 12 million years ago, at which time they diverged, with the site 116 foraminifera significantly enriched in ^{13}C relative to the southwest Pacific foraminifera. Blanc *et al.* concluded that, in the North Atlantic, production of oxygenated deep water similar to present-day production commenced 12 million years ago. This comparison of the isotopic histories of two oceans was limited by the core material available at the time (*14*). I present here the results of a detailed comparison between Late Neogene stratigraphies of low-latitude DSDP sites in the Caribbean Sea and the Pacific Ocean. Stable isotopic results reveal significant events in the late Neogene ocean which led to the establishment of modern oceanographic patterns by 3 million years ago.

Cores were collected with the newly developed hydraulic piston corer at western Caribbean site 502 and eastern Pacific site 503. The cores, each about 230 m in length, represented apparently continuous records of pelagic and hemipelagic sediment accumulation over the past 8 million years (*15*). Complete data and a detailed account of sample selection, preparation, and analysis are presented elsewhere (*16*). At each location, specimens of the benthic foraminifera *Cibicidoides* and the planktonic foraminifera *Globigerinoides sacculifera* (175 to 295 μm) were analyzed (*17*) at intervals estimated to range between 40,000 and 125,000 years (*18–20*).

The oxygen and carbon isotopic data were divided into four time-stratigraphic intervals (8 to 6, 6 to 5, 5 to 3, and 3 to 2 million years ago) on the basis of biostratigraphic and stable isotopic criteria (*16*). These intervals were chosen because 6 million, 5 million, and 3 million years ago mark times of significant change in many stable isotopic and biostratigraphic records. The mean stable isotopic compositions of foraminifera from these intervals were calculated and the results were compared between the two sites (Fig. 1) and between the planktonic and benthic foraminifera at each site (Fig. 2). In Figs. 1 and 2 the dashed lines mark the 95 percent confidence interval about the difference between data sets. The confidence limits are large—especially for the interval from 3 million to 2 million years ago—because of increased isotopic variability resulting from Northern Hemisphere glaciation, but there are several significant differences.

It is assumed that the benthic foraminiferal results for Caribbean site 502 reflect oceanographic conditions of the North Atlantic in general. Although other Neogene DSDP sites are more centrally located in the North Atlantic, detailed stable isotopic results for a continuous late Neogene sequence are available only from site 502. Bottom water in the Caribbean is composed primarily of North Atlantic Deep Water (NADW), which flows across a 1600-m sill at the Windward Passage (*21*). It is further assumed, in the absence of evidence to the contrary, that 1600 m has been the minimum depth of this sill throughout the latest Neogene.

Differences between the Atlantic and the Pacific in the carbon isotopic composition of benthic foraminifera reveal an overall increase to 1 per mil during the latest Neogene (Fig. 1). A value of 1 per mil is similar to the modern Atlantic-Pacific difference in the δ^{13}C (*22*) of total CO_2 based on hydrocast data (*2*). Holocene *Cibicidoides* from core tops also show a 1 per mil decrease from North Atlantic to North Pacific cores (*20*) as do the core-top *Cibicidoides* from sites 502 and 503 (*16*). Planktonic Δ^{13}C shows no overall increase, but rather two temporary increases coincident with permanent changes in benthic Δ^{13}C.

Benthic Δ^{13}C appears as two steps at 6 million and 3 million years ago (Fig. 1). These steps probably are not an artifact of dividing a gradually changing record because no change is recorded at the

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Miocene-Pliocene boundary (~ 5 million years). Even in the oldest time interval (8 million to 6 million years ago), Atlantic benthic foraminifera are significantly enriched in ^{13}C (by 0.60 per mil) relative to those of the Pacific, probably owing to an origin of net deep water flow from the Atlantic to the Pacific before 8 million years ago (*23*). The first step in $\Delta^{13}C$ (at 6 million years ago) may represent an increase to 75 percent of the modern basin-basin fractionation due to increased production of NADW. Increased NADW production 6 million years ago was suggested previously on grounds that the $\delta^{13}C$ decrease 6 million years ago is generally larger in Pacific than in Atlantic benthic foraminifera (*24*). The increase may be related to high-latitude cooling at that time. However, since the Mediterranean Sea was isolated from the world ocean between 6 million and 5 million years ago (*11*) and since the outflow of highly saline water from the Mediterranean may contribute to the production of NADW (*25*), increased NADW production in the latest Miocene may not be indicated (*26*). Alternatively, the $\Delta^{13}C$ step 6 million years ago may have resulted from termination of deep to intermediate water exchange between the Atlantic and the Pacific across a sill at Panama. Possible evidence for this mechanism is the presence of "Pacific-like" sedimentologic, mineralogic, and physical properties in the lower 30 m of site 502 (*15*).

The second $\Delta^{13}C$ increase is probably due to increased NADW production, because by 3 million years ago the Panama land bridge was largely completed. Vertical carbon isotopic differences also reveal significant ^{13}C enrichment in site 502 benthic foraminifera during the Pliocene, whereas there is no significant change at site 503 (Fig. 2). Thus, carbon isotopic changes in the Caribbean and the Pacific document evolving deep-sea circulation patterns that may have resulted from uplifting of Central America and cooling at high latitudes.

Oxygen isotopic differences between the Caribbean and the Pacific show a sharp decrease from the interval 8 million to 6 million years ago to the interval 6 million to 5 million years ago, when the average $\delta^{18}O$ values for planktonic foraminifera are nearly identical (Fig. 1). Thereafter the difference increases throughout the Pliocene. Benthic foraminifera reveal a similar pattern, although the magnitude of the change is reduced. Since the stable isotopic effects of continental ice volume are the same at each location for any time interval (within the mixing time of the oceans), the observed changes in oxygen isotopic contrast must reflect differing temperature and salinity histories between the eastern Pacific and the western Caribbean. Weyl (*27*) examined contrasting patterns of salinity in Atlantic and Pacific surface waters and found that the average 1 per mil difference in salinity increases to 2 per mil on either side of the Panama isthmus due to net transport of water vapor from the Atlantic to the Pacific by the trade winds across low-lying Panama. According to Weyl, as long as there was an open seaway across Central America, mixing of surface waters prevented the modern salinity contrast.

Biogeographic data on planktonic foraminifera indicate that the exchange of surface waters between the Atlantic and the Pacific began to become increasingly restricted 4 million to 3 million years ago (*12*). Similarly, the decrease in planktonic and benthic $\Delta^{18}O$ 6 million years ago may reflect slightly divergent temperature histories of surface and deep waters in the Caribbean and eastern Pacific, even with an open seaway. Restricted circulation of surface waters between these two bodies of water in the early Pliocene probably led to increased salinity in surface waters of the Caribbean Sea, which may be represented by the 0.7 per mil $\Delta^{18}O$ increase 6 million to 2

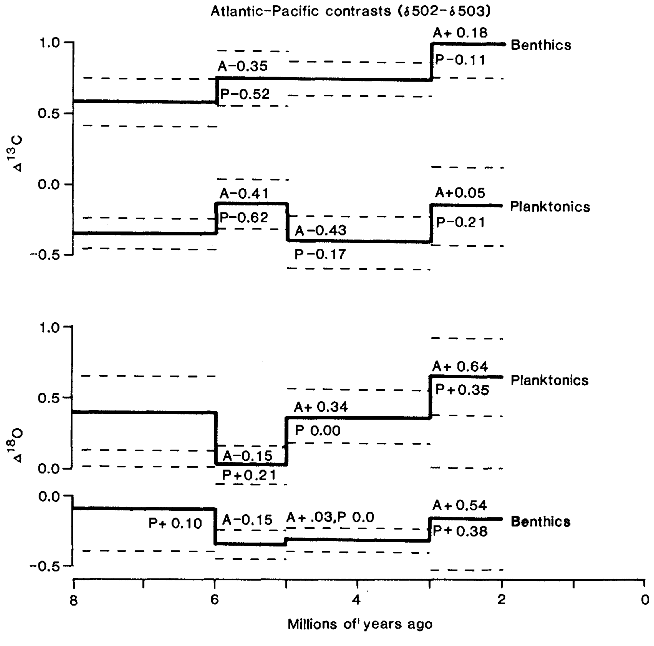

Fig. 1 (left). History of stable isotopic contrasts between DSDP sites 502 and 503 ($\delta_{502} - \delta_{503}$) calculated for four time-stratigraphic intervals in the late Neogene. Numbers preceded by *A* and *P* show the magnitude of Atlantic and Pacific isotopic change between each interval. Results are based on benthic foraminifera *Cibicidoides* sp. and planktonic *Globigerinoides sacculifera*. Benthic $\Delta^{13}C$ shows stepwise growth to modern values of the $\delta^{13}C$ contrast, which is maintained by the net flow of deep waters from the North Atlantic to the North Pacific. The history of the contrast in Atlantic-Pacific planktonic foraminiferal $\delta^{18}O$ is dominated by large Pliocene increases in Caribbean planktonic foraminiferal $\delta^{18}O$, which may reflect increasing salinity of Caribbean surface waters.

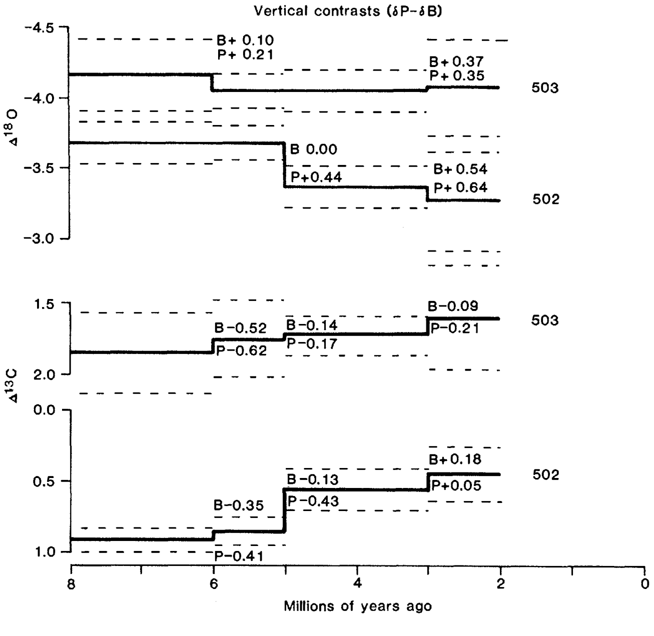

Fig. 2 (right). History of vertical stable isotopic contrasts ($\delta_{\text{planktonic}} - \delta_{\text{benthic}}$) calculated for four time-stratigraphic intervals at DSDP sites 502 and 503. Numbers preceded by *P* and *B* show the magnitude of planktonic (*Globigerinoides sacculifera*) and benthic (*Cibicidoides* sp.) isotopic change between each interval. Decreasing $\Delta^{18}O$ values at site 502 between 5 million and 2 million years ago result from an ^{18}O enrichment in planktonic foraminifera which may reflect increasing salinity of Caribbean surface waters. Decreasing $\Delta^{13}C$ values at site 502 result from increasing benthic foraminiferal $\Delta^{13}C$, perhaps signaling increased production of NADW.

million years ago (Fig. 1). Such an increase is also seen in the difference in the oxygen isotopic composition between planktonic and benthic foraminifera at site 502, whereas there is no significant difference at the Pacific site (Fig. 2). This is interpreted as increased salinity in surface waters rather than as decreased temperature because early Pliocene planktonic foraminifera of the Caribbean and tropical Atlantic are marked by the origin of endemic, warmwater *Globorotalia* species. The proposed increase in salinity may be only a regional (Caribbean) effect. Since NADW is formed by the sinking of North Atlantic surface waters, an increase in the salinity of those waters would not result in an increase in the vertical oxygen isotopic contrast of Caribbean waters during the Pliocene, as is evident at site 502 (Fig. 2).

Exact timing of the inferred salinity increase in Caribbean surface waters can best be seen by graphing isotopic data for sites 502 and 503 against absolute age (Fig. 3) (*28*). It is evident that site 502 planktonic foraminifera became significantly enriched in ^{18}O with respect to site 503 planktonic foraminifera beginning about 4 million years ago. This is in excellent agreement with biogeographic data on planktonic foraminifera (*12*) which suggest restricted communication between the surface waters of the tropical Atlantic and Pacific beginning at this time due to uplifting of the Central American isthmus. This is also in agreement with biogeographic studies of North and South American land mammals which reveal interchange across the Panama straits beginning in the late Miocene, with extensive faunal interchange by about 3 million years ago (*29*).

Before completion of the Panama isthmus, a large component of the Atlantic North Equatorial Current is thought to have reached the eastern Pacific (*30*). As the isthmus emerged, it must have deflected this current to the northeast, ultimately strengthening the Gulf Stream. Evidence for this is increased winnowing and erosion of sediments in the Yucatán Channel (*31*) and on the Blake Plateau (*32*) in the latest Miocene and in the Pliocene. Kaneps (*32*) inferred that an overall increase in Gulf Stream intensity began in the latest Miocene and culminated about 3.8 million years ago due to gradual emergence of the isthmus. Permanent glaciation of Northern Hemisphere continents appears to have begun about 3 million years ago (*8*). The intensified Gulf Stream may have been an important source of moisture to high northern latitudes at about that time, perhaps through a mechanism similar to that proposed by Ruddiman and McIntyre (*33*) for the Quaternary.

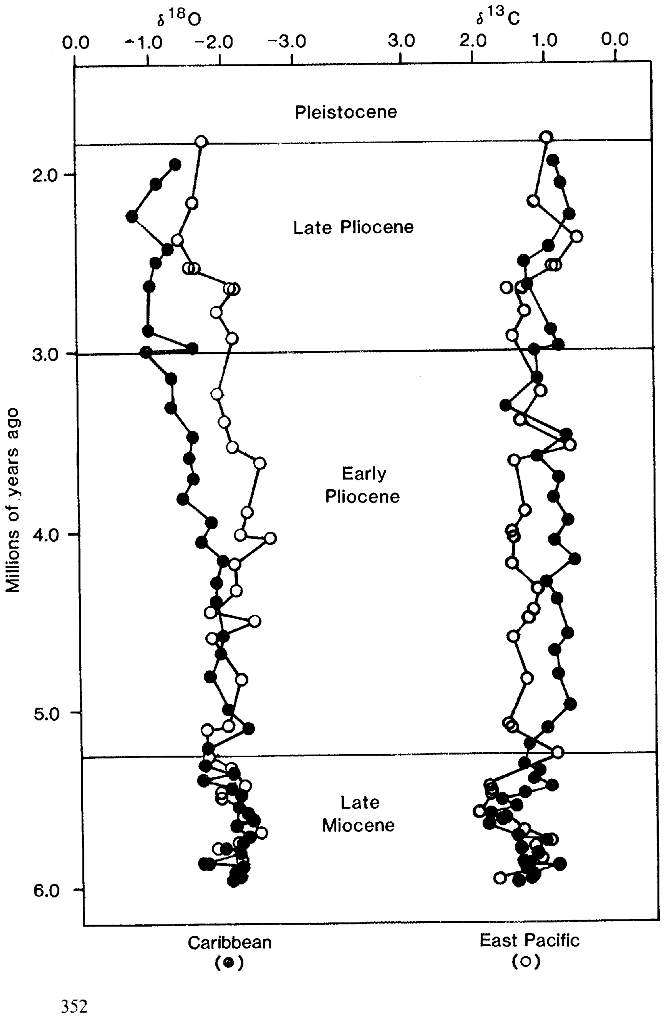

Fig. 3. Planktonic foraminiferal (*Globigerinoides sacculifera*) stable isotopic results at sites 502 and 503, plotted against age for the interval 6 million to 2 million years ago. The increase in site 502 $\delta^{18}O$ values at about 4 million years ago may reflect increasing salinity of Caribbean surface waters due to restricted circulation through the Panama straits.

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22. The value $\delta^{13}C = [(R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}]$ 1000, where $R = {}^{13}C/{}^{12}C$ of Pee Dee belemnite standard. Differences between two δ values are presented as Δ values.
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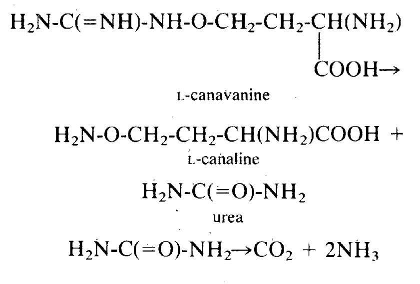
L-Canavanine, a Dietary Nitrogen Source for the Seed Predator *Caryedes brasiliensis* (Bruchidae)

Abstract. *Larvae of the bruchid beetle* Caryedes brasiliensis *(Bruchidae) develop entirely within the seed of the neotropical legume* Dioclea megacarpa. *The seed contains an appreciable concentration of L-canavanine, a potent antimetabolite and structural analog of L-arginine. This bruchid beetle uses the nitrogen stored in this toxic allelochemical as an effective dietary nitrogen source for amino acid biosynthesis.*

Maturing larvae of the bruchid beetle *Caryedes brasiliensis* (Bruchidae) develop entirely within the seed of the neotropical legume *Dioclea megacarpa* (*1*) (Fig. 1). More than 95 percent of the free amino acid nitrogen of this leguminous seed accumulates as L-canavanine, an insecticidal structural analog of L-arginine (*2*). This seed predator is distinctive in its synthesis of appreciable urease (E.C. 3.5.1.5) which makes possible effective mobilization of the nitrogen stored in canavanine via hydrolysis of urea; the latter is derived from canavanine by the action of arginase (E.C. 3.5.3.1).



$$H_2N\text{-}C(=NH)\text{-}NH\text{-}O\text{-}CH_2\text{-}CH_2\text{-}\underset{\displaystyle COOH}{\underset{|}{CH}}(NH_2) \rightarrow$$

L-canavanine

$$H_2N\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH(NH_2)COOH +$$

L-canaline

$$H_2N\text{-}C(=O)\text{-}NH_2$$

urea

$$H_2N\text{-}C(=O)\text{-}NH_2 \rightarrow CO_2 + 2NH_3$$

It has been proposed that these hydrolytic reactions not only detoxify canavanine, but also make ammonia available as a dietary nitrogen source for the developing larva (*3*). If this hypothesis is correct, it would represent a significant finding since, with the possible exception of cyanide incorporation into L-asparagine (*4*), no instance is known of insects using a toxic higher plant allelochemical in amino acid synthesis. The ease with which this insect can convert canavanine to canaline and urea and the availability of ^{15}N-labeled urea have made possible an experimental verification of this hypothesis which is important to our understanding of the basic biochemical interaction between higher plants and their insect predators.

To test this hypothesis, living terminal stadium larvae (9 g, fresh weight) were washed thoroughly with deionized water to remove adhering plant material; each larva was then injected with 1 μl of 150 m*M* ^{15}N-labeled urea (*5*). The treated larvae were maintained in the dark for 48 hours at 28°C before storage at −60°C. The frozen larvae were ground for 60 seconds with 50 ml of freshly distilled acetone (Sorvall Omnimixer, full power). The larval acetone powder was collected by vacuum filtration, and reground as above for 120 seconds and dried in air overnight at 22°C. The free amino acids of the acetone powder (2.7 g) were obtained by mechanical stirring at 3°C for 20 hours with 250 ml of 50 percent aqueous ethanol containing 0.15*N* HCl. The ethanolic extract was clarified by centrifugation at 18,000*g* for 20 minutes, adjusted to *p*H 7.0 with 1*N* NaOH, and concentrated by rotary evaporation at reduced pressure. Particulate materials deposited from the extract during concentration were removed by centrifugation as above. Finally, the ethanolic extract was reduced to 35 ml, adjusted to *p*H 2.5, and filtered (Millipore GS membrane).

The clarified larval extract was placed on a column (20 by 495 mm) of Dowex-50 (H^+) and washed with 3 liters of deionized H_2O at 3°C. Amino acids were eluted fully with 1.2 liters of 0.3*N* NH_4OH

Table 1. Percent ^{15}N incorporation into the free amino acids of the larvae of the bruchid beetle *Caryedes brasiliensis*. The values presented for percent of ^{15}N incorporation were obtained by three independent determinations of the same sample. The fragment structures are based on the work of Gelpi *et al.* (*8*). The amino acids were analyzed as their *N*-TFA-*n*-butyl ester derivatives. See Fig. 2 legend for the amino acid designations.

Amino acid	^{15}N incorporation (%)	Fragment used in calculations		
		*m/e**	Relative abundance (%)	Structure
Ala	35, 33, 33	140	100	$M - C_4H_9COO$
Gly	18, 18, 16	126	98.9	$M - C_4H_9COO$
2-ABA	30, 31, 28	154	100	$M - C_4H_9COO$
Thr	0, 0, 0	152	33.5	$CF_3CONH \overset{\cdots}{-} C \overset{\cdots}{-} CHCH_3$
Ser	16, 20, 19	138	49.2	$CF_3CONH \overset{\cdots}{-} C \overset{\cdots}{-} CH_2$
Val	7, 5, 7	168	100	$M - C_4H_9COO$
3-Ala	23, –, 21	168	100	$M - OC_4H_9$
Leu	0, 0, 0	182	59.6	$M - C_4H_9COO$
Ile	0, 0, 0	182	50.5	$M - C_4H_9COO$
H-Ser	11, 6, 7	152	100	$CF_3CONH \overset{\cdots}{-} C \overset{\cdots}{-} CHCH_3$
Pro	25, 25, 25	166	100	$M - C_4H_9COO$
Hy-Pro	0, 0, 0	164	100	$(M - C_4H_9COO) - CF_3COOH$
Met	11, 9, 10	227	64.8	$M - (CH_2CH - S - CH_3)$
Asp/Asn	24, 22, 25	240	79.7	$M - C_4H_9COO$
Lys	0, 0, 0	293	14.4	$M - C_4H_9COO$
Glu/Gln	44, 49, 48	198	100	$(M - C_4H_9COO) - C_4H_8$
His	0, 0, 0	206	75.8	$M - C_4H_9COO$

*Ratio of mass to charge.

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