

1 - 5 . ジカルボン酸

1 - 5 - 1 . Introduction

It has been proposed that the massive extinction of organisms, ranging from dinosaurs to marine plankton, at the end of the Cretaceous period (approximately 65 million years ago) was caused by a global fallout of debris and dust due to the impact of an extraterrestrial body or bolide^{6, 7)} or to extensive volcanism^{8, 9)}. Findings from organic geochemical studies support the bolide impact theory. For example, enrichments of soot, charcoal PAHs and fullerenes in the K/T boundary sediments have been suggested to be due to global fires triggered by the impact¹⁷⁻²²⁾, and an unusually high occurrence of α -aminoisobutyric acid and isovaline in sediments around the K/T boundary at Stevns Klint, Denmark, was attributed to a bolide²⁶⁾ because these two amino acids have been found in abundance in carbonaceous chondrites²³⁻²⁵⁾ and are rare in terrestrial materials. However, these two amino acids were not detected in the K/T boundary sediments at Kawaruppu, Hokkaido, Japan. Therefore, further studies are necessary to clarify the situation regarding the presence of extraterrestrial organic compounds in the K/T boundary sediments.

Many dicarboxylic acids are water-extractable and have been found in the Murchison^{42, 61-63)} and Yamato-791198 carbonaceous chondrites⁴²⁾. In this section, water-soluble dicarboxylic acids were analyzed in the K/T boundary sediments at Kawaruppu and compared their characteristics with those found in the Neogene Shinjo sediments, which are undoubtedly not of extraterrestrial origin. Although the results of several studies of water-soluble dicarboxylic acids in sediments have been reported⁶⁴⁻⁶⁸⁾, the Shinjo dicarboxylic acids were analyzed for normal, branched and unsaturated forms using a method similar to the one used in the present study. The characteristics of the K/T dicarboxylic acids were compared with those from the two carbonaceous chondrites⁴²⁾ and from other terrestrial sediments.

1 - 5 - 2 . Experiments

1-5-2-1. Samples

The K/T boundary sediments occur in the upper part of the Katsuhira Formation exposed in the bed of a shallow stream from the Mokawaruppu River, about 4 km upstream of Kawaruppu Town, Tokachi District, Hokkaido³⁰⁾. The sedimentary sequence at this locality consists predominantly of a marine, dark gray siltstone, bearing occasional calcareous concretions. A distinct grayish-black claystone, about 14 cm thick, which is similar in appearance to the well-known "boundary clay" of the classical K/T sections in Europe, is the only lithological break in this otherwise monotonous sedimentary succession. Thirteen sediment samples from different horizons in the K/T boundary claystone at Kawaruppu (0 - 13.7 cm), 5 samples above (40 - 495 cm) and 6 samples below (-395 - 0 cm) the boundary claystone were analyzed for dicarboxylic acids. The locality and stratigraphic sequence of the samples are shown in Fig. 1-1.

1-5-2-2. Analyses

For each analysis, 1 g of powdered boundary claystone or 2.5 g of powdered sediment above and below the boundary claystone was extracted with 10 ml water by sonication for 1 h and then, twice with 5 ml water for 30 min. The extracts were combined and divided into two parts. One part of the solution was dried and treated with 15 wt%

BF₃/methanol to make dimethyl esters of dicarboxylic acids. The other part was dried and treated with 2 mol l⁻¹ HCl/(*S*)-2-butanol to make the optically active dibutyl esters of the dicarboxylic acids.

A GC-MS (Shimadzu GC-MS QP-5000) was used for separation and detection of the dicarboxylic acids. The GC was equipped with a FFAP bonded FS-WCOT capillary column (60 m x 0.25 mm i.d.) and operated with a ramp rate of 10 °C min⁻¹ from 50 to 90 °C and 2 °C min⁻¹ from 90 to 200 °C. Helium was used as carrier gas with a flow rate of 2.2 ml min⁻¹. The MS was scanned every 1.0 s over m/z 60 to 300 in the chemical ionization mode at 200 eV with isobutane. Identification and quantification of compounds were generally made by comparison of peak retention time and area, respectively, of mass fragmentograms for selected ions with those of standard compounds.

All glassware was heated at 500 °C for at least 3 h prior to use in order to eliminate organic contaminants. The water was purified by a sequence of distillation, deionization, and then distillation twice more. The 15 wt% BF₃/methanol and 2 mol l⁻¹ HCl/(*S*)-2-butanol were prepared by bubbling BF₃ and HCl gas into twice distilled methanol and into (*S*)-2-butanol, respectively. A procedural blank was carried out with 0.5 g pre-ignited sand powder.

1 - 5 - 3 . Results and discussion

1-5-3-1. Identification and concentration of dicarboxylic acids

A total of 27 dicarboxylic acids were identified including 8 normal, 14 branched, and 5 unsaturated dicarboxylic acids. The mass numbers for identification and abbreviations used are shown in Table 1-5-1. The mass fragmentograms of these dicarboxylic acids in the middle horizon (5.5 - 6.3 cm) of the boundary claystone are shown in Fig. 1-5-1. The concentrations of the dicarboxylic acids are listed in Tables 3-2-2 to 3-2-4. Concentrations of the total normal, total branched, and total unsaturated dicarboxylic acids at each sample horizon are shown in Fig. 1-5-2, together with total organic carbon content. Recovery test of dimethyl esters showed 88% for oxalic acid, 98% for malonic acid, and 102% for succinic acid on the basis of 100% recovery for glutaric acid. Because the chromatogram of the procedural blank showed only small peaks of dicarboxylic acids, there was no significant contamination during the analysis.

The total concentrations of the normal, branched, and unsaturated dicarboxylic acids at the lowest horizon (0 - 0.8 cm) of the boundary claystone were 17, 0.40 and 0.71 nmol g⁻¹, respectively, which were the lowest concentrations of all the samples analyzed. In contrast, those at the other horizons (0.8 - 13.7 cm) in the boundary claystone were in the ranges, 80 - 310, 0.41 - 3.4 and 1.6 - 5.6 nmol g⁻¹, respectively, and were higher than those above and below the boundary claystone (29 - 82, 0.37 - 1.3 and 0.73 - 3.2 nmol g⁻¹, respectively). Such small concentrations of dicarboxylic acids at the lowest horizon of the boundary claystone are probably related to the decreased biomass caused by the extinction event. The higher concentrations in the boundary claystone relative to horizons above and below most likely result from higher adsorption by the clay, although another possibility is increased precipitation of dicarboxylic acids as insoluble salts due to increased alkaline earth elements in the ocean as a result of the increased continental weathering. It has been suggested that a bolide impact would have produced significant amounts of nitrogen oxides by shock heating of the atmosphere and that the resulting acid rain greatly increased continental weathering¹¹). If so, the dicarboxylate formation and precipitation could have occurred in the ocean as suggested for their formation and precipitation in the present eastern Pacific Ocean waters⁶⁹).

1-5-3-2. Normal dicarboxylic acids

The normal dicarboxylic acids found ranged from C₂ (oxalic acid) to C₉ (azeleic acid). Oxalic acid was the most abundant acid of the dicarboxylic acids analyzed in this study (Table 1-5-2). This acid has also been found to be the most concentrated low molecular weight dicarboxylic acid in the surface sediments of the Santa Barbara Basin and the Cariaco Trench⁶⁷). Molecular distribution patterns of the carbon numbers of the molecules at representative sample horizons are shown in Fig. 1-5-3. These molecular distribution patterns are very similar throughout all sample horizons. Log plots of the concentrations normalized to the C₄ acid as 100 versus carbon number give roughly straight lines in the range from C₂ to C₇ except for malonic acid (C₃). The slopes of these lines are -0.64, -0.58 and -0.65 for dicarboxylic acids above, in, and below the boundary claystone, respectively. These numbers are not significantly different from those found in the Neogene Shinjo sediments (-0.62 to -0.91). These distributions are probably due to chemical changes of biological compounds deposited with the sediments after undergoing diagenesis therein. It is apparent that the diagenetic time period needed for these acids to reach the straight-line distribution was sufficient for the K/T boundary sediments. It should be noted that not all of the samples analyzed by this method show the straight line. For example, the molecular distribution pattern of dicarboxylic acids in *Escherichia coli* was different from that for the sediments, malonic acid being the most abundant followed by succinic, glutaric, oxalic, and adipic acids in order of decreasing abundance.

1-5-3-3. Branched dicarboxylic acids

Branched dicarboxylic acids were found among the C₄ to C₇ acids. The optical isomers of methylsuccinic acid were resolved as their di-(*S*)-*s*-butyl esters as shown in Fig. 1-5-4. In this analysis, water was used as the solvent for extracting dicarboxylic acids from the sediment samples rather than the commonly used KOH-methanol solution, which promotes racemization of the dicarboxylic acids. As to the optical isomer predominance of dicarboxylic acids in biological matter, the author is aware of only one case, i.e., methylsuccinic acid from human urine which occurs as the *R*-enantiomer⁷⁰). Although the peak of *R*-enantiomer partly overlaps with an unknown peak in this analysis (b to e in Fig. 1-5-4), it appears that methylsuccinic acid is nearly racemic throughout the sample horizons. Methylsuccinic acid in the Neogene Shinjo sediments showed a slight predominance of the *R*-enantiomer in the upper part of the sedimentary sequence and was racemic in the lower part. Therefore, the presence of the racemic methylsuccinic acid indicates that the dicarboxylic acids found in this study are ancient and probably as old as the sediments. Although they were observed as dimethyl esters, it was not generally possible to determine the optical isomers (as di-(*S*)-*s*-butyl esters) of the other branched dicarboxylic acids, ethylsuccinic, 2,3-dimethylsuccinic, 2-methylglutaric, 2-ethylglutaric, and 3-methyladipic acids, because of their low concentrations, although 2-methylglutaric acid was found to be racemic in one sample horizon (11.0 - 11.7 cm).

1-5-3-4. Unsaturated dicarboxylic acids

The C₄ and C₅ unsaturated dicarboxylic acids were found, the C₅ acids being more abundant. *Cis* isomers of C₄ (maleic acid) and C₅ (citraconic acid) acids were more abundant than the corresponding *trans* isomers, fumaric acid and mesaconic acid, respectively, at all sample horizons. The ratios of *cis* to total isomers for C₄ and C₅ are 0.83 and 0.99, respectively (mean values of all sample horizons). Although isomerization takes place

between *cis* and *trans* isomers, they are generally transformed to the acid anhydrides via the *cis* form during diagenesis of sediments due to the anhydrous conditions. Acid anhydride forms were recovered as *cis* isomers in this analytical procedure. Therefore, the *cis* predominance with C₄ and C₅ is only apparent. Similar *cis* predominance was found in the Neogene Shinjo sediments. The ratios for C₄ and C₅ in the lower sequences of the Shinjo sediments were 0.73 and 0.94, respectively. The higher values for the K/T boundary sediments than for the Shinjo sediments probably indicate a longer period of diagenesis.

1-5-3-5. Comparison with dicarboxylic acids in carbonaceous chondrites

Twenty-six and twenty-five dicarboxylic acids were detected and quantified in the Murchison and Yamato-791198 carbonaceous chondrites, respectively⁷¹). All of these dicarboxylic acids were also detected at all sample horizons in this study and also in the Neogene Shinjo sediments; therefore, it is not possible to use any dicarboxylic acid as an indicator of extraterrestrial origin, as done with α -aminoisobutyric acid and isovaline in the case of amino acids²⁶).

The logarithmic plots of the concentrations versus carbon number of normal dicarboxylic acids in the Murchison and Yamato-791198 carbonaceous chondrites gave straight lines whose slopes were -0.74 and -0.63, respectively⁷¹). These numbers are not significantly different from those (between -0.58 and -0.65) found in this study and in the Neogene Shinjo sediments, although the dicarboxylic acids in the carbonaceous chondrites are abiotic in origin while those in the sediments are biological; therefore, the molecular distribution patterns are not useful for distinguishing extraterrestrial dicarboxylic acids from terrestrial ones.

Racemic methylsuccinic, 2,3-dimethylsuccinic, ethylsuccinic, 2-methylglutaric, 2,4-dimethylglutaric, and 2-ethylglutaric acids were found in the two carbonaceous chondrites⁷¹). Likewise, racemic methylsuccinic acid was found in the K/T boundary sediments; however, because the acids were racemic even in the Neogene Shinjo sediments, the racemic methylsuccinic acid in the K/T boundary sediments can not be used as an indicator of an extraterrestrial origin. It will be necessary to find optical isomers whose racemization is improbable, as in the case of isovaline²⁶) or four other α -methyl amino acids recently analyzed in Murchison⁷²).

Unsaturated C₅ dicarboxylic acids were more abundant than the C₄ acids in the Murchison and Yamato-791198 carbonaceous chondrites⁷¹). The K/T boundary sediments showed similar relative abundances of the unsaturated acids; however, the ratios of *cis* to total isomers differ between the K/T boundary sediments and the two chondrites. The ratios were 0.11 and 0.91 for the C₄ and C₅ acids, respectively, in Murchison, and 0.17 and 0.88, respectively, in Yamato-791198⁷¹). On the other hand, the ratios found in the K/T boundary sediments are 0.83 and 0.99, respectively. However, the difference does not completely rule out the possibility of extraterrestrial origin of the dicarboxylic acids, since the C₄ ratios, if originally chondritic, might have increased during the 65 million year diagenesis in the sediments. Thus, these ratios also do not provide a clear means of distinguishing dicarboxylic acids of extraterrestrial origin from terrestrial ones in the K/T boundary sediments.

The carbon chain-formation mechanism for dicarboxylic acids in the carbonaceous chondrites was suggested to be by progressive addition of one carbon species as inferred from the molecular distribution pattern⁷¹), and a similar mechanism was suggested for carbon chain elongation of light hydrocarbons and monocarboxylic acids from a carbon isotope study⁷³). If so, one carbon species were added not only to the terminal carbon but also to the

interior carbons, making chemically more stable secondary and tertiary carbons. This suggestion is in accordance with the observation that the normal dicarboxylic acid contents were generally lower with respect to branched ones in the carbonaceous chondrites. Molar ratios of normal to normal plus branched dicarboxylic acid contents at C₅, C₆ and C₇ are shown in Fig. 1-5-5 for the K/T boundary sediments along with those for the Murchison and Yamato-791198 carbonaceous chondrites. The ratios in the Neogene Shinjo sediments were 0.56, 0.71 and 0.58 (mean values) for C₅, C₆ and C₇ acids, respectively. The ratios in all the samples analyzed, except those of C₆ acids at the horizon (60 cm), are clearly higher than those in the two carbonaceous chondrites. Because the normal and branched saturated structures are relatively stable, the ratios, if originally due to a carbonaceous chondrite, would not have changed significantly during the 65 million year diagenesis of the K/T boundary sediments. Therefore, the clear difference in the ratios (Fig. 1-5-5) indicates that the dicarboxylic acids in the K/T boundary sediments are not entirely of extraterrestrial origin, although it is possible that an extraterrestrial contribution is hidden by an overlay of terrestrial dicarboxylic acids in the sediments.

It seems that the recognition of an extraterrestrial contribution is very difficult. It suggests that stable carbon and hydrogen isotope analyses might be useful. The meteoritic dicarboxylic acids are heavier in ¹³C by about 18‰ and in ²H about 500‰ than terrestrial ones⁶³). If an extraterrestrial contribution is hidden by an overlay of terrestrial dicarboxylic acids in the sediments, the contribution could raise the values significantly.

1 - 5 - 4 . Conclusions

Dicarboxylic acids found in the K/T boundary sediments at Kawaruppu included 8 normal (from C₂ to C₈), 14 branched (from C₄ to C₇), and 5 unsaturated ones (C₄ and C₅). Examinations of their concentrations, and structural and optical isomer ratios indicate the following:

11. Their total concentrations were lowest at the lowest horizon of the boundary claystone among horizons in, above and below the boundary claystone.
12. At most of the horizons, the normal dicarboxylic acids were more abundant than the branched isomers.
13. The normal isomers showed a roughly logarithmic decrease in concentration with increase in carbon number.
14. In two cases, the branched ones (methylsuccinic and methylglutaric acids) were racemic.
15. The unsaturated ones showed an apparent *cis*-form predominance over *trans*-one.

It appears that these features reflect the results of the 65 million year long diagenesis of the terrestrial bioorganic materials in the sediments. No clear evidence for the presence of extraterrestrial dicarboxylic acid(s) could be derived from the present study of the K/T boundary sediments at Kawaruppu.

Table 1-5-1: Compound names, their abbreviations and mass numbers for identification of dicarboxylic acids as dimethyl esters in the K/T boundary sediments at Kawaruppu.

No.	compounds	abbreviations	mass numbers for identification	
			(M+H) ⁺	(M-OCH ₃) ⁺
1	oxalic acid	Oxa	119	
2	methylmalonic acid	MMal	147	115
3	malonic acid	Mal	133	
4	ethylmalonic acid	EMal	161	129
5	2,2-dimethylsuccinic acid	2,2DMSuc	175	143
6	(<i>meso</i>)-2,3-dimethylsuccinic acid	(<i>m</i>)DMSuc	175	143
7	(<i>D,L</i>)-2,3-dimethylsuccinic acid	(<i>dl</i>)DMSuc	175	143
8	fumaric acid	Fuma	145	113
9	methylsuccinic acid	MSuc	161	129
10	succinic acid	Suc	147	115
11	mesaconic acid	Mesa	159	127
12	itaconic acid (2-propene-1,2-dicarboxylic acid)	Itac	159	127
13	citraconic acid	Citr	159	127
14	ethylsuccinic acid	ESuc	175	143
15	2-methylglutaric acid	2MGlu	175	143
16	3-methylglutaric acid	3MGlu	175	143
17,18	(<i>meso</i>)- & (<i>D,L</i>)- 2,4-dimethylglutaric acid	2,4DMGlu	189	157
19	maleic acid	Male	145	113
20	glutaric acid	Glu	161	129
21	adipic acid	Adi	175	143
22	2-ethylglutaric acid	2EGlu	189	157
23	2-methyladipic acid	2MAdi	189	157
24	3-methyladipic acid	3MAdi	189	157
25	pimelic acid	Pim	189	157
26	suberic acid	Sub	203	171
27	azeleic acid	Aze	217	185

M stands for mass number of molecular ion.

Table 1-5-2. Concentrations of normal dicarboxylic acids in the K/T boundary sediments at Kawaruppu.

relative depth / cm	concentration / nmol g ⁻¹							
	Oxa	Mal	Suc	Glu	Adi	Pim	Sub	Aze
495	78	1.0	2.3	0.46	0.11	0.035	0.022	0.041
225	37	0.98	1.8	0.43	0.078	0.021	0.014	0.010
120	27	0.60	1.2	0.25	0.050	0.012	0.014	0.018
60	34	1.1	1.0	0.27	0.030	0.027	0.020	0.033
40	49	1.6	2.3	0.56	0.21	0.10	0.072	0.10
12.7 - 13.7	290	3.2	9.1	3.7	1.9	0.24	0.32	0.44
11.7 - 12.7	290	4.0	9.7	3.1	2.4	0.25	0.33	0.49
11.0 - 11.7	180	2.3	4.6	1.6	0.51	0.084	0.091	0.11
10.2 - 11.0	75	0.93	2.1	0.79	0.54	0.15	0.24	0.36
8.7 - 10.2	150	2.9	5.4	2.4	0.77	0.20	0.32	0.43
7.5 - 8.7	120	2.5	5.1	2.6	0.65	0.17	0.28	0.33
6.3 - 7.5	130	2.4	4.3	2.3	0.57	0.10	0.23	0.26
5.5 - 6.3	190	1.3	5.3	3.1	0.67	0.15	0.34	0.57
4.3 - 5.5	160	1.9	4.1	2.2	0.47	0.085	0.20	0.26
2.8 - 4.3	120	0.86	2.4	0.99	0.36	0.11	0.25	0.42
1.8 - 2.8	88	1.1	1.6	0.87	0.20	0.10	0.19	0.30
0.8 - 1.8	120	1.3	2.4	1.7	0.34	0.13	0.36	0.61
0.0 - 0.8	15	0.44	1.2	0.31	0.13	0.042	0.048	0.095
-3 - 0.0	43	0.61	1.6	0.31	0.058	0.017	0.014	0.024
-10	42	1.2	2.9	0.85	0.26	0.10	0.13	0.20
-85	49	1.2	3.3	0.79	0.12	0.030	0.029	0.032
-165	41	0.85	2.2	0.46	0.059	0.012	0.009	0.006
-235	45	0.85	2.4	0.50	0.077	0.021	0.018	0.033
-395	31	0.43	1.4	0.29	0.057	0.015	0.017	0.025

Abbreviations of compound names are shown in Table 1-5-1.

Table 1-5-3. Concentrations of branched dicarboxylic acids in the K/T boundary sediments at Kawaruppu.

relative depth / cm	concentration / nmol g ⁻¹												
	MMal	EMal	MSuc	2,2DMSuc	(m)DMSuc	(dl)DMSuc	ESuc	2MGlu	3MGlu	2,4DMGlu	2EGlu	2Madi	3MAdi
495	0.033	0.003	0.30	0.044	0.002	0.005	0.030	0.059	0.043	0.004	0.004	0.001	0.008
225	0.032	0.004	0.32	0.074	0.002	0.010	0.047	0.062	0.048	0.002	0.006	0.004	0.008
120	0.019	0.002	0.18	0.051	0.008	0.006	0.028	0.037	0.028	n.d.	0.004	n.d.	0.005
60	0.027	0.003	0.26	0.079	0.014	0.010	0.031	0.051	0.073	0.007	0.008	0.004	0.010
40	0.039	0.005	0.39	0.095	0.009	0.012	0.049	0.079	0.069	0.002	0.008	0.011	0.021
12.7 - 13.7	0.049	0.009	1.3	0.20	0.030	0.027	0.15	0.47	0.98	0.043	0.047	0.036	0.066
11.7 - 12.7	0.042	0.007	1.3	0.22	0.018	0.021	0.14	0.39	0.67	0.036	0.039	0.034	0.063
11.0 - 11.7	0.025	0.003	0.70	0.14	0.008	0.011	0.073	0.21	0.35	0.006	0.017	0.011	0.024
10.2 - 11.0	0.009	n.d.	0.37	0.11	n.d.	0.005	0.081	0.14	0.24	n.d.	0.070	0.039	0.065
8.7 - 10.2	0.025	n.d.	0.99	0.20	0.020	0.030	0.12	0.44	0.96	0.028	0.13	0.045	0.076
7.5 - 8.7	0.016	n.d.	0.96	0.058	n.d.	n.d.	0.054	0.47	1.0	n.d.	0.056	0.048	0.071
6.3 - 7.5	0.019	n.d.	0.87	0.16	n.d.	0.034	0.15	0.47	0.96	0.022	0.12	n.d.	0.037
5.5 - 6.3	0.016	n.d.	0.91	0.20	0.022	0.031	0.13	0.48	1.2	0.027	0.11	0.018	0.035
4.3 - 5.5	0.017	n.d.	0.76	0.16	0.030	0.025	0.094	0.34	0.81	0.029	0.067	0.015	0.032
2.8 - 4.3	0.010	0.004	0.45	0.10	0.034	0.022	0.10	0.20	0.42	0.041	0.097	0.054	0.083
1.8 - 2.8	0.010	n.d.	0.33	0.056	0.016	0.004	0.056	0.17	0.42	0.023	0.055	0.034	0.059
0.8 - 1.8	0.011	0.002	0.48	0.095	0.016	0.012	0.094	0.34	0.89	0.040	0.082	0.017	0.056
0.0 - 0.8	0.009	0.004	0.16	0.043	0.007	0.007	0.024	0.041	0.072	0.008	0.008	0.006	0.011
-3 - 0.0	0.025	0.002	0.22	0.050	0.007	0.005	0.027	0.033	0.028	0.002	0.003	0.001	0.005
-10	0.048	0.008	0.53	0.12	0.022	0.022	0.099	0.16	0.15	0.019	0.061	0.029	0.046
-85	0.046	0.005	0.51	0.072	0.010	0.014	0.065	0.11	0.073	0.005	0.009	0.004	0.013
-165	0.033	0.004	0.35	0.048	0.006	0.009	0.039	0.058	0.054	0.002	0.006	n.d.	0.011
-235	0.035	0.003	0.34	0.059	0.001	0.011	0.036	0.062	0.044	0.002	0.003	0.005	0.005
-395	0.025	0.003	0.26	0.054	0.008	0.009	0.030	0.049	0.039	0.002	0.004	0.004	0.007

Abbreviations of compound names are shown in Table 1-5-1.

n.d. : not detected

Table 1-5-4. Concentrations of unsaturated dicarboxylic acids in the K/T boundary sediments at Kavaruppu.

relative depth / cm	concentration / nmol g ⁻¹				
	Fuma	Male	Mesa	Itac	Citr
495	0.031	0.15	0.001	0.005	0.55
225	0.042	0.14	0.001	0.002	0.91
120	0.039	0.093	0.003	0.005	0.68
60	0.040	0.16	0.005	0.014	0.89
40	0.13	0.24	0.012	0.032	1.5
12.7 - 13.7	0.37	1.8	0.032	0.026	3.1
11.7 - 12.7	0.53	2.1	0.031	n.d.	2.8
11.0 - 11.7	0.25	1.6	0.026	n.d.	2.2
8.7 - 10.2	0.19	1.7	0.032	n.d.	3.6
7.5 - 8.7	0.10	0.91	n.d.	n.d.	1.1
5.5 - 6.3	0.19	1.3	0.031	0.034	2.6
4.3 - 5.5	0.14	1.1	0.022	0.022	1.9
2.8 - 4.3	0.11	0.58	0.005	n.d.	1.4
1.8 - 2.8	0.069	0.45	0.011	n.d.	1.1
0.8 - 1.8	0.11	0.66	0.015	n.d.	1.9
0.0 - 0.8	0.099	0.33	0.005	n.d.	0.28
-3 - 0.0	0.014	0.13	0.029	n.d.	0.66
-10	0.067	0.35	0.012	0.023	2.7
-85	0.071	0.23	0.007	0.009	1.5
-165	0.043	0.13	0.003	0.001	0.81
-235	0.032	0.16	0.004	0.011	0.96
-395	0.025	0.14	0.006	0.017	1.2

Abbreviations of compound names are shown in Table 1-5-1.

n.d. : not detected

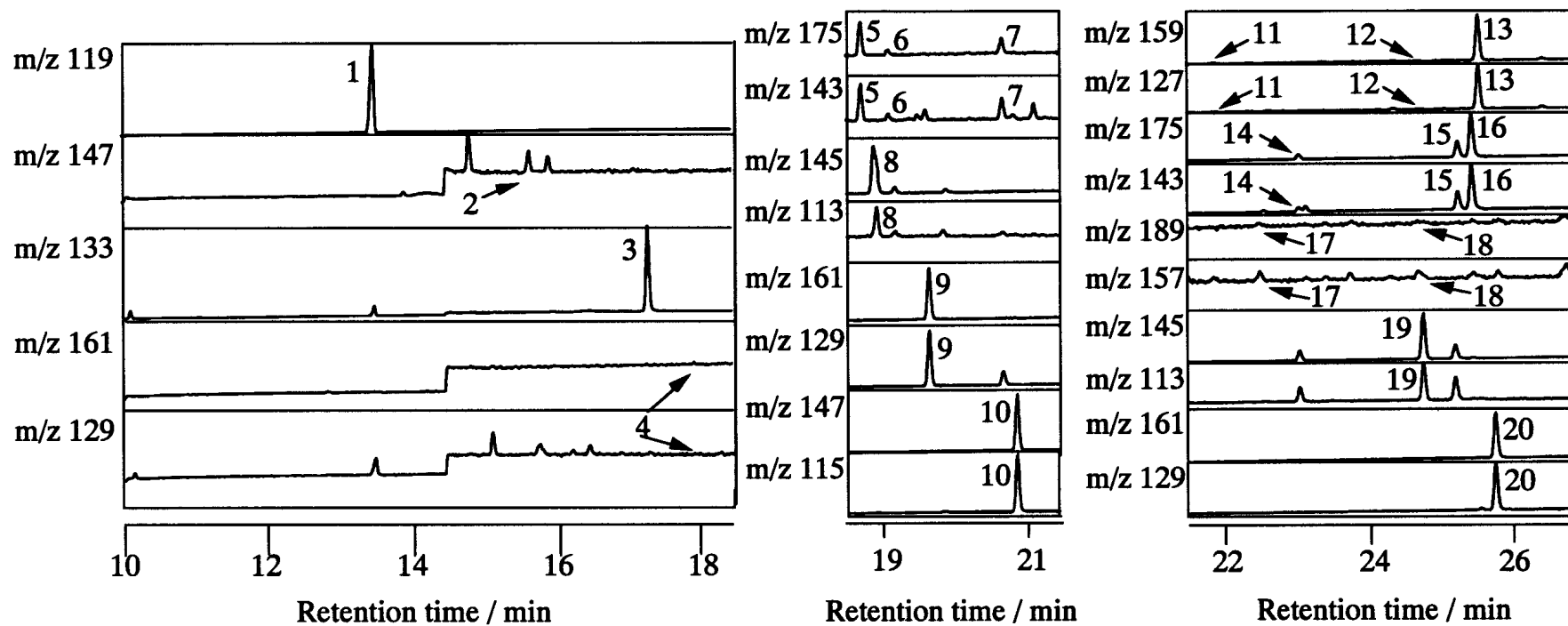


Fig. 1-5-1. Mass fragmentograms of dicarboxylic acid dimethyl esters in the K/T boundary claystone (5.5 to 6.3 cm) at Kawaruppu. Peak numbers correspond to those of the compounds in Table 1-5-1.

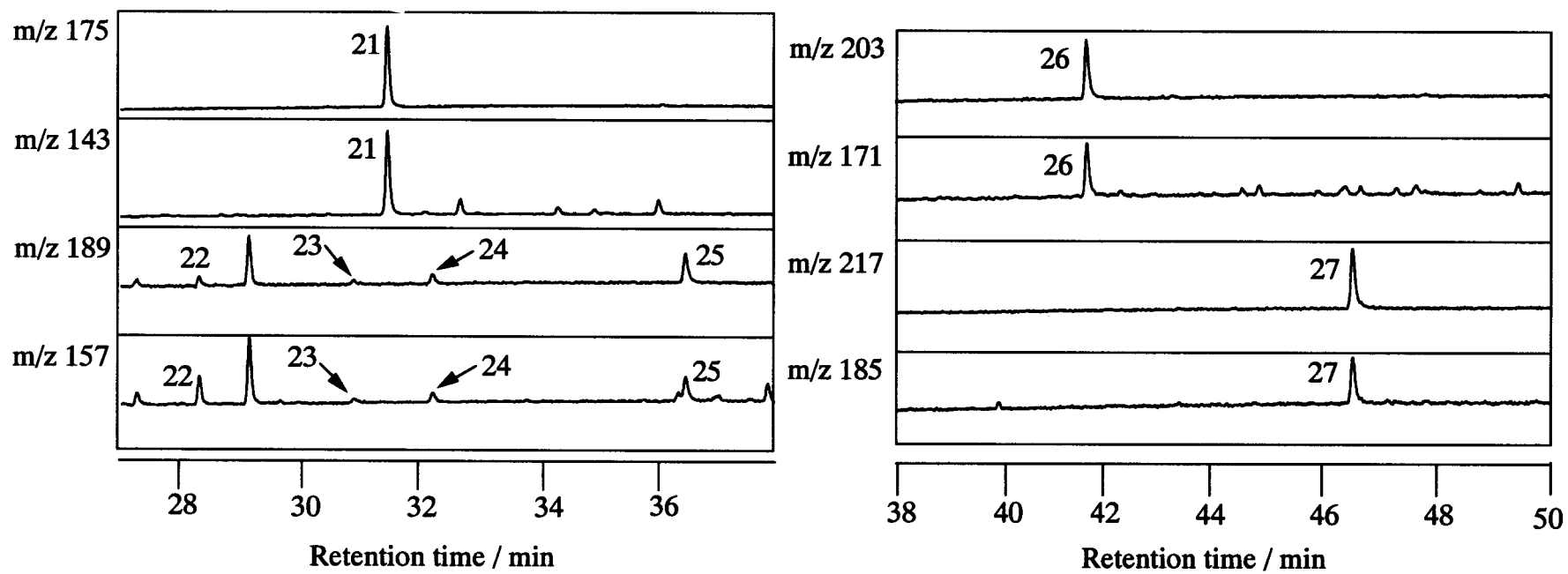


Fig. 1-5-1. (continued)

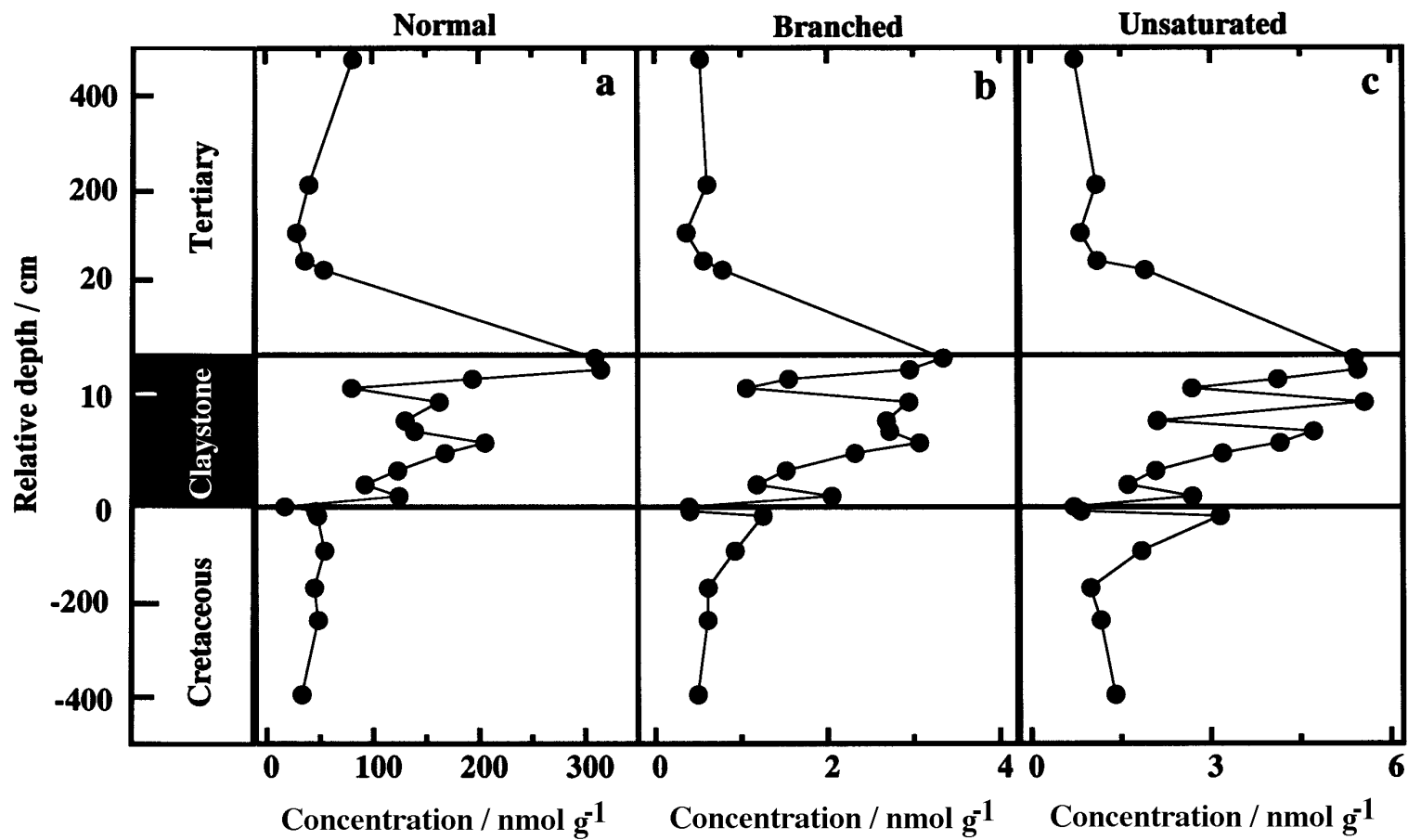


Fig. 1-5-2. Depth distributions of a: total concentrations of normal dicarboxylic acid, b: those of branched ones, and c: those of unsaturated ones in the K/T boundary sediments at Kawaruppu.

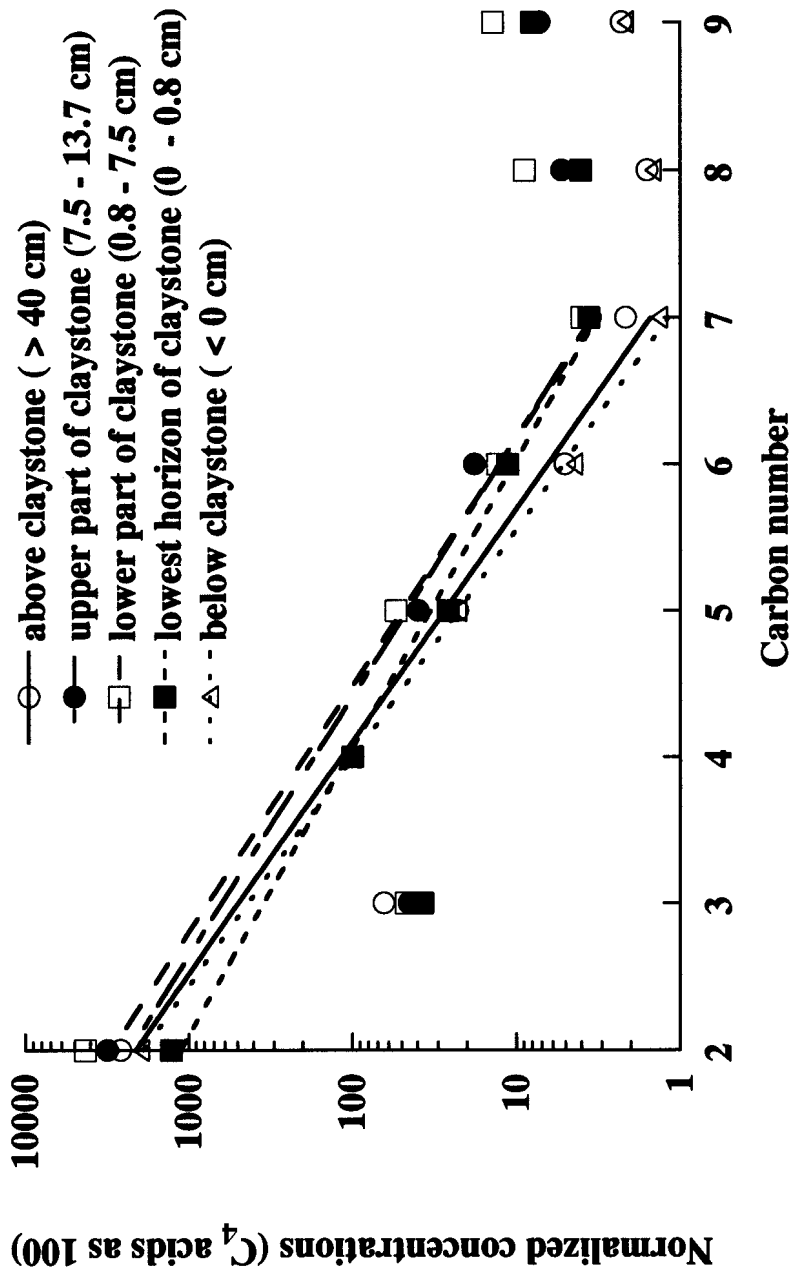


Fig. 1-5-3. Molecular distribution patterns of normal dicarboxylic acids in the K/T boundary sediments at Kawaruppu. Concentrations are normalized to succinic acid (C₄) as 100.

m/z=245

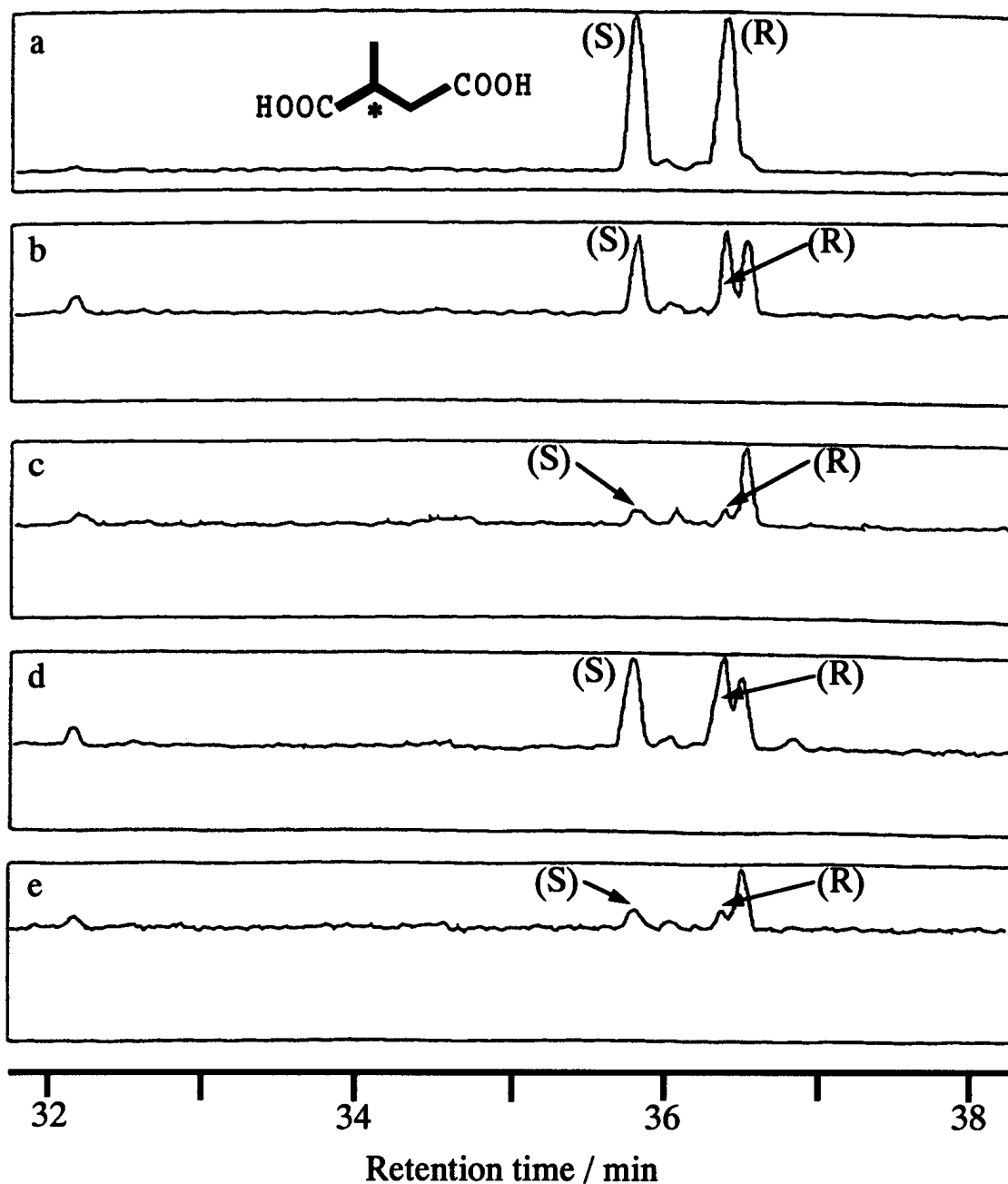


Fig. 1-5-4. Mass fragmentograms of methylsuccinic acid di-(S)-s-butyl esters in the K/T boundary sediments at Kawaruppu. (a) standard sample, (b) above the boundary claystone (495 cm), (c) above the boundary claystone (60 cm), (d) within the boundary claystone (0 to 13.7 cm), and (e) below the boundary claystone (-235 cm).

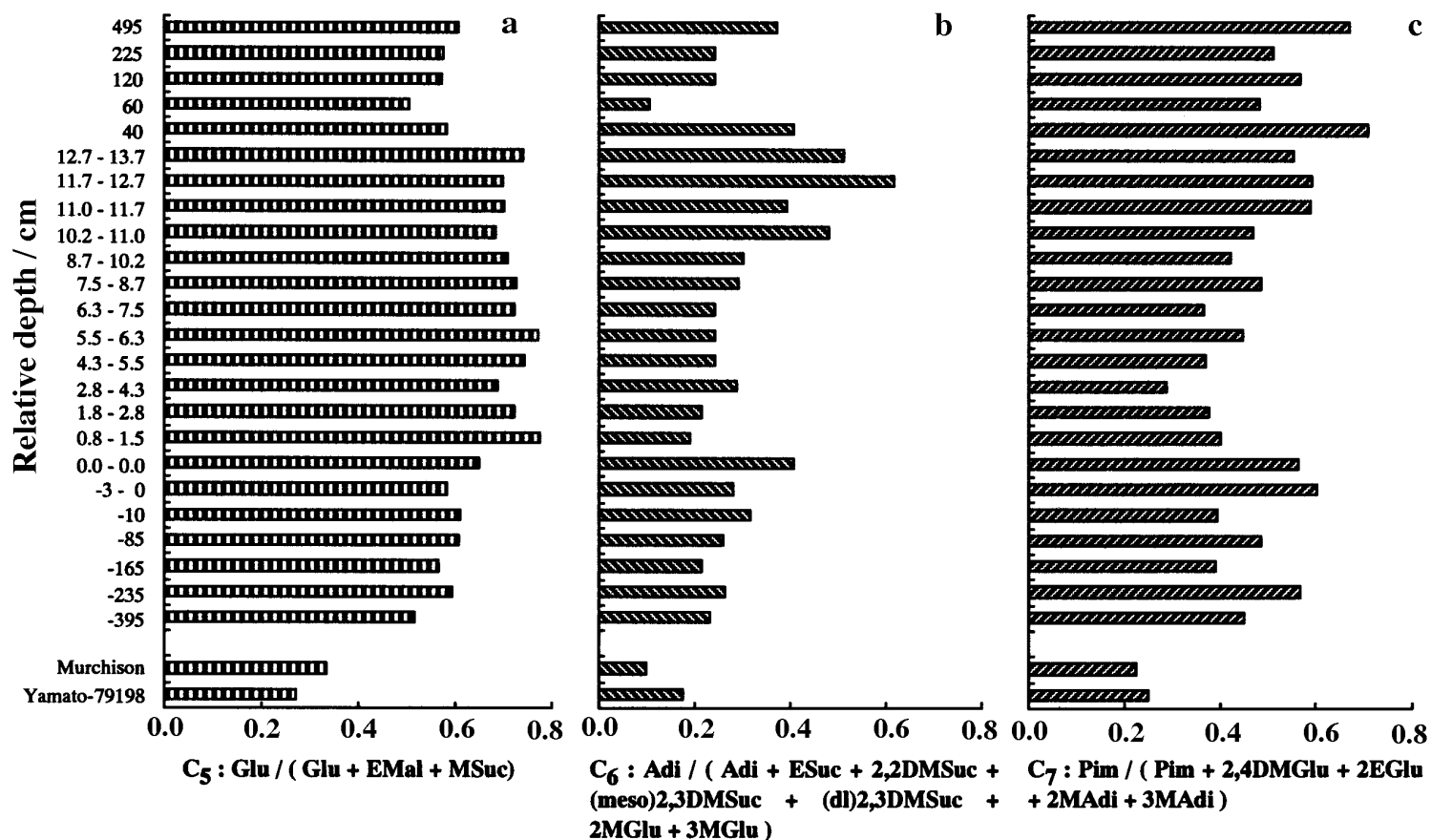


Fig. 1-5-5. Ratios of normal to normal plus branched dicarboxylic acid contents in the K/T boundary sediments at Kawaruppu and carbonaceous chondrites. (a) for C₅ acids, (b) for C₆ acids, and (c) for C₇ acids. Abbreviations are shown in Table 3-2-1. Data of the Murchison and Yamato-791198 were from Shimoyama and Shigemastu (1994).