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Full Title:

Stable carbon isotopic composition of low molecular weight dicarboxylic acids and ketoacids in remote marine aerosols

Running head:

$\delta^{13}\text{C}$ of dicarboxylic acids in marine aerosols

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Abstract

We determined stable carbon isotopic composition ($\delta^{13}\text{C}$) of C_2 to C_9 dicarboxylic acids (DCAs) and some ketoacids in the marine aerosols from the western Pacific and Southern Ocean ($35^\circ\text{N} - 65^\circ\text{S}$). On average, oxalic (mean: -16.8‰), adipic (-17.2‰) and glyoxylic (-17.6‰) acids showed heavier $\delta^{13}\text{C}$, whereas, maleic (-24.2‰), methylmalonic (-23.6‰) and phthalic (-23.1‰) acids were more depleted in ^{13}C . Oxalic acid presented very diverse $\delta^{13}\text{C}$ values (-27 to -7‰), which increased from mid latitudes towards the Equator. A similar latitudinal trend of $\delta^{13}\text{C}$ was also found for malonic, succinic and adipic acids. However, such a trend was not observed for phthalic, maleic and glyoxylic acids. We suggest that the $\delta^{13}\text{C}$ increase towards the Equator is associated with photochemically aged air masses, in which kinetic isotope effects for photochemical degradation of DCAs may be important. Differences in $\delta^{13}\text{C}$ of some saturated DCAs were also found to increase from mid latitudes to the Equator.

Key words: Carbon isotopic composition; Decarboxylation; Latitudinal change; Photochemical aging;

1. Introduction

Compound-specific stable carbon isotope analysis (CSCIA) of organic compounds has been widely used in many scientific fields [*Hayes et al.*, 1990; *Lichtfouse*, 2000; *Schmidt et al.*, 2004]. Its applications to atmospheric aerosols include the studies on long-chain fatty acids, n-alkanes, n-alcohols and polycyclic aromatic hydrocarbons [*Conte and Weber*, 2002; *Fang et al.*, 2002; *Norman et al.*, 1999; *Schefuß et al.*, 2003; *Simoneit*, 1997]. This technique is very useful for investigating sources and long-range atmospheric transport of aerosols, due to a conservative character of these biomarker

compounds. In contrast, CSCIA of small hydrocarbons can provide highly valuable information to determine the extent of photochemical processing that individual target compounds have experienced in the atmosphere. This approach also has a possibility to differentiate the impact of local sources from long-rang transported air masses [Anderson *et al.*, 2004; Iannone *et al.*, 2003; Rudolph and Czuba, 2000; Rudolph *et al.*, 2000; 2002; 2003; Saito *et al.*, 2002].

Low molecular weight (LMW) dicarboxylic acids (DCAs) and related polar compounds comprise a significant fraction of organic aerosols and can play an important role in atmospheric chemistry and on the radiative forcing of the Earth's climate [Kawamura and Usukura, 1993; Saxena and Hildemann, 1996; Saxena *et al.*, 1995]. Although LMW DCAs and related polar compounds can be generated from primary sources including incomplete combustion of fossil fuels [Kawamura and Kaplan, 1987] and biomass burning [Narukawa *et al.*, 1999], they are thought to be formed mainly by secondary processes in the atmosphere and have been used as tracers for secondary aerosols [Fisseha *et al.*, 2004; Kawamura *et al.*, 1996; Sheesley *et al.*, 2004]. They are also subjected to photochemical degradation in the atmosphere [Kawamura *et al.*, 2005; Zuo and Hoigne, 1994]. Recently, Kawamura and Watanabe [2004] reported a novel method for CSCIA of LMW DCAs and ketoacids using gas chromatography/isotope ratio mass spectrometry (GC/irMS). Before this work, related research had been confined to the measurements of stable carbon isotope ratio ($\delta^{13}\text{C}$) of oxalic acid in marine aerosols at Bermuda [Turekian *et al.*, 2003] and that of formic and acetic acids in rainwater samples from Los Angeles [Sakugawa and Kaplan, 1995].

Here we report the stable carbon isotopic compositions of LMW DCAs and one α -ketoacid and their latitudinal changes in the marine aerosols collected from the western

Pacific and Southern Ocean. The data sets are discussed in terms of photochemical aging of the organic acids in the atmosphere. The results are also discussed using air mass back trajectories.

2. Experimental Methods

2.1. Aerosol Sampling and Analysis for Concentrations of DCAs and Ketoacids

Marine aerosols were collected during a cruise between Tokyo and Antarctica conducted from November 22, 1994 to February 11, 1995 (KH94-4, R/V *Hakuho Maru*). The cruise track and surface wind conditions are shown in Fig.1. A high volume air sampler loaded with a preheated (450° C, > 3 hours) quartz fiber filter (20 × 25 cm²) was deployed for aerosol collection on an upper deck of the ship. The samples were analyzed for water-soluble DCAs and ketoacids using the methods reported previously [Kawamura, 1993; Kawamura and Ikushima, 1993]. Briefly, an aliquot (typically one eighth) of a filter was cut in small pieces and extracted with ultra-pure organic-free water in an ultrasonic bath. The water extracts were then concentrated to nearly dryness by a rotary evaporator under vacuum, and then derivatized to butyl esters and/or dibutyl acetals by reacting with 14% BF₃ in n-butanol. Lastly the derivatives were determined using a HP 6890 gas chromatograph equipped with a fused silica capillary column (HP-5, 0.2 mm × 25 m × 0.52 μm) and an FID detector. Using this technique, aerosol concentrations were measured for 11 linear saturated α,ω-DCAs (C₂ to C₁₂) and 17 branched/unsaturated DCAs or ketoacids. Their aerosol concentrations and molecular distributions are presented elsewhere [Wang *et al.*, 2005].

2.2. Determination of δ¹³C for DCAs and Ketoacids

δ¹³C values of water-soluble DCAs and ketoacids relative to Pee Dee Belemnite (PDB) were measured using the method developed by Kawamura and Watanabe [2004].

Briefly, after an appropriate amount of internal standard (n-C₁₃ alkane) was spiked to the derivatized fraction of each sample, $\delta^{13}\text{C}$ of the derivatives were determined using GC/irMS (HP 6890 GC and Finnigan-MAT Delta plus irMS). $\delta^{13}\text{C}$ of free organic acids in the sample were then calculated using a mass balance equation based on the measured $\delta^{13}\text{C}$ of the derivatives and the derivatizing agent (1-butanol). Each sample was analyzed in replicate and the mean $\delta^{13}\text{C}$ is reported. Difference in $\delta^{13}\text{C}$ of free acids for replicate analyses is generally below 1 ‰. But for minor species, the difference is sometimes up to 1.5 ‰ and occasionally over 2 ‰. Whether a reliable $\delta^{13}\text{C}$ can be obtained for a compound in a sample depends on its concentration and properties of the sample. We thus only report $\delta^{13}\text{C}$ for nine compounds (eight DCAs and one α -ketoacid) in this work although $\delta^{13}\text{C}$ for some other organic acids were also determined.

2.3. Air Mass Back Trajectory

Backward air mass trajectories were conducted using the 40-year reanalysis data of the European Center of Medium-range Weather Forecast (ERA40). The trajectory calculation was based on backward tracking of selected air parcels, assuming that they were moving along the ambient airflow [*Hatsushika and Yamazaki, 2003*]. The flow pattern was updated every 6 hours.

3. Results and Discussion

3.1. Summary of $\delta^{13}\text{C}$ for DCAs and Ketoacids

$\delta^{13}\text{C}$ values for nine organic acids are given in Table 1. On average, oxalic (C₂), adipic (C₆) and glyoxylic (ω C₂) acids are more enriched in ¹³C while maleic (M), methylmalonic (iC₄) and phthalic (Ph) acids are more depleted in ¹³C. It should be born in mind that unlike biomarkers that can faithfully reflect $\delta^{13}\text{C}$ values in their sources

because of their stable character, LMW organic acids are subjected to both photochemical production and degradation in the atmosphere [Chebbi and Carlier, 1996; Kawamura *et al.*, 2005]. Consequently, significant carbon isotopic fractionation of these LMW molecules may have occurred during atmospheric transport (see discussion below). Cautions should thus be taken for the interpretation of their potential sources based on their $\delta^{13}\text{C}$ values determined in samples. On the other hand, rich information on atmospheric chemical processes may exist behind the isotopic fractionation.

3.2. Latitudinal Changes in $\delta^{13}\text{C}$ of Individual Organic Acids

Fig. 2 presents latitudinal variations of $\delta^{13}\text{C}$ for the detected organic acids. Interestingly, $\delta^{13}\text{C}$ of the saturated DCAs especially for C_2 , C_3 (malonic) and C_4 (succinic) increase from mid latitudes towards the Equator with the exception of two samples (QFF659 and 687 collected near Papua New Guinea, further discussion is given later on them). Except for C_2 in the Northern Hemisphere, all the correlations between $\delta^{13}\text{C}$ of C_2 to C_4 DCAs and latitudes (from mid latitudes to the Equator) are significant at a level of $p < 0.05$ or $p < 0.08$. Several possible atmospheric processes could contribute to the latitudinal changes in the isotopic composition. Those include evaporation, isotope exchange with inorganic carbon, and photochemical reactions. In addition, global distribution of C_3 and C_4 plants might also have some effects on the latitudinal changes in $\delta^{13}\text{C}$.

Semi-volatile properties of DCAs have been reported [Limbeck *et al.*, 2001]. During evaporation isotopically lighter molecules are generally enriched in the vapor phase, the extent depending on the temperature [Hoefs, 1997]. Since the evaporation-related isotopic fractionation arises from the differences in the vapor pressures of

isotopic compounds [Hoefs, 1997], it appears that this type of isotopic fractionation is only significant for very small molecules such as water molecules. For example, it has been found that carbon isotopic fractionation effects due to evaporation for monoaromatic hydrocarbons are very small (around +0.2 ‰) [Harrington *et al.*, 1999]. Although it cannot be ruled out completely, evaporation-related isotopic fractionation for DCAs at ambient temperature is likely insignificant.

Inorganic carbon species (CO_2 , HCO_3^- and CO_3^{2-}) have much heavier $\delta^{13}\text{C}$ values than most organic compounds [Hoefs, 1997]. Under high temperature conditions (above several hundreds °C), kinetic isotope effects (KIEs, ratios of reaction rate constants for ^{12}C and ^{13}C and commonly expressed as $(k_{12}/k_{13} - 1) \times 1000$, ‰) will be very small and isotope exchange between organic and inorganic carbon species may be significant [Dias *et al.*, 2002a; Dias *et al.*, 2002b]. However, we have not found any reports in which such isotope exchange takes place significantly at ambient temperature and pressure.

In general, C_4 plants have much heavier $\delta^{13}\text{C}$ than C_3 plants (with a mean of -13 and -27 ‰, respectively) [Hoefs, 1997]. Although there is a very dense coverage of C_4 plants in northern Australia, the coverage of C_4 plants around the western Pacific Equatorial is quite low [Still *et al.*, 2003]. Ten days' backward air mass trajectories found that during the sampling period no significant air masses flowed out of northern Australia to the sampling areas. Thus, the distribution of C_3 and C_4 plants cannot be used to successfully explain the latitudinal changes in $\delta^{13}\text{C}$ of the saturated DCAs particularly in the Northern Hemisphere.

During the sampling, ambient temperature maximized around the Equator and solar radiation generally increased from mid latitudes towards the Equator except for

the areas where the two “outliers” (i.e. QFF659 and 687) were collected. The $\delta^{13}\text{C}$ increase of the saturated DCAs is possibly associated with photochemically aged air masses since photochemical reactions should be more active towards the Equator. It is generally accepted that KIEs seem more plausible than thermodynamic equilibrium effects being responsible for carbon isotopic fractionation at least in most biochemical reactions [Hoefs, 1997]. Unidirectional chemical reactions always show a preferential enrichment of the lighter isotope in the reaction products with the remaining reactants being heavier [Hoefs, 1997]. Laboratory experiments and ambient measurements have found that remaining small aliphatic and aromatic hydrocarbons as well as isoprene become more enriched in ^{13}C after the photochemical reactions with OH radicals and the $\delta^{13}\text{C}$ increase has been ascribed to the KIEs for their photochemical destruction [Rudolph *et al.*, 2000; 2002; 2003;]. Hence, the increasing trends of $\delta^{13}\text{C}$ towards the Equator for the saturated DCAs (Fig. 2) may be resulted mainly from KIEs for their photochemical degradation. This is seemingly supported by a positive correlation between $\delta^{13}\text{C}$ values of C_2 to C_4 DCAs and solar radiation obtained for the samples collected in the areas from mid latitudes to the Equator (see Fig. 3).

Fig. 4 plots $\delta^{13}\text{C}$ of C_2 to C_4 and C_6 DCAs in the western Pacific aerosols as a function of relative abundance (in terms of molar ratio to total DCAs) of oxalic acid. The relative abundance of C_2 has been proposed as a measure of photochemical processing in the remote marine atmosphere [Kawamura and Sakaguchi, 1999]. As seen in Fig. 4, isotopic values of C_2 to C_4 and C_6 DCAs positively correlate with relative abundance of C_2 . Although relative abundance of oxalic acid increases with the increment of its $\delta^{13}\text{C}$, its concentrations decrease towards the Equator (see Fig. 5). The latitudinal change patterns for aerosol concentrations of all other organic acids in this

work are very similar to oxalic acid. On average, in the Northern Hemisphere, concentrations of C₂, C₃ and C₄ decreased from mid latitudes towards the Equator by 94%, 94% and 98%; in contrast, their $\delta^{13}\text{C}$ increased by 55%, 25% and 20%, respectively. Similarly, the concentrations in the Southern Hemisphere decreased by 39%, 63% and 90% for C₂, C₃ and C₄, respectively; whereas their $\delta^{13}\text{C}$ increased by 46%, 29% and 22%. This further suggests that photochemical decomposition of the saturated DCAs is one of key factors responsible for the increase in their $\delta^{13}\text{C}$ towards the Equator.

No latitudinal trend was observed in $\delta^{13}\text{C}$ of the saturated DCAs for the samples from the Southern Ocean (south of 50 °S). In this region average ambient temperatures were below 6 °C during the sampling and the latitudinal change is small (within 15 degrees). Backward air mass trajectories found that the air masses for the Southern Ocean samples originated from the Southern Ocean and Antarctica. This suggests that aerosol organic acids over the Southern Ocean may have been produced mainly via *in situ* photochemical reactions with insignificant contribution from polluted terrestrial air masses. Their precursors may be predominantly derived by sea-to-air emissions of marine organics including unsaturated fatty acids, phenolic compounds [Kawamura *et al.*, 1996] and olefins [Warneck, 2003].

As mentioned above, there are two “outliers” near the Equator (QFF659 and 687, see Fig. 2) showing lighter $\delta^{13}\text{C}$ than what might be expected for the saturated DCAs in terms of latitudinal change. It was found that the two “outliers” experienced weaker solar radiation (22.2 and 23.9 MJ/m²/day) than the nearby Southern Hemisphere samples (25.2 and 26.3 MJ/m²/day). This may be a major reason for their lighter $\delta^{13}\text{C}$. This also suggests that the two samples were photochemically relatively fresh (less

aged). Interestingly, the two samples were found to contain significantly higher concentrations of fatty acids than the nearby samples, especially C₁₈ unsaturated fatty acids being over ten times more abundant [Niwai, 1996]. Unsaturated fatty acids are major lipid components in marine algae and enriched in the micro-layers of sea surfaces [Marty *et al.*, 1979] but are subjected to quick photo-oxidation after emitted to the atmosphere [Kawamura and Gagosian, 1987]. Air mass back trajectories did not show any significant air outflow from Papua New Guinea during the sampling (see Fig 6). Although some air masses for the two samples came over nearby small islands, a significant amount of organics might have been emitted into the air from local ocean sources.

3.3. Possible Effect of Decarboxylation on $\delta^{13}\text{C}$

Fig. 7 plots the differences in $\delta^{13}\text{C}$ ($\Delta\delta^{13}\text{C}$) of C₂ to C₄ DCAs as a function of latitude. Interestingly, $\Delta\delta^{13}\text{C}$ (C₂ – C₃) and $\Delta\delta^{13}\text{C}$ (C₂ – C₄) over the western Pacific increase from mid latitudes towards the Equator. Actually, we found that $\Delta\delta^{13}\text{C}$ (C₂ – C₆) also have a similar trend ($R^2 = 0.90$, the data are not shown since only four data points are available).

Oxalic acid (C₂) contains only carboxyl carbon but larger saturated DCAs have additional alkyl carbon. KIEs for alkyl carbon have been studied for the photochemical oxidation of methane [Cantrell *et al.*, 1990] and some small non-methane saturated hydrocarbons [Rudolph *et al.*, 2000]. KIEs for alkyl carbon in the non-methane alkanes are below +4 ‰ despite +5.4 ‰ for methane. In contrast, KIEs of carboxyl carbon in photochemical decarboxylation of organic acids are not available at present. However, thermal or spontaneous decarboxylation under various conditions has been extensively studied for the KIEs, which are in the range of +30 to +60 ‰ at room temperature

[Lewis *et al.*, 1993]. Although reaction conditions such as solvent types, temperature and enzyme addition may greatly affect the decarboxylation reaction rate, they have little effects on KIEs for the thermal/spontaneous decarboxylation [Huang *et al.*, 1975; Lewis *et al.*, 1993; Marlier and O'leary, 1986]. When an organic acid undergoes decarboxylation, it will lose one carboxyl group and forms a carbon dioxide molecule. It has been concluded that rupture of a carbon-carbon bond to the carboxyl carbon is the rate-determining step for the decarboxylation [Fry, 1970].

It is impossible to use the small isotopic fractionation of alkyl carbon to successfully explain the significant increase in $\delta^{13}\text{C}$ of the saturated DCAs. If we assume that KIEs for carboxyl carbon in photochemical decarboxylation of the saturated DCAs have a similar value to those of thermal/spontaneous decarboxylation of organic acids described above, KIEs for the photochemical decarboxylation of the saturated DCAs might play a key role in controlling their stable carbon isotopic composition. With this hypothesis, we can reasonably explain the observed trends of $\Delta\delta^{13}\text{C}$ (Fig. 7). As the molecular weight of saturated DCAs increases, carboxyl carbon will be isotopically “diluted” by the presence of additional alkyl carbon. Hence, larger DCA molecules will have less opportunity to undergo reactions of the carboxyl carbon. Since KIEs for carboxyl carbon in photochemical decarboxylation would be much greater than those for oxidation of alkyl groups, oxalic acid will have the largest isotopic fractionation among saturated DCAs during photochemical degradation in the atmosphere. It should be noted that since the mechanisms for photochemical decarboxylation of the saturated DCAs are not very clear and the KIEs are not available at present, the above hypothesis is subjected to further research.

4. Summary and Conclusions

Marine aerosols collected from the western Pacific and Southern Ocean have been analyzed using GC/irMS for the stable carbon isotopic composition of saturated DCAs and ketoacids. $\delta^{13}\text{C}$ values of the saturated DCAs especially oxalic, malonic and succinic acids were found to increase from mid latitudes towards the Equator although such a trend was not observed for phthalic, maleic and glyoxylic acids. Interestingly, difference in $\delta^{13}\text{C}$ between oxalic and malonic acids and that between oxalic and succinic acids were also found to increase from mid latitudes to the Equator. Based on these observations, we propose that the $\delta^{13}\text{C}$ increase may be associated with photochemically aged air masses and might have resulted mainly from kinetic isotope effects (KIEs) for their photochemical degradation.

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References

Anderson, R.S., R. Iannone, A.E. Thompson, J. Rudolph, and L. Huang (2004), Carbon kinetic isotope effects in the gas-phase reactions of aromatic hydrocarbons with the OH radical at 296 ± 4 K, *Geophysical Research Letters*, 31, L15108, doi:10.1029/2004GL020089.

- Cantrell, C.A., R.E. Shetter, A.H. McDaniel, J.G. Calvert, J.A. Davidson, D.C. Lowe, S.C. Tyler, R.J. Cicerone, and J.P. Greenberg (1990), Carbon kinetic isotope effect in the oxidation of methane by the hydroxyl radical, *Journal of Geophysical Research*, *95*, 22455-62.
- Chebbi, A., and P. Carlier (1996), Carboxylic acids in the troposphere, occurrence, sources, and sinks: A review, *Atmospheric Environment*, *30*, 4233-4249.
- Conte, M.H., and J.C. Weber (2002), Long-range atmospheric transport of terrestrial biomarkers to the western North Atlantic, *Global Biogeochemical Cycles*, *16*, 1142, doi:10.1029/2002GB001922.
- Dias, R.F., K.H. Freeman, and S.G. Franks (2002a), Gas chromatography-pyrolysis-isotope ratio mass spectrometry: a new method for investigating intramolecular isotopic variation in low molecular weight organic acids, *Organic Geochemistry*, *33*, 161-168.
- Dias, R.F., K.H. Freeman, M.D. Lewan, and S.G. Franks (2002b), $\delta^{13}\text{C}$ of low-molecular-weight organic acids generated by the hydrous pyrolysis of oil-prone source rocks, *Geochimica et Cosmochimica Acta*, *66*, 2755-2769.
- Fang, J., K. Kawamura, Y. Ishimura, and K. Matsumoto (2002), Carbon isotopic composition of fatty acids in the marine aerosols from the western North Pacific: Implication for the source and atmospheric transport, *Environmental Science & Technology*, *36*, 2598-2604.
- Fisseha, R., J. Dommen, M. Sax, D. Paulsen, M. Kalberer, R. Maurer, F. Hofler, E. Weingartner, and U. Baltensperger (2004), Identification of organic acids in secondary organic aerosol and the corresponding gas phase from chamber experiments, *Analytical Chemistry*, *76*, 6535-6540.
- Fry, A. (1970), Heavy atom isotope effects in organic reaction mechanism studies, in *Isotope Effects in Chemical Reactions*, edited by C. J. Collins and N. S. Bowman, VNR, New York.
- Hatsushika, H., and K. Yamazaki (2003), Stratospheric dehydration within the tropical tropopause layer diagnosed by air parcel trajectories, *Journal of Geophysical Research*, *108*, D19, 4610, doi:10.1029/2002JD002986.
- Harrington, R.R., S.R. Poulson, J.I. Drever, P.J.S. Colberg, and E.F. Kelly (1999), Carbon isotope systematics of monoaromatic hydrocarbons: vaporization and adsorption experiments, *Organic Geochemistry*, *30*, 765-775.
- Hayes, J.M., K.H. Freeman, B.N. Popp, and C.H. Hoham (1990), Compound-specific isotopic analyses - A novel tool for reconstruction of ancient biogeochemical processes, *Organic Geochemistry*, *16*, 1115-1128.
- Hoefs, J. (1997), *Stable Isotope Geochemistry*, Springer, Berlin.
- Huang, T.T.S., R.W. Kidd, and P.E. Yankwich (1975), Intermolecular ^{13}C kinetic isotope effects in the decarboxylation of oxalic acid in dioxane solution, *Journal of Chemical Physics*, *62*, 4757-63.
- Iannone, R., R.S. Anderson, J. Rudolph, L. Huang, and D. Ernst (2003), The carbon kinetic isotope effects of ozone-alkene reactions in the gas-phase and the impact of ozone reactions on the stable carbon isotope ratios of alkenes in the atmosphere, *Geophysical Research Letters*, *30*, 1684, doi:10.1029/2003GL017221.
- Kawamura, K. (1993), Identification of C2-C10 ω -oxocarboxylic acids, pyruvic acid C2-C3 α -dicarbonyls in wet precipitation and aerosol samples by capillary GC and GC-MS, *Analytical Chemistry*, *65*, 3505-3511.
- Kawamura, K., and R. B. Gagosian (1987), Implications of ω -oxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids, *Nature*, *325*, 330-332.
- Kawamura, K., and K. Ikushima (1993), Seasonal change in the distribution of dicarboxylic acids in the urban atmosphere, *Environmental Science & Technology*, *27*, 2227-2235.
- Kawamura, K., Y. Imai, and L.A. Barrie (2005), Photochemical production and loss of organic acids in high Arctic aerosols during long-range transport and polar sunrise ozone depletion events, *Atmospheric Environment*, *39*, 599-614.

- Kawamura, K., and I.R. Kaplan (1987), Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air, *Environmental Science & Technology*, *21*, 105-110.
- Kawamura, K., H. Kasukabe, and L.A. Barrie (1996), Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in Arctic aerosols: one year of observations, *Atmospheric Environment*, *30*, 1709-1722.
- Kawamura, K., and F. Sakaguchi (1999), Molecular distribution of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, *Journal of Geophysical Research*, *104*, 3501-3509.
- Kawamura, K., and K. Usukura (1993), Distributions of low molecular weight dicarboxylic acids in the North Pacific aerosol samples, *Journal of Oceanography*, *49*, 271-283.
- Kawamura, K., and T. Watanabe (2004), Determination of stable carbon isotopic compositions of low molecular weight dicarboxylic acids and ketocarboxylic acids in atmospheric aerosol and snow samples, *Analytical Chemistry*, *76*, 5762-5768.
- Lewis, C., P. Paneth, M.H. O'Leary, and D. Hilvert (1993), Carbon kinetic isotope effects on the spontaneous and antibody-catalyzed decarboxylation of 5-nitro-3-carboxybenzisoxazole, *Journal of American Chemical Society*, *115*, 1410-1413.
- Lichtfouse, E. (2000), Compound-specific isotope analysis. Application to archaeology, biomedical sciences, biosynthesis, environment, extraterrestrial chemistry, food science, forensic science, humic substances, microbiology, organic geochemistry, soil science and sport, *Rapid Communications in Mass Spectrometry*, *14*, 1337-1344.
- Limbeck, A., H. Puxbaum, L. Otter, and M.C. Scholes (2001), Semivolatile behavior of dicarboxylic acids and other polar organic species at a rural background site (Nylsvley, RSA), *Atmospheric Environment*, *35*, 1853-1862.
- Marlier, J.F., and M.H. O'leary (1986), Solvent dependence of the carbon kinetic isotope effect on the decarboxylation of 4-pyridylacetic acid. A model for enzymatic decarboxylations, *Journal of American Chemical Society*, *108*, 4896-4899.
- Marty, J.C., A. Saliot, P. Buat-Menard, R. Chesselet, and R.A. Hunter (1979), Relationship between the lipid composition of marine aerosols, the sea surface microlayers, and subsurface water, *Journal of Geophysical Research*, *84*, 5707-5716.
- Narukawa, M., K. Kawamura, N. Takeuchi, and T. Nakajima (1999), Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires, *Geophysical Research Letters*, *26*, 3101-3104.
- Niwai, T. (1996), Distributions and behaviors of lipid class compounds in the marine aerosols from the western Pacific and Southern Oceans, M Sc thesis, Tokyo Metropolitan University, Tokyo.
- Norman, A.L., J.F. Hopper, P. Blanchard, D. Ernst, K. Brice, N. Alexandrou, and G. Klouda (1999), The stable carbon isotope composition of atmospheric PAHs, *Atmospheric Environment*, *33*, 2807-2814.
- Rudolph, J., R.S. Anderson, K.V. Czapiewski, E. Czuba, D. Ernst, T. Gillespie, L. Huang, C. Rigby, and A.E. Thompson (2003), The stable carbon isotope ratio of biogenic emissions of isoprene and the potential use of stable isotope ratio measurements to study photochemical processing of isoprene in the atmosphere, *Journal of Atmospheric Chemistry*, *44*, 39-55.
- Rudolph, J., and E. Czuba (2000), On the use of isotopic composition measurements of volatile organic compounds to determine the "photochemical age" of an air mass, *Geophysical Research Letters*, *27*, 3865-8.
- Rudolph, J., E. Czuba, and L. Huang (2000), The stable carbon isotope fractionation for reactions of selected hydrocarbons with OH-radicals and its relevance for atmospheric chemistry, *Journal of Geophysical Research*, *105*, 29329-46.
- Rudolph, J., E. Czuba, A.L. Norman, L. Huang, and D. Ernst (2002), Stable carbon isotope composition of nonmethane hydrocarbons in emissions from transportation related

- sources and atmospheric observations in an urban atmosphere, *Atmospheric Environment*, 36, 1173-1181.
- Saito, T., U. Tsunogai, K. Kawamura, T. Nakatsuka, and N. Yoshida (2002), Stable carbon isotopic compositions of light hydrocarbons over the western North Pacific and implication for their photochemical ages, *Journal of Geophysical Research*, 107, ACH 2-1-9, doi:10.1029/2000JD000127.
- Sakugawa, H., and I.R. Kaplan (1995), Stable carbon isotope measurements of atmospheric organic acids in Los Angeles, California, *Geophysical Research Letters*, 22, 1509-1512.
- Saxena, P., and L.M. Hildemann (1996), Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds, *Journal of Atmospheric Chemistry*, 24, 57-109.
- Saxena, P., L.M. Hildemann, P.H. McMurry, and J.H. Seinfeld (1995), Organics alter hygroscopic behavior of atmospheric particles, *Journal of Geophysical Research*, 100, 18,755-18770.
- Schefuß, E., V. Ratmeyer, J.-B.W. Stuut, J.H.F. Jansen, and J.S. Sinninghe Damste (2003), Carbon isotope analyses of n-alkanes in dust from the lower atmosphere over the central eastern Atlantic, *Geochimica et Cosmochimica Acta*, 67, 1757-1767.
- Schmidt, T.C., L. Zwank, M. Elsner, M. Berg, R.U. Meckenstock, and S.B. Haderlein (2004), Compound-specific stable isotope analysis of organic contaminants in natural environments: a critical review of the state of the art, prospects, and future challenges, *Analytical and Bioanalytical Chemistry*, 378, 283-300.
- Sheesley, R.J., J.J. Schauer, E. Bean, and D. Kenski (2004), Trends in secondary organic aerosol at a remote site in Michigan's upper peninsula, *Environmental Science & Technology*, 38, 6491-6500.
- Simoneit, B.R.T. (1997), Compound-specific carbon isotope analyses of individual long-chain alkanes and alkanolic acids in Harmattan aerosols, *Atmospheric Environment*, 31, 2225-2233.
- Still, C.J., J.A. Berry, G.J. Collatz, and R.S. DeFries (2003), Global distribution of C3 and C4 vegetation: Carbon cycle implications, *Global Biogeochemical Cycles*, 17, 1006, doi:10.1029/2001GB001807.
- Turekian, V.C., S.A. Macko, and W.C. Keene (2003), Concentrations, isotopic compositions, and sources of size-resolved, particulate organic carbon and oxalate in near-surface marine air at Bermuda during spring, *Journal of Geophysical Research*, 108, 4157, doi:10.1029/2002JD002053.
- Wang, H., K. Kawamura, and K. Yamazaki (2005), Water-soluble dicarboxylic acids, ketoacids and dicarbonyls in the atmospheric aerosols over the Southern Ocean and western Pacific Ocean, *Journal of Atmospheric Chemistry*, in press.
- Warneck, P. (2003), In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, *Atmospheric Environment*, 37, 2423-2427.
- Zuo, Y.G., and J. Hoigne (1994), Photochemical decomposition of oxalic, glyoxalic and pyruvic-acid catalyzed by iron in atmospheric waters, *Atmospheric Environment*, 28, 1231-1239.

FIGURE CAPTIONS

FIGURE 1. A figure showing the cruise track of KH94-4 and surface wind conditions. The numbers shown in the maps represent quartz fiber filter identification numbers used in the corresponding cruise periods. Arrows indicate surface wind directions with bold and regular arrows corresponding to the wind speeds above and below 7 m s^{-1} respectively. (a) Legs 1 and 2: Leg 1 started from Tokyo, Japan in Nov. 22, 1994 and ended in Lyttelton, New Zealand in Dec. 9, 1994; Leg 2 started from the Southern Ocean in Dec. 19, 1994 and ended in Hobart, Australia in Jan. 4, 1995. (b) Legs 3 and 4: Leg 3 started from Hobart in Jan. 9, 1995 to the Southern Ocean and then back to Sydney, Australia in Jan. 28, 1995; Leg 4 started from Sydney in Feb. 1, 1995 and ended in Tokyo in Feb. 13, 1995.

FIGURE 2. Latitudinal variations of $\delta^{13}\text{C}$ values (relative to PDB) for individual dicarboxylic acids and α -ketoacid (glyoxylic acid). For abbreviations, see Table 1. Open diamonds indicate the two “outliers” (QFF659 and 687), which show lighter $\delta^{13}\text{C}$ than what might be expected.

FIGURE 3. Relationships between solar radiation and $\delta^{13}\text{C}$ (relative to PDB) of saturated DCAs (C_2 to C_4); (a) for the samples collected in the areas from northern mid latitudes to the Equator, and (b) for those from southern mid latitudes to the Equator.

FIGURE 4. Relationships between relative abundance of oxalic acid (in terms of molar ratio to total dicarboxylic acids) and $\delta^{13}\text{C}$ values of C_2 to C_4 and C_6 diacids (relative to PDB) over the western Pacific. For abbreviations, see Table 1.

FIGURE 5. Latitudinal changes of atmospheric aerosol concentrations of oxalic acid.

FIGURE 6. Ten days' backward air mass trajectories for QFF659 and QFF687. The trajectory calculation was based on backward tracking of selected air parcels, assuming that they were moving with the ambient airflow. The flow pattern was updated every 6 h (The back trajectory analysis was performed by Prof. K. Yamazaki).

FIGURE 7. Relationships between latitude and the differences in $\delta^{13}\text{C}$ ($\Delta\delta^{13}\text{C}$); (a) for oxalic and malonic acids ($\text{C}_2 - \text{C}_3$) and (b) for oxalic and succinic acids ($\text{C}_2 - \text{C}_4$). Dots indicate data points from the Northern Hemisphere and triangles represent data points from the Southern Hemisphere (the two "outliers", i.e. QFF659 and 687, are not included here).

Table 1. $\delta^{13}\text{C}$ Values (Relative to PDB, permil) of Water-soluble DCAs and One α -Ketoacid in Individual Samples

<i>Filter Name</i>	<i>Collection Dates (JST)</i>	<i>Oxalic (C₂)</i>	<i>Malonic (C₃)</i>	<i>Succinic (C₄)</i>	<i>Adipic (C₆)</i>	<i>Azelaic (C₉)</i>	<i>Methylmalonic (iC₄)</i>	<i>Maleic (M)</i>	<i>Phthalic (Ph)</i>	<i>Glyoxylic (oC₂)</i>
QFF655	Nov. 22-25, 94	-19.9	-22.0	-20.3	-13.8	-14.0	-30.7	-14.3	-22.4	-14.5
QFF657	Nov. 25-27, 94	-13.1	-18.6	-16.2	-12.2	-13.0	-18.2	-15.4		-37.3
QFF658	Nov. 27-29, 94	-6.7	-15.4	-17.0		-23.5				-23.5
QFF659	Nov. 29-Dec. 1, 94	-17.5	-21.8	-18.6	-13.9		-26.4	-23.6	-26.4	-35.7
QFF660	Dec. 1-3, 94	-13.3	-19.5	-18.7	-14.0		-20.8		-21.3	-25.5
QFF662	Dec. 5-7, 94	-18.7	-23.7	-23.2	-16.5	-11.5	-25.7	-13.8	-29.6	-17.2
QFF663	Dec. 7-9, 94	-18.8	-23.5	-22.9	-14.0	-18.7	-20.8			
QFF668	Dec. 19-23, 94	-17.9	-25.1	-24.4	-19.6	-23.2		-33.2	-24.3	-21.9
QFF669	Dec. 23-27, 94	-18.2	-23.2	-23.5	-22.4	-15.3				-17.0
QFF670	Dec. 27-29, 94	-16.4	-24.1	-22.5	-21.2	-17.2			-24.1	-8.7
QFF671	Dec. 29, 94-Jan. 1, 95	-17.7	-24.8	-22.1		-18.1			-22.3	-26.7
QFF672	Jan. 1-4, 95	-27.1	-24.3	-20.5				-30.5		-14.3
QFF674	Jan. 9-11, 95	-20.5	-25.7	-20.5	-17.3			-32.0	-25.1	-11.2
QFF675	Jan. 11-13, 95	-16.7	-22.2	-20.9	-19.2	-22.9			-23.7	-8.3
QFF676	Jan. 13-16, 95	-19.8	-26.1	-25.3	-20.1					-27.5
QFF677	Jan. 16-18, 95	-17.9	-21.9	-21.8	-19.1	-18.6				-13.0
QFF678	Jan. 18-20, 95	-17.3	-19.8	-20.2	-19.6	-25.0		-17.2		-12.9
QFF680	Jan. 20-22, 95	-17.9	-19.5	-21.3	-16.4					-40.0
QFF682	Jan. 24-26, 95	-14.4	-21.9	-19.5					-18.6	-7.3
QFF683	Jan. 26-28, 95	-15.2	-21.7	-19.9			-28.8		-23.9	-5.9
QFF685	Feb. 1-3, 95	-22.6	-24.0	-20.5	-15.5		-17.7	-31.7		
QFF686	Feb. 3-5, 95	-9.1	-14.5	-15.4						
QFF687	Feb. 5-7, 95	-17.1	-18.9	-19.3	-17.1	-17.1			-22.9	-13.5
QFF688	Feb. 7-9, 95	-11.2	-17.5	-15.7					-33.9	-3.1
QFF689	Feb. 9-11, 95	-14.1	-16.7	-18.4				-19.0	-19.8	-1.0
Mean \pm Standard error		-16.8 \pm 0.8	-21.5 \pm 0.6	-20.3 \pm 0.5	-17.2 \pm 0.7	-18.3 \pm 1.2	-23.6 \pm 1.6	-24.2 \pm 0.9	-23.1 \pm 2.6	-17.6 \pm 2.3

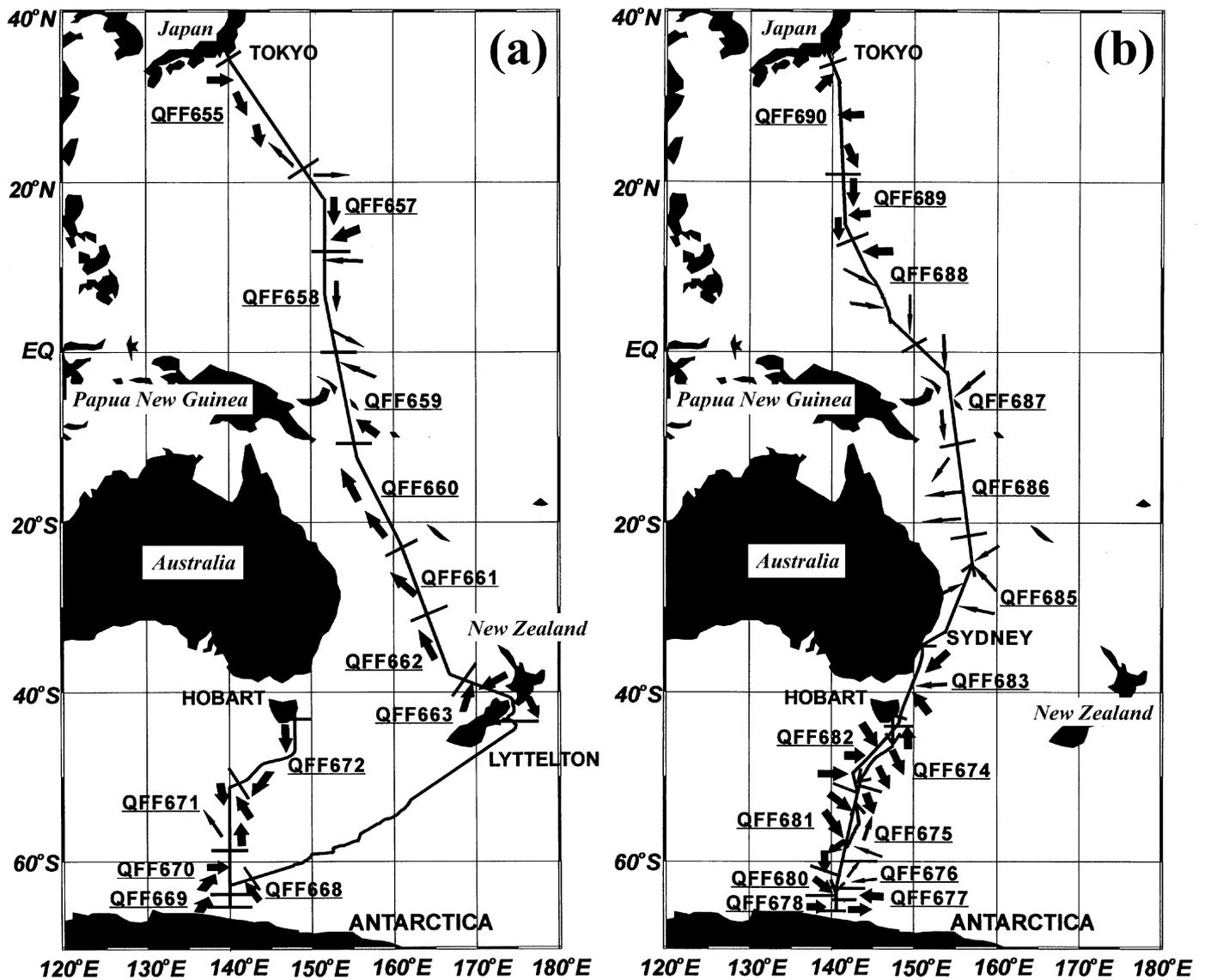


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Fig. 2 (Wang & Kawamura)

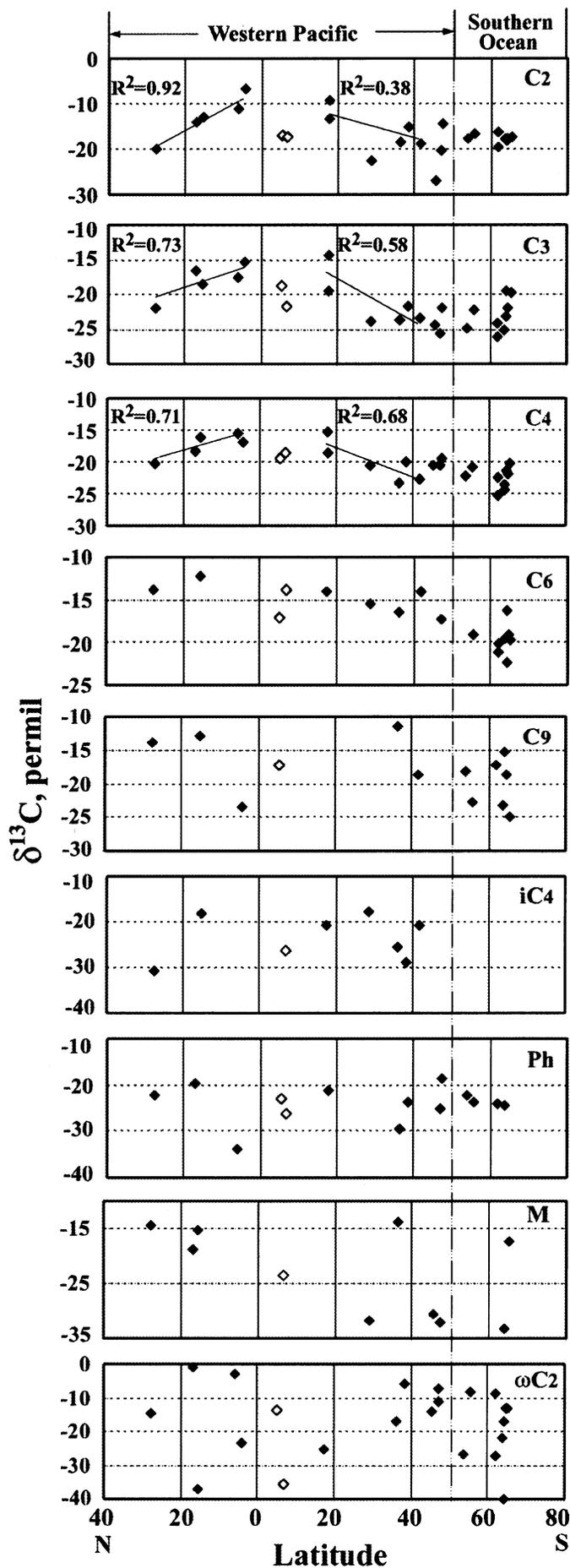


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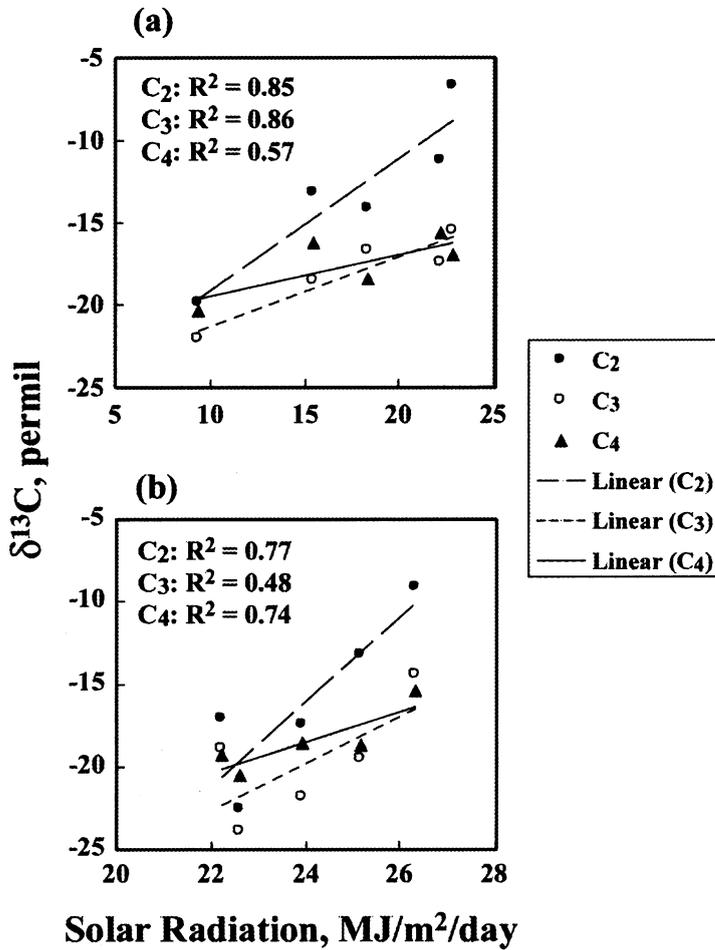


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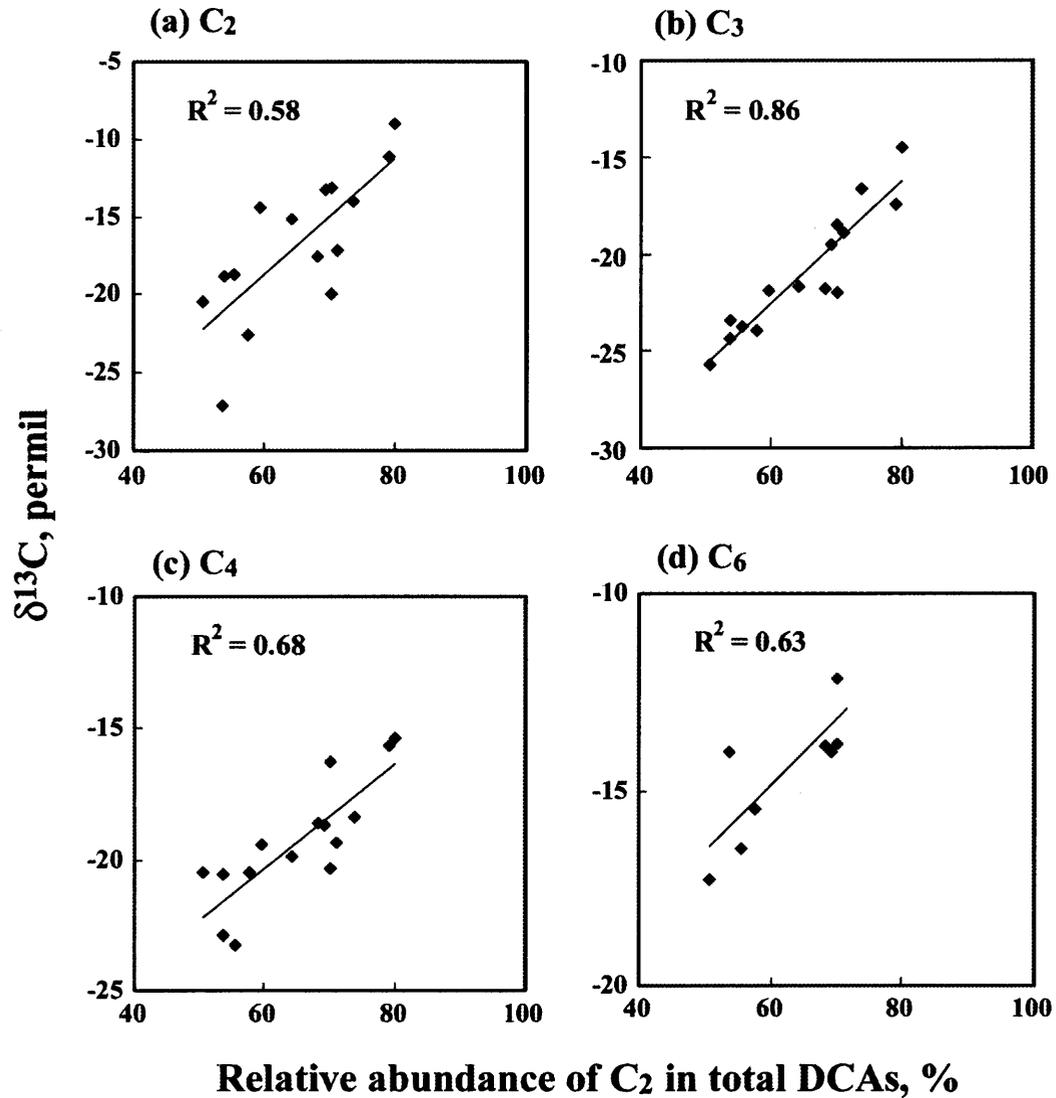


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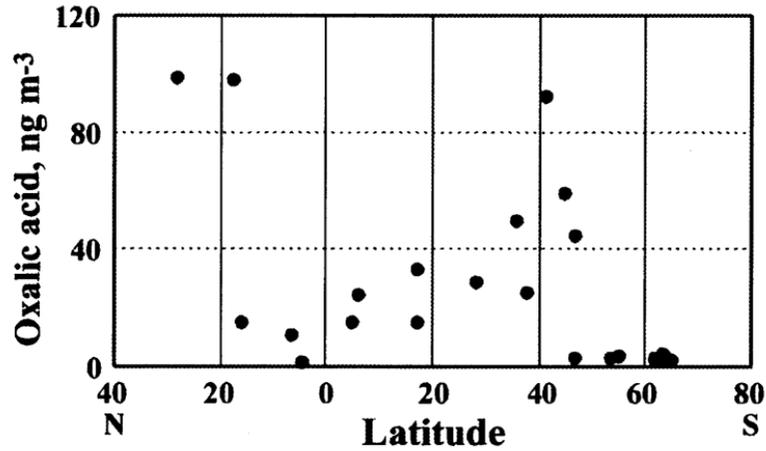


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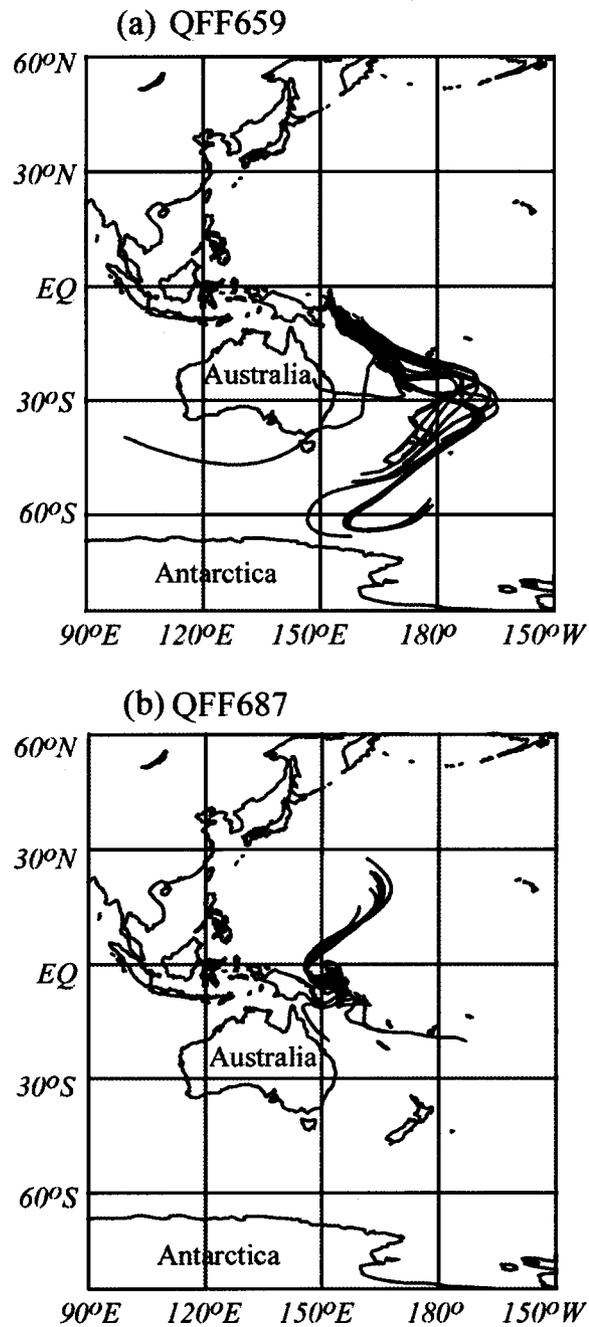


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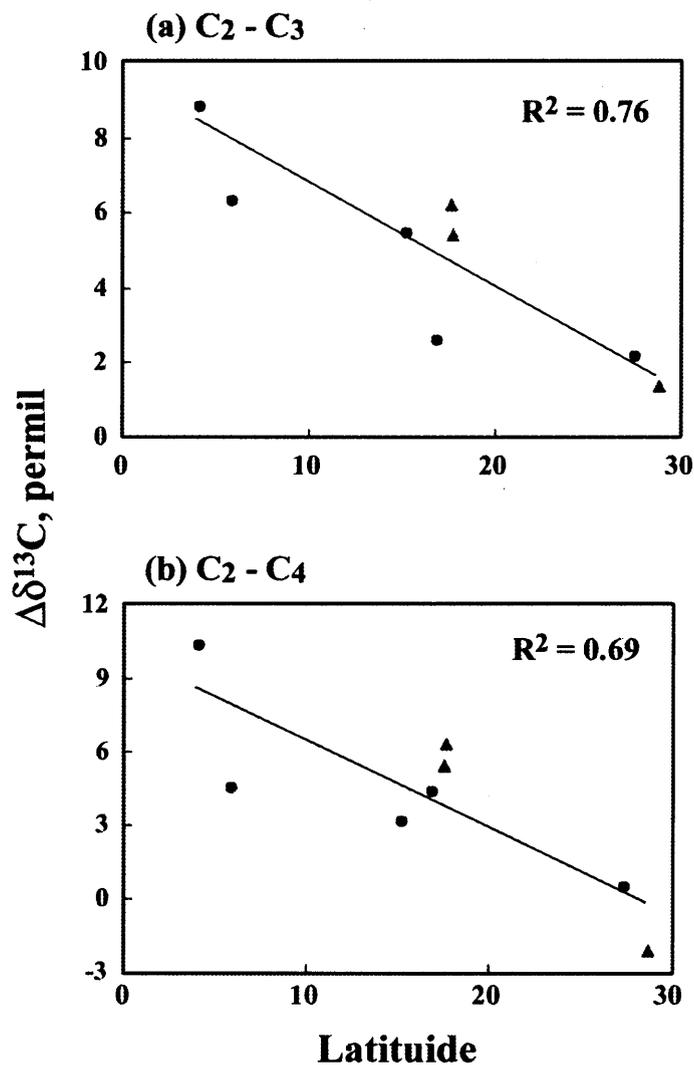


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