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

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

Running head:
$\delta^{13}C$ of dicarboxylic acids in marine aerosols

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Abstract

We determined stable carbon isotopic composition ($\delta^{13}$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$^\circ$N – 65$^\circ$S). On average, oxalic (mean: -16.8 ‰), adipic (-17.2 ‰) and glyoxylic (-17.6 ‰) acids showed heavier $\delta^{13}$C, whereas, maleic (-24.2 ‰), methylmalonic (-23.6 ‰) and phthalic (-23.1 ‰) acids were more depleted in $^{13}$C. Oxalic acid presented very diverse $\delta^{13}$C values (-27 to -7 ‰), which increased from mid latitudes towards the Equator. A similar latitudinal trend of $\delta^{13}$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 $\delta^{13}$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 $\delta^{13}$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 (δ^{13}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-C_{13} alkane) was spiked to the derivatized fraction of each sample, δ^{13}C of the derivatives were determined using GC/irMS (HP 6890 GC and Finnigan-MAT Delta plus irMS). δ^{13}C of free organic acids in the sample were then calculated using a mass balance equation based on the measured δ^{13}C of the derivatives and the derivatizing agent (1-butanol). Each sample was analyzed in replicate and the mean δ^{13}C is reported. Difference in δ^{13}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 δ^{13}C can be obtained for a compound in a sample depends on its concentration and properties of the sample. We thus only report δ^{13}C for nine compounds (eight DCAs and one α-ketoacid) in this work although δ^{13}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 δ^{13}C for DCAs and Ketoacids

δ^{13}C values for nine organic acids are given in Table 1. On average, oxalic (C_{2}), adipic (C_{6}) and glyoxylic (ωC_{2}) acids are more enriched in ^{13}C while maleic (M), methylmalonic (iC_{4}) and phthalic (Ph) acids are more depleted in ^{13}C. It should be born in mind that unlike biomarkers that can faithfully reflect δ^{13}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 $\delta^{13}$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 $\delta^{13}$C of Individual Organic Acids

Fig. 2 presents latitudinal variations of $\delta^{13}$C for the detected organic acids. Interestingly, $\delta^{13}$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 $\delta^{13}$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 $\delta^{13}$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 mono-aromatic 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 $\delta^{13}$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 $\delta^{13}$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 $\delta^{13}$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 $\delta^{13}C$ 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 $\delta^{13}C$ increase has been ascribed to the KIEs for their photochemical destruction [Rudolph et al., 2000; 2002; 2003;]. Hence, the increasing trends of $\delta^{13}C$ 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 $\delta^{13}C$ 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 $\delta^{13}C$ 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 $\delta^{13}C$, 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 \(\text{C}_2\), \(\text{C}_3\) and \(\text{C}_4\) 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 \(\text{C}_2\), \(\text{C}_3\) and \(\text{C}_4\), 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 \textit{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 \textit{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 C_{18} 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 $\delta^{13}C$

Fig. 7 plots the differences in $\delta^{13}C$ ($\Delta\delta^{13}C$) of C$_2$ to C$_4$ DCAs as a function of latitude. Interestingly, $\Delta\delta^{13}C$ (C$_2$ – C$_3$) and $\Delta\delta^{13}C$ (C$_2$ – C$_4$) over the western Pacific increase from mid latitudes towards the Equator. Actually, we found that $\Delta\delta^{13}C$ (C$_2$ – C$_6$) also have a similar trend ($R^2 = 0.90$, the data are not shown since only four data points are available).

Oxalic acid (C$_2$) 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 δ^{13}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 Δδ^{13}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. $\delta^{13}$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 $\delta^{13}$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 $\delta^{13}$C increase may be associated with photochemically aged air masses and might have resulted mainly from kinetic isotope effects (KIEs) for their photochemical degradation.

Acknowledgments

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References


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


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

FIGURE 3. Relationships between solar radiation and $\delta^{13}$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 $\delta^{13}$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 $\delta^{13}C$ ($\Delta \delta^{13}C$); (a) for oxalic and malonic acids (C$_2$ – C$_3$) and (b) for oxalic and succinic acids (C$_2$ – 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. δ\(^{13}\)C Values (Relative to PDB, permil) of Water-soluble DCAs and One \(\alpha\)-Ketoacid in Individual Samples

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<th>Malonic (C(_3))</th>
<th>Succinic (C(_4))</th>
<th>Adipic (C(_6))</th>
<th>Azelaic (iC(_4))</th>
<th>Methylmalonic (M)</th>
<th>Maleic (M)</th>
<th>Phthalic (Ph)</th>
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<td>-16.7</td>
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<td>-1.0</td>
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<td>Mean ± Standard error</td>
<td>-16.8 ± 0.8</td>
<td>-21.5 ± 0.6</td>
<td>-20.3 ± 0.5</td>
<td>-17.2 ± 0.7</td>
<td>-18.3 ± 1.2</td>
<td>-23.6 ± 1.6</td>
<td>-24.2 ± 0.9</td>
<td>-23.1 ± 2.6</td>
<td>-17.6 ± 2.3</td>
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FIGURE 1. A figure showing the cruise track of KH94-4 and surface wind conditions.
FIGURE 2. Latitudinal variations of $\delta^{13}C$ values (relative to PDB) for individual dicarboxylic acids and $\alpha$-ketoacid (glyoxylic acid). For abbreviations, see Table 1. Open diamonds indicate the two "outliers" (QFF659 and 687), which shows lighter $\delta^{13}C$ than what might be expected.
FIGURE 3. Relationships between solar radiation and $\delta^{13}$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 $\delta^{13}C$ 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 trajectory 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 6h (The back trajectory analysis was performed by Prof. K. Yamazaki).
FIGURE 7. Relationships between latitude and the differences in $\delta^{13}C (\Delta \delta^{13}C)$; (a) for oxalic and malonic acids ($C_2 - C_3$) and (b) for oxalic and succinic acids ($C_2 - C_4$). 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).