1 **Tracing the sources of carbon in clay minerals: an**
2 **example from western Taiwan**

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Abstract

Radiocarbon has been widely used in determining the age of various geological materials and events. The validity of ages, particularly for sediments, has often been questioned due to the incorporation of carbon-bearing components with different abundances of ^{13}C and ^{14}C . This study examines carbon contained in clay minerals (kaolinite, illite and illite-smectite) extracted by temperature-stepped combustion experiments, ranging from 350°C to 1100°C. Distinct carbon components were identified in the samples using both their ^{13}C and ^{14}C contents. Two carbon end-members were observed for all of the clay minerals: a low temperature component (<400°C), relatively depleted in ^{13}C and enriched in ^{14}C ; and a high temperature component (>550°C), relatively enriched in ^{13}C and depleted in ^{14}C . The high temperature carbon component is relatively old and not released until the clay is completely oxidized. This observation suggests that this carbon was incorporated into the clay mineral when it first formed [by weathering](#).

We applied the same procedure to sediments collected from terraces along the Kueichung River, in southwestern Taiwan, sieved to < 64 μm . We obtained results similar to the pure clay minerals, with distinct low temperature (relatively young) and high temperature (relatively old) end members. One of the sediments also contained a third carbon component, possibly detrital carbon. The radiocarbon dates on these various carbon fractions provide a range of dates enabling us to place constraints on the timing of terrace development in Taiwan.

Keywords: clay minerals, radiocarbon dating, sediments, size fractionation,
temperature-stepped combustion

Introduction

The major geological structure that underlies the Central Mountain belt in Taiwan is oriented from northeast to southwest in accordance with a zone of active subduction of the Philippine Sea plate under the Eurasian continental plate. The western boundary of this mountain belt is composed of a series of continuous fault planes (Shyu et al., 2005). The Mw 7.6 Chi-Chi earthquake occurred on one of these faults, Chelungpu fault, 15 years ago and caused major casualties in central Taiwan (Chen et al. 2001). Therefore, it is important to understand and quantify the timing of fault movements in Taiwan to help mitigate future earthquake hazards. In Taiwan, reverse faults are generally responsible for uplift and subsequent river incision. One approach to understand past fault movements is to study fluvial channel morphology and estimate river incision rates (Yanites et al., 2010). This can be done along rivers that follow active faults using multiple radiocarbon dates from terraces. However, dating the formation and abandonment of river terraces is made difficult in Taiwan due to the generally poor preservation of plant matter and charcoal. These dating materials are either degraded in a short period of time or washed away by frequent floods.

Charcoals are easily decomposed in sediments where the water table fluctuates repeatedly, and charcoals that are chemically altered by such a process can produce

70 “aberrant” radiocarbon ages (Bird et al., 2002). In Taiwan, sudden and large amounts
71 of rainfall are characteristic of the annual monsoon and typhoon seasons, causing
72 substantial water table fluctuations, repeatedly oxidizing the sediments. Hence, it is
73 often the case that sediments from Taiwan contain poorly preserved charcoal that
74 has experienced post-depositional degradation. This leaves what we refer to here as
75 “organic nodules”, because their original plant fragment textures are no longer
76 clearly identifiable under a microscope. Since radiocarbon ages of these organic
77 nodules are uncertain, a combination of dating techniques is needed to constrain the
78 ages of terraces. Such an approach has been used successfully, for example, in a
79 study of Holocene and late Pleistocene soil profiles from the European Alps, which
80 included dates on both charcoal and soil organic matter (Favilli et al., 2009).

81 It is well known that organic carbon contained in bulk sediments is often a
82 heterogeneous mixture from different sources. These can include relatively old
83 inherited radiocarbon, radiocarbon that is contemporaneous with terrace formation,
84 and modern carbon that has infiltrated the sediments. The sources of the pool could
85 be further complicated by active and ongoing exchange of organic carbon in surface
86 sediments. Physical and chemical extraction techniques have been used to separate
87 some of these carbon sources (Christensen, 1992; von Lützow et al., 2007). For
88 example, grain size separation has been demonstrated to show that the residence
89 time of organic matter can depend on particle size (Schöning and Kögel-Knabner,
90 2006). Another useful physical separation approach is density separation. Dense
91 forms of soil organic carbon have been found to be relatively inert and resistant to
92 post-depositional exchange (Trumbore 2009; Trumbore and Zheng 1996). Chemical
93 pretreatments offer another effective means to separate sediment organic carbon in

the form of humic acids and humin (Hajdas et al. 2009). However, consistent age relationships between these two fractions can be ambiguous if the sediments aren't also subjected to physical separations before chemical pretreatment (Anderson and Paul, 1984).

In addition to physical and chemical separations, Thermogravimetry analysis (TGA) combined with other analyses have been used to characterize organic compounds in humic acid fractions of sediments (Plante et al., 2009). An analogous method, temperature-stepped combustion, was used by McGeehin et al. (2001). Their study extracted carbon in humic acids and humin ($<64\ \mu\text{m}$) from the fine fraction of sediments at two temperature increments ($<400^{\circ}\text{C}$ and $>400^{\circ}\text{C}$). We applied the same technique in Taiwan and found that ages from humic acids were consistently younger than those of low temperature humin, both of which produced younger ages than the high temperature humin fraction (Burr et al. 2009; Wang et al. 2013). Thus, the combination of size separation, chemical pretreatment and thermal analysis successfully separated distinguishable pools of organic carbon.

In this work, we extend the method by increasing the number of combustion steps, with smaller (50°C) temperature increments. We then apply the temperature-stepped combustion method to well-crystallized kaolinite, illite and illite-smectite samples to characterize their carbon content. Organic matter has a well-known affinity for clays (Christenson, 1992), and clay minerals are a major component of fine-grained sediments. Hence, we applied the same experimental protocol to analyze the fine fraction of terrace sediments from the Liuchia fault area. This area has the highest risk of earthquake in western Taiwan (Steer et al., 2014). Our goal is

to understand more about how carbon is stored in the clay minerals, and how this carbon can be used to date fluvial terrace sediments.

Material and sample sites

1. Clay Minerals

Standardized clay mineral samples were procured from The Clay Mineral Society, Aurora, CO, USA. For this study, kaolinite (KGa-1b), illite (IMt-1) and Illite-smectite (ISCz-1) (detailed composition shown in Table 1) were chosen for further analyses. These clay minerals represent a spectrum of basic structural types. All clay minerals have structures composed of some combination of tetrahedrally and octahedrally coordinated layers. Kaolinite has the simplest clay structure, with alternating tetrahedral and octahedral layers (1:1 tetrahedral-octahedral structure), with no interlayer ions. Illite has a 2:1 tetrahedral-octahedral-tetrahedral structure, with tightly bound monovalent interlayer ions. Both kaolinite and illite are non-swelling clays. Smectites have a 2:1 tetrahedral-octahedral-tetrahedral structure, with loosely bound interlayer ions with a variety of charge states, as well as hydrous molecules (Velde, 1992). Smectites are swelling clays. Their structures can expand substantially with increases in humidity and interlayer ions and molecules can exchange at room temperature.

Table 1. Clay mineral formulae for the clay standards used in this study (Compositions from the American Clay Mineral Society, Aurora, CO USA.)

141 Kaolinite KGa-1

143 Illite IMt-1

145 Illite-Smectite ISCz-1

147

148 **2. Terrace Sediment Samples - Structural setting and sample sites**

149 Terrace samples were collected along the Liuchia fault, which is a blind fault in
150 southwestern Taiwan, 30 kilometers south of the Chelungpu Fault. In the study area,
151 the Niushan anticline and Chiendapu syncline are in the hanging wall block of, and
152 parallel to, the Liuchia fault due to the Philippine Sea plate and Eurasian continental
153 plate convergence (Fig. 1). The Kueichung River runs over the syncline and anticline,
154 and the surface of the Liuchia fault. We opened five trenches along the river,
155 denoted as VC, PG, SY, JH and NN. Locations of tectonic structures and the five
156 trenches are marked in Fig. 1. These 5 trenches are on different terrace levels, from
157 Terrace 1 to Terrace 5, respectively. The terrace numbers indicate relative ages, and
158 do not imply correlation of the terraces along the river. The trenches were
159 approximately 3 meters deep and situated on terraces composed of discrete fluvial
160 sediment layers. The PG trench on Terrace 2 is the only terrace with a thick gravel
161 layer. Sediment samples from that trench were collected from the fine-grained
162 matrix. The other four trenches - VC, SY, JH and NN, were from terraces with thick
163 layers of fine-grained fluvial sediments that were yellow in color, topped with a thin
164 layer (<50 cm) of soil. These four sediment samples were collected at depths

between 1.5 m and 2 m below the terrace surface. Grain sizes of samples from the VC and SY trenches were slightly smaller (more muddy) than those from the NN and JH trenches.

Methods

The terrace sediments were wet sieved to less than 64 μm because this fraction contains the major portion of total organic carbon and avoids plant fragments trapped in sand (von Lutzow et al., 2007). A small portion of this fraction was used for X-ray diffraction (XRD) analyses and the remainder was dried in an oven at $\sim 60^\circ\text{C}$ for a week. We used an acid-alkali-acid (AAA) pretreatment to extract humic acid (alkali-soluble, acid-insoluble) and humin (alkali-acid-insoluble) for radiocarbon dating (Hajdas, 2008). The AAA pretreatment consisted of a heated bath at 70°C with 0.1M HCl overnight, 0.1M NaOH overnight and 0.1M HCl for 2 hours. After each chemical cleaning step, the fraction was rinsed with ultrapure Milli-Q water to a neutral pH and dried in an oven at $\sim 60^\circ\text{C}$ after the final rinse. The base wash was repeated several times until the humic acids were fully extracted. The humic acids separated during the base step were re-acidified and re-precipitated for separate analysis. This solid humic acid was then centrifuged to remove the solution, rinsed repeatedly with Milli-Q water and dried in a warm oven (60°C) prior to combustion. The clay minerals were washed in 0.1M HCl at 70°C to remove any inorganic carbon, then rinsed repeatedly and dried. We used a temperature-stepped combustion method modified from McGeehin et al (2001). The humin fraction of sediment was

188 placed in 9 mm quartz tube, 20 cm in length. The tube was evacuated under high
189 vacuum and then heated to 90°C to remove any water vapor, until the pressure
190 reached 10⁻⁵ torr. We filled the tube with 0.5 atmosphere ultrapure O₂ (99.99%) and
191 heated the sample in a combustion furnace, increasing the temperature at a rate of
192 5°C /min until the target temperature was reached. Samples were combusted for 20
193 min and the CO₂ produced was collected cryogenically using a vacuum line with a
194 similar design to the extraction line shown in Figure 1 of McGeehin et al (2001). The
195 sample tube was then pumped under a high vacuum, recharged with 0.5 atmosphere
196 ultrapure O₂, and heated to the next target temperature. About 4 to 7 grams of the
197 humin fraction for sediments and ~2 grams of the acid-insoluble fraction for clays
198 was combusted, at successive temperatures, from 300°C to 1000°C, in 50°C
199 increments where sufficient carbon was present. In sediment samples with
200 insufficient carbon for 50°C increments, we used 100°C increments, and in a few
201 cases 150°C increments. Whichever temperature increment was used, it is
202 referenced by the highest oxidation temperature used for oxidation. This method
203 allowed us to quantify the relative amounts of carbon in each temperature
204 increment and to characterize their ¹³C and ¹⁴C contents. A portion of CO₂ produced
205 in each combustion step was used to measure δ¹³C with an isotopic ratio mass
206 spectrometer (IRMS: MAT253, Thermo-Finnigan, Bremen, Germany) and the carbon
207 isotopic composition was normalized to the Vienna PEE DEE Belemnite and
208 expressed as δ values ($\delta = [({}^{13}\text{C}/{}^{12}\text{C})_{\text{sample}}/({}^{13}\text{C}/{}^{12}\text{C})_{\text{standard}} - 1] \times 1000 \text{ ‰}$) with a
209 external precision of 0.2 ‰ (1σ) from repeat measurements of our Oxalic Acid
210 standard. The remaining gas was reduced to graphite by Zn reduction for ¹⁴C AMS
211 analysis (Burr and Jull, 2010). The measured fraction modern carbon (F) is defined as

$F = (^{14}\text{C}/^{13}\text{C})_S / (^{14}\text{C}/^{13}\text{C})_{\text{STD}}$, where $(^{14}\text{C}/^{13}\text{C})_S$ is the measured ratio in the sample,
 normalized to $\delta^{13}\text{C} = -25 \text{ ‰}$, and $(^{14}\text{C}/^{13}\text{C})_{\text{STD}}$ is the calculated modern standard ratio
 at AD 1950, determined from measurements of NBS oxalic acid standards, also
 normalized to $\delta^{13}\text{C} = -25 \text{ ‰}$ (Donahue et al., 1990). Then the ^{14}C age of the sample
 was calculated from the background-corrected F values as $^{14}\text{C age} = -8033 \ln F$.
 Conventional radiocarbon ages were calibrated to cal BP via CALIB v 7.1 (Stuiver and
 Reimer, 2015). All sediment samples were pretreated, combusted, and converted to
 graphite at National Taiwan University and the clay minerals were processed at the
 AMS facility at the University of Arizona. Graphite targets were analyzed either with
 the HVE 1 MV Tandetron AMS at National Taiwan University, or the NEC 3 MV AMS
 in Arizona. We made measurements at both laboratories on standard sample P from
 the Fifth International Radiocarbon Intercomparison (VIRI) standard set (Scott et al.,
 2010). The VIRI P charcoal was subjected to the same chemical pretreatment as the
 unknowns.

Figure 1 (a) Tectonic setting of Taiwan and adjacent regions. The study area is shown as the blue square. DF, deformation front; LCS, Lishan-Chaochou suture; LVS, Longitudinal Valley suture; WF, Western Foothills; CeR, Central Range; CoR, Coastal Range (modified from Shyu et al., 2005); (b) Enlarged view of the study area. Trench sites of the terrace sediment samples are marked with black dots (modified from Du, 2013).
(a)

(b)

Results

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239 **1. Carbon in well-crystallized clay minerals**

240 We combusted the clay minerals using a temperature increment of 50°C, and the
241 percentage of total carbon released from each increment was recorded (Table 2).

242 The results show that varying proportions of carbon were oxidized at each
243 temperature increment, with most of the carbon being released within two
244 temperature ranges: $\leq 400^{\circ}\text{C}$ and $\geq 550^{\circ}\text{C}$ (in Fig. 2 (a), (c) and (e)).

245

246 **Figure 2. (a), (c) and (e) are percent of carbon released from clay minerals during stepped**
247 **temperature combustion. (b) and (d) are TGA (Thermogravimetry Analysis) and DTA (Differential**
248 **Thermal Analysis) profiles of kaolinite and illite (modified from Kuo et al., 2011). TGA is shown as a**
249 **solid line with weight percent left, and DTA is shown as a dashed line with temperature difference**
250 **to standard. These figures show that carbon is released at distinct temperature ranges.**

251 (a)

252

253 (b)

(c)

(d)

(e)

By combining the radiocarbon (F , fraction modern carbon) and $\delta^{13}\text{C}$ measurements we were able to identify two carbon components in the clay minerals. The carbon from all clay minerals has lower $\delta^{13}\text{C}$ values and higher F values at lower combustion temperatures. The isotopic composition shifts towards higher $\delta^{13}\text{C}$ and lower F values with increasing combustion temperature. Mixing curves are plotted in Fig. 3, and two components are easily identified from the mixing curves. The mixing trend for kaolinite (KGa-1b) and illite (IMt-1) resulted in a nearly linear fit, likely due to the fact that these two clay minerals are very pure. In contrast, the trend for illite-smectite mixed layer (ISCz-1) is curved. This curved trajectory likely represents a composite of two linear trends, as the sample is known to contain two interlayered clay mineral phases.

Figure 3. Fraction modern carbon (F) and $\delta^{13}\text{C}$ values of carbon extracted from clay minerals. Errors for the $\delta^{13}\text{C}$ values are contained within the markers. The temperature of each increment is labeled. The mixing curve is calculated from a general mixing equation for two components and the

equation* (Langmuir et al., 1978) is given below. Data points are fitted in a mixing hyperbolic curve between LT (low temperature) and HT (high temperature) end members.

(a)

(b)

(c)

* $Ax+Bxy+Cy+D=0$, A, B, C, D are coefficients,

$$x=\delta^{13}\text{C}=[(^{13}\text{C}/^{12}\text{C})_{\text{sample}}/(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}-1]*1000\text{‰}$$

$$y=F=(^{14}\text{C}/^{13}\text{C})_{\text{sample}}(\delta^{13}\text{C}_{\text{corr.}})/(^{14}\text{C}/^{13}\text{C})_{\text{OxII(1950)}}$$

Table 2. Percent of carbon released at successive oxidation temperatures, $\delta^{13}\text{C}$ values, fraction modern carbon (F) of clay minerals.

sampleID	%C	$\delta^{13}\text{C}(\text{‰})$	error	F	dF	sampleID	%C	$\delta^{13}\text{C}(\text{‰})$	error	F	dF	sampleID	%C	$\delta^{13}\text{C}(\text{‰})$	error	F	dF
KGa-1b kaolin						lmt-1 illite						ISCz-1 illite-smectite					
300°C	8.0					300°C	26.8	-28.1	0.02	0.296	0.005	300°C	7.8	-30.3	0.02	0.561	0.008
350°C	17.5	-27.6	0.02	0.462	0.019	350°C	9.9	-25.3	0.02	0.206	0.012	350°C	5.6	-27.6	0.02	0.530	0.009
400°C	17.5	-25.0	0.02	0.421	0.028	400°C	25.4	-27.6	0.02	0.180	0.005	400°C	3.7	-26.0	0.02	0.490	0.015
450°C	4.7					450°C	8.5	-27.0	0.02	0.231	0.013	450°C	6.2	-25.2	0.02	0.439	0.009
500°C	6.2	-23.9	0.02	0.462	0.013	500°C	5.6					500°C	5.8	-24.9	0.02	0.366	0.006
550°C	6.2	-21.6	0.02	0.343	0.031	550°C	4.2					550°C	18.7	-24.2	0.02	0.317	0.005
600°C	6.2	-22.7	0.02	0.224	0.040	600°C	2.8					600°C	7.7	-24.1	0.02	0.316	0.017
650°C	19.3	-21.7	0.02	0.150	0.038	650°C	7.1					650°C	5.5	-24.3	0.02	0.329	0.015
700°C	6.2					700°C	4.2					700°C	4.7				
750°C	3.3	-20.3	0.02	0.203	0.036	750°C	2.8					750°C	1.4				
800°C	1.5					800°C	1.3					800°C	1.9				
1100°C	3.3	-19.6	0.02	0.169	0.037	1100°C	1.3	-21.2	0.02	0.062	0.018	1100°C	0.4	-24.0	0.02	0.270	0.011
TOC%	0.018						0.047						0.022				

2. Carbon in <64 μm terrace sediments

The results for the terrace sediment samples are given in Table 3. These include radiocarbon dates on humic acids extracted as described above, and measurements of each temperature-step increment. The percent carbon released from each

increment for all samples is shown in Fig. 4. The amount of carbon from the VC terrace sample was not sufficient for 5 temperature steps, so we combined CO₂ from two fractions, ≤400°C and ≥500°C. These are identified in Table 3 as VC 400 and VC 1000, and their maximum combustion temperatures are quoted.

Table 3. Percent of carbon released at successive oxidation temperatures, $\delta^{13}\text{C}$ values, fraction modern carbon (F), radiocarbon age BP, and calibrated BP (2 σ) of all fractions of sediment samples.

sampleID	%C	$\delta^{13}\text{C}$ (‰)	error	F	dF	^{14}C ageBP	error	calBP(2 σ)
JH (height(m): 21.8)								
JH1HA		-15.3	0.01	0.545	0.006	4870	90	5330-5890
JH300	20.0	-17.5	0.01	0.726	0.005	2570	50	2490-2770
JH400	27.7	-16.5	0.01	0.470	0.003	6060	60	6750-7160
JH500	15.0	-16.1	0.02	0.313	0.004	9320	100	10240-10760
JH600	22.0	-17.4	0.01	0.419	0.003	6990	70	7690-7950
JH1000	15.0	-16.6	0.01	0.063	0.003	22200	300	25910-27170
TOC%	0.072							
PG (height(m): 3.4)								
PG1HA		-18.5	0.01	0.718	0.006	2660	70	2510-2950
PG300	32.9	-20.2	0.01	0.937	0.005	520	45	500-640
PG400	25.6	-18.9	0.01	0.819	0.005	1600	40	1390-1570
PG500	24.2	-19.3	0.00	0.665	0.004	3280	45	3400-3610
PG600	10.0	-19.1	0.01	lost				
PG1000	7.3	-17.3	0.01	0.218	0.003	12200	90	13770-14490
TOC%	0.255							
SY (height(m): 23.2)								
SYHA		-16.5	0.01	0.572	0.003	4490	40	4980-5300
SY300	19.9	-20.8	0.01	0.357	0.003	8280	60	9040-9440
SY400	24.4	-21.9	0.02	0.081	0.002	20200	250	23690-25040
SY500	25.9	-23.4	0.01	0.034	0.002	27200	500	30340-32420
SY600	13.9	-18.2	0.02	0.027	0.004	29000	1100	30990-34980
SY1000	15.9	-17.4	0.01	0.038	0.004	26300	700	28870-31430
TOC%	0.028							
NN (height(m): 35.3)								
NN1HA		-17.5	0.01	0.875	0.003	1070	30	930-1050
NN300	20.4	-20.7	0.01	0.751	0.004	2300	50	2150-2430
NN400	17.8	-20.0	0.01	0.555	0.004	4720	60	5320-5580
NN500	47.4	-18.8	0.02	0.200	0.002	12900	80	15160-15700
NN1000	14.5	-17.0	0.02	0.114	0.005	17500	300	20390-21920
TOC%	0.025							
VC (height(m): 21.3)								
VC1HA		-18.8	0.01	0.662	0.003	3300	30	3450-3590
VC400		-20.3	0.02	0.326	0.003	9000	80	9790-10370
VC1000		-19.3	0.01	0.085	0.002	19800	160	23430-24230

The percent carbon released from the JH terrace sample has two temperature ranges, $\leq 400^{\circ}\text{C}$ and $\geq 500^{\circ}\text{C}$, and produced results similar to the illite profile (IMt-1). Terrace PG and SY have broad temperature ranges from 300°C to 600°C of carbon released, and are similar to the Illite-Smectite profile (ISCz-1). The terrace NN sample was composed mainly of silt, without enough clay for XRD analysis. The carbon oxidized in this sample is dominated by the 500°C fraction. In general, the CO_2 -oxidation temperature profiles for the sediments are similar to the clay results, and consistent with their respective clay contents (Table 4).

Figure 4. Percent carbon released versus stepped-temperature of sediment in JH, PG, SY and NN trenches.

Table 4. XRD results of terrace sediments

Sample ID	Illite	Smectite	Chlorite	Quartz
PG	39.5%	28.5%	22.7%	9.3%
JH	41%	16.7%	24.5%	17.8%
SY	38%	29.4%	26.6%	6%

We also plotted $\delta^{13}\text{C}$ values versus F, for each trench location in Fig. 5. These plots generally follow a trend from lower $\delta^{13}\text{C}$ and higher F values at lower temperatures, to higher $\delta^{13}\text{C}$ and lower F values at higher temperatures. Two components of carbon sources can be clearly identified in the sediments from the PG, NN and JH terraces. Moreover, the grain sizes of the sediments from these three trenches are larger than from trenches SY and VC. Combustion of sediment samples from the SY terrace yielded two fractions of 400°C and 500°C, departing from a simple two component mixing curve and pointing to a third carbon component. A third component was also observed in sediments from Nanfu terrace, with lower F and lower $\delta^{13}\text{C}$ values in the 500°C fraction (Wang et al., 2013).

Figure 5. Fraction modern carbon (F) and $\delta^{13}\text{C}$ values of each temperature increment from sediment samples. Errors are contained within the markers.

(a)

(b)

337

338 (c)

339

340 (d)

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342

343 **Discussion**

344

1. Carbon in Clay Minerals

Clay minerals that form in soils are the product of weathering of silicate minerals, such as feldspar or mica. The weathering process dissolves the soluble portion of the high temperature minerals to form secondary clay minerals that contain water in their crystalline structures (Velde, 1992). Since clay minerals form in soils near the surface and they are in close contact with soil organic matter, some of this carbon can be incorporated into the clay minerals as they form. Moreover, clay minerals are stable at surface conditions, so it is reasonable to assume that once carbon is incorporated into the crystal lattice of a clay mineral, it will remain there as long as the clay minerals remain within surface conditions of temperature and pressure.

In general, there are several potential sites for water in clay minerals: 1) in interlayer sites (for certain clay minerals) that can freely exchange water and other molecules, 2) as OH^- shared by linked octahedral units (inner hydroxyls), and 3) as OH^- attached to the summits of octahedral sites, on the edge of an octahedral sheet (outer hydroxyls) (Velde, 1992). The release of interlayer water from clay as a result of heating is referred to as dehydroxylation and this phenomenon can be observed with Thermogravimetry Analysis (TGA) and Differential Thermal Analysis (DTA). These thermal analyses are often used to identify thermal stability temperature ranges in clay minerals and are analogous to our temperature-stepped combustion approach.

In the profiles of temperature-stepped combustion for well-crystalized clay minerals (Fig. 2), we observe two carbon sites: a low temperature site ($\leq 400^\circ\text{C}$) and a high temperature site ($\geq 550^\circ\text{C}$). TGA and DTA profiles from the same clay minerals

used here (from the Clay Mineral Society) show analogous behavior. Illite (IMt-1) has a mass loss below 400°C (Fig. 2). Our result show that 25% of the total carbon was oxidized at 400 °C and the remaining carbon was released between 500°C and 800°C, which is also observed in the corresponding DTA experiment. The JH terrace sample contained the highest proportion of illite to smectite, among the sediments studied here and this sample showed two distinct carbon-release peaks at 400°C and 600°C. Illite-Smectite (ISCz-1) is a mixed layer structure, and the temperature of carbon release is broad, from 500°C to 700°C, with a distinct peak at 550°C. Kaolinite (KGa-1b) has a single mass loss higher than 500°C in the TGA profile (Fig. 2), where we observe two peaks in our temperature-stepped combustion experiment: at low temperature (<400°C) and high temperature (>550°C). The higher temperature fraction of our data match those from TGA and DTA, however the carbon produced in the lower temperature range may be from carbon sources that were not removed by the acid-leach pretreatment of our clay mineral samples.

The correspondence between TGA and stepped-temperature combustion results points to a common source of carbon within the clays. The advantage of the stepped-temperature combustion results is that they provide a means to fingerprint these sources, in terms of their ^{13}C and ^{14}C isotopic compositions. All of the clay data can be explained in the context of two carbon end-members - a low temperature site and a high temperature site, both of which are clearly identified from the ratio ($\delta^{13}\text{C}$) to ratio (F) plots in Fig. 3. This is consistent with a number of published studies. For example, it has been shown previously that clay mineralogy exerts a control over the thermal stability of organo-mineral complexes (Plante et al., 2009). It has also been shown that there are at least two carbon components in organo-mineral complexes,

and that one is less stable and younger, and the other is more stable and older (Trumbore and Zheng, 1996; Kleber et al., 2007). Our low temperature site may be related to hydroxyl ions in the clay minerals. Binding sites for water, either in the interlayers of swelling clays, or on the edge of non-swelling clays, could accommodate organic carbon (Theng et al., 1986; Schulten et al., 1996; Chorover et al., 2004; Skiba et al., 2011). Such sites can exchange carbon at surface temperatures. Hence we interpret the radiocarbon age of the low temperature fraction to represent the most recent time of active exchange (a minimum age). Our high temperature carbon end member must be lattice-bound however, because it is not released until the clay is completely oxidized. Hence we infer that the radiocarbon age of the high temperature fraction dates to the time that the clay mineral formed (a maximum age). We expect that the tightly bound carbon in the high temperature fraction must also be protected from biodecomposition, as has been suggested by other studies (Kleber et al., 2005; Eusterhues et al., 2007).

2. Radiocarbon results from the fine fraction of sediments

The radiocarbon ages of all the fractions of sediment dated in this study range from 500 to 35000 Cal BP (Table 3). Based on the similarity between carbon in clay minerals and sediments, the low temperature carbon component in the sediments can be associated with relatively recent carbon exchange, after terrace formation, and the high temperature component may be expected to date the formation of the clays, before terrace formation. Temperature increments between the low- and high-temperature fractions are mixtures of the two end-members. Thus, we can consider the ages of the highest and the lowest increments to bracket the age range

for terrace formation. In addition, we can consider dates on humic acids extracted from the sediment for an indicator of the time of soil development.

In Fig. 7, we show the range of uplift rates determined from the ages of humic acids and the lowest and the highest increments in temperature-stepped combustion with other published results. The terraces, the Niushan anticline and the Chiendapu syncline are arranged according to their respective distances from the Liuchia fault. The uplift rates were calculated from terrace heights (mm) divided by their calibrated ages (Cal yr BP). [We used the 2 \$\sigma\$ range of calibrated ages for the uplift rate calculation of each fraction \(Fig. 7\).](#) The broad range of radiocarbon ages is reflected in the calculated range of possible uplift rates, from 0.4 to 33.6 mm/yr. The apparent high uplift rates for the NN, JH and PG terraces result from very young 300°C increment radiocarbon ages. Ages from lowest temperature increments are consistently the youngest for both clay minerals and sediments, suggesting that this carbon is acquired after the uplift of the terrace.

The apparent high uplift rates can be excluded based on GPS analysis. The entire western Taiwan orogenic belt is absorbing a horizontal convergence rate of up to 30 mm/yr (Hsu et al., 2003), and this convergence is likely distributed along at least three active faults in southwestern Taiwan (Shyu et al., 2005), all of which are low-angle (<30°) faults (Suppe, 1976, 1980; Hung et al., 1999). It is unlikely that the Liuchia fault would absorb a significant part of the horizontal convergence. With this, the uplift rate of its hanging wall is likely less than 10 mm/yr. Thus, an uplift rate of terraces higher than 10 mm/yr is excluded from Fig. 7. Considering the close proximity of the SY terrace to the anticline, the uplift rate appears to be lower than expected. The third component in the SY terrace is possibly detrital carbon that was

able to pass through the 64 μm sieve during pretreatment. This could be any form of organic material. The data indicate that this component formed at a very early stage, comparable to the age of the clays.

Figure 7. Uplift rates of humic acid and temperature-stepped combustion of humin derived from calibrated ages analyzed in this study. Only the lowest temperature (300°C in SY, NN, JH and PG terraces and 400°C in VC terrace) and the highest temperature (1000°C) increments of humin are plotted. Blue (humic acid), red (step combustion) and green (organic nodules) symbols indicate the uplift rates calculated from the 2 σ range of calibrated ages. In some cases the error bars are smaller than the symbol. The modeled uplift curve (dashed line) and uplift rates of organic nodules (green bar from Du, 2013 and green cross from Chang, 2005) are plotted for comparison. Gray shaded area is bounded by humic acid as upper limit and high temperature increments as lower limit for possible range of uplift rates.

The range of uplift rates of sediment fractions from the five terraces is broadly consistent with the proposed uplift curve of Du (2013), except for the omitted low temperature increments suspected of recent carbon input. The dashed uplift curve was modeled by a detailed channel topographic analysis along the Kueichung River and by the radiocarbon ages dated from organic nodules collected from the VC, JH and PG terraces with an additional data point (green cross) from Chang (2005). Some of the low temperature humin fractions show the continuity of carbon input on terrace sediment, so it is difficult to extract the age information. Organic nodules are altered plant fragments whose ages are closer to the age of terrace formation. Uplift rates based on humic acids are close to those of the organic nodules, and reflect similar ages and similar carbon exchange between humic acid, organic nodules and soil. Thus, we can also consider humic acids as minimum ages for terrace formation. Uplift rates based on low temperature fractions from the two terraces, SY and VC, are close to their humic acid fractions, and reflect the different depositional environment of these terraces, when compared with the other three terraces. The high temperature humin fraction represents the age of clay mineral formation, which occurs upstream from the terrace site. Hence, the high temperature dates provide maximum ages for terrace formation. Although we cannot say precisely how much this maximum overestimates the age of the terrace, it is worth noting that the time it takes for clay to form and then be transported downstream will be minimized by the topography and climate of the broader study area in Taiwan, with steep mountains and substantial rainfall during the monsoon season and from typhoons.

Instead of a single curve, we can draw a band of possible age ranges, confined by upper and lower boundaries derived from minimum and maximum radiocarbon

ages measured from the fine sediment fractions. This band could be refined with more radiocarbon ages from sediments on other terraces along the Kueichung River, and this technique has the potential to provide age constraints on the formation of terraces at other rivers, especially those running across important faults without reliable absolute ages.

Concluding remarks and future research

We combusted both well-crystallized clay minerals and terrace sediments sieved to silt and clay size in incrementally increased temperature steps. Oxidation temperature ranges of the carbon in the samples are similar to their dehydroxylation temperatures, based on clay contents. Based on temperature-stepped combustion results we identify two carbon sites in three different clay minerals, as defined by their ^{13}C and ^{14}C compositions: 1) low temperature ($\leq 400^\circ\text{C}$) and 2) high temperature ($\geq 550^\circ\text{C}$). The high temperature carbon component is only released when the clay is completely destroyed, and therefore must be contained within the clay mineral lattice. In the fine fraction of sediments (sieved to $<64\ \mu\text{m}$) we also find these two types of carbon, and in one case a third type, which is possibly detrital. As a rule, the radiocarbon ages of the fine sediment humin fraction increase with increasing combustion temperature. We can use dates from sediment humic acids and corresponding high temperature fine sediment humin fractions to provide quantitative minimum and maximum ages to constrain terrace formation ages. A virtue of this technique is that any terrace can be studied with the ubiquitous nature

of clay minerals, even under the circumstance of very few or poorly preserved charcoal found.

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