Using continental margin organic geochemical stratigraphy to reconstruct watershed history– Lessons from the Waipaoa Sedimentary System, New Zealand

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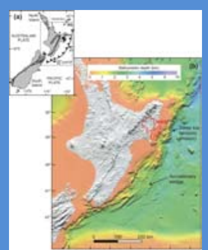
Introduction– Recognizing the organic geochemical signatures of terrestrial erosion in offshore sediments

Sedimentary organic matter buried on the continental margins has the potential provide information about the relative roles of various geomorphic processes in watersheds over time. In the Waipaoa watershed, New Zealand, for example, gully erosion, earthflows, shallow landslides, and sheet wash deliver organic matter from derived from different depths in the regolith, and therefore of different composition and age.

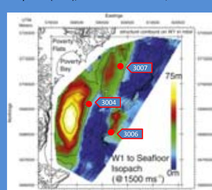
Gully erosion and **earthflows** access sedimentary bedrock, which in the Waipaoa watershed has a mean OC content of 0.27 ± 0.18 and $\delta^{13}C$ of -25.1 ± 1.3 (n=11). Because of its age, organic carbon (kerogen) from these rocks contains no ^{14}C (Fm=0)

Shallow landslides have failure planes near the soil/bedrock interface. Typical soil profiles in the Waipaoa watershed are built on volcaniclastic material. Organic contents are high at the surface (~≈5-10%) and decrease downward asymptotically. Soil $\delta^{13}C$ values are variable, but a common pattern is that $\delta^{13}C$ values at the surface are close to that of plants and become more positive with depth. The depth-integrated ^{14}C age of OC in the typical soil profile is about 1000 years (Fm≈0.8)

Sheet wash mobilizes surficial material, including relatively recent plant debris (Fm≈1.0-1.1). C3 plants dominate the Waipaoa watershed. Typical $\delta^{13}C$ values are between -27 and -28‰.



Location map for the Waipaoa Sedimentary System (WSS), from Litchfield et al., 2009



Isopach map from Gerber et al. (2010) showing location of Holocene depocenters and coring sites

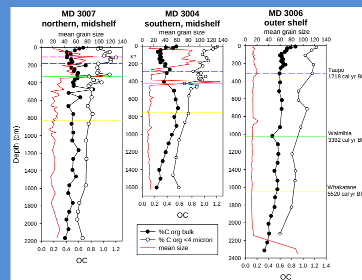
Methods– teasing apart the clues

The Waipaoa Sedimentary System on the North Island of New Zealand is an ideal location in which to explore the organic geochemical stratigraphic signals of watershed change. The Waipaoa River discharges abundant sediment and associated organic carbon to the ocean, where it has accumulated to 10's of meters thickness in a number of offshore depocenters (Orpin et al., 2006; Gerber et al., 2010).

Samples from each of three depocenters on the Waipaoa shelf were obtained from giant piston cores recovered in 2006 by the R/V Marion Dufresne as part of the MATACORE program (Proust et al., 2006; Gerber et al., 2010). Tephra layers identified in the cores include those from the Whakatane (5530 cal yr BP), Waimihia (3410 cal yr BP), and Taupo (1717 cal yr BP) eruptions (Lowe et al., 2008; Gerber et al., 2010). Detailed sampling of the cores, designated MD3004, MD3006, and MD3007, was undertaken for this study in June 2007, under the auspices of the NSF Margins Source-to-Sink Initiative.

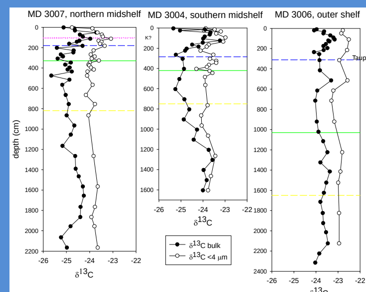
Bulk sediments as well as size and density isolates from the MD cores have been analyzed for this study. Charcoal, woody plant fragments, pumice, and biological skeletal debris have been isolated from the >25 micron fraction by flotation in an aqueous solution of sodium polytungstate (SPT, ρ=1.6 gm cm^{-3}). Clay-sized material has been isolated by settling. Following acidification to remove inorganic carbon, samples were analyzed for %OC and $\delta^{13}C$ using a Thermo-Electron EA 1112 elemental analyzer coupled to a Thermo Delta V IRMS. Bulk sediment, clay, wood, and charcoal from the MD3007 core were analyzed for ^{14}C at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS), Woods Hole, MA.

Results– OC, $\delta^{13}C$, and ^{14}C trends in Waipaoa shelf sediments

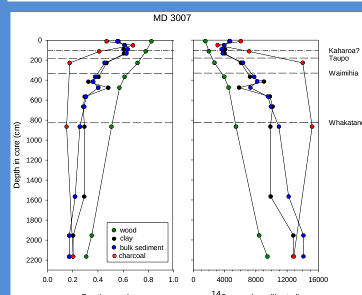


The **organic carbon** content of bulk sediments in the MD cores is partly a function of particle size. OC content in the clay-sized fraction is generally higher by a factor of 2 and shows a downward decrease suggestive of a diagenetic effect. A subtle, stepped upward increase in clay-associated OC beginning just below the Waimihia tephra in MD3007 and MD3004 may signal a source change

Note that in this study we have tentatively identified a coarse, pumiceous horizon at ~ 105 cm in the MD3007 core as the Kaharoa tephra (636 cal. yr BP)

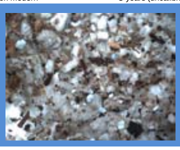


$\delta^{13}C$ values are more positive for the clay-sized fraction than for bulk sediments in all three cores, but the two sets of samples show similar trends. The most distinctive feature in all three cores is an "excursion" toward more positive values above the Taupo tephra layer.

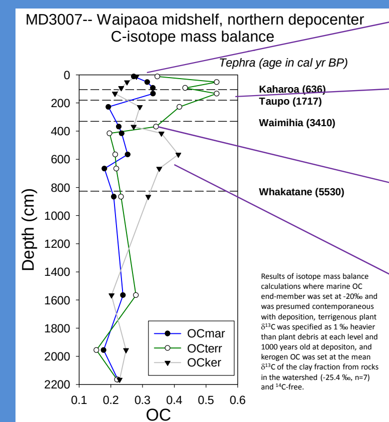


Radiocarbon dating of sediment fractions in MD3007 points to their derivation from multiple sources. Wood fragments are the youngest fraction, but based on comparison to calibrated ages to established ages of tephras, were about 400-500 years old when they were deposited on the shelf. Both the bulk sediments and the clay fraction are older than wood fragments by an average of about 4000 years. Charcoal in the lower part of the core is very old, but becomes dramatically younger in the upper part of the core, most likely due to an increased contribution from coeval biomass burning. The timing of this change is consistent with the first phases of anthropogenic deforestation of the watershed by Maori settlers about 700 years ago (Wilmshurst et al., 2008).

Low density isolate from the Waipaoa shelf containing woody plant debris, charcoal, pumice, and skeletal debris



Resolving sources of OC using an isotope mass balance



Results of isotope mass balance calculations where marine OC end-member was set at -20‰ and was presumed contemporaneous with deposition, terrigenous plant $\delta^{13}C$ was specified as 1 ‰ heavier than plant debris at each level and 1000 years old at depositon, and kerogen OC was set at the mean $\delta^{13}C$ of the clay fraction from rocks in the watershed (-25.4 ‰, n=7) and ^{14}C-free.

Investigations of the modern Waipaoa sedimentary system have revealed that the primary sources of organic carbon buried on the continental shelf are sedimentary rocks, terrestrial plant debris, and marine algae (Blair et al., 2010; Brackley et al., 2010). Assuming that the same sources have dominated throughout the Holocene, we have applied a three end-member mixing model and the following isotope mass balance equations (Blair et al., 2003) to resolve what the $\delta^{13}C$ and ^{14}C variations in the MD3007 may indicate about changing sources of organic matter over time:

$$1 = f_t + f_k + f_m$$
$$\delta_s = \delta_t f_t + \delta_k f_k + \delta_m f_m$$
$$F_s = F_t f_t + F_k f_k + F_m f_m$$

where f_t, f_k, and f_m are the fractions of terrestrial (non-rock), kerogen (rock), and marine carbon, and δ_s, δ_t, δ_k, and δ_m represent the $\delta^{13}C$ values of samples, the terrestrial, kerogen, and marine end-members respectively. Similarly, F_s, F_t, F_k, and F_m are the $^{14}C/^{12}C$ ratios of the samples and three end-members expressed as Fraction modern (Fm), and "modern" is defined as 95% of the radiocarbon concentration in AD 1950 of a standard (Olson, 1970).

In order to minimize the effects of particle size on OC concentrations, the mass balance calculations have been carried out for the clay-sized fraction. Mass balance equations were solved simultaneously to estimate the proportions of the three end-members at various levels in the MD3007 core. End-member values were varied in different model runs as indicated below.

OC Source	$\delta^{13}C$	^{14}C age
Marine	-19 to -21 ‰	Contemporaneous with depositional age as determined from tephra chronology
Terrestrial	$\delta^{13}C$ of plant debris at each level (ca. -27‰) or 1‰ heavier	500-1000 years older than depositional age (reflects residence time in trees and soils)
Kerogen (rock carbon)	-25.4 ‰ (average for clay fraction in watershed rocks)	>50,000 years– contains no ^{14}C

What does this tell us about watershed history?

- Recent increase is **kerogen OC** coincides with deforestation of headwaters by Europeans and development of *deep gully complexes* into bedrock
- Note that kerogen is a smaller proportion of the OC buried on the shelf than during the mid Holocene.

- Increased contribution of **terrestrial carbon,** and possibly also marine OC– coincides with $\delta^{13}C$ "excursion" observed in all 3 shelf cores
- Timing is about the same as the influx of young charcoal (see ^{14}C results)
- Consistent with more frequent *shallow landsliding* that may have resulted from biomass burning following human immigration about 700 years ago
- Soil erosion may have released nutrients that stimulated marine productivity

- Abrupt increase in **terrestrial carbon** coincides with decreased sediment accumulation rates on the midshelf and greater pumice contribution to sediments.
- As earthflow activity slowed, *occasional landslides* delivering pumiceous soils may have become relatively more important sources of OC

- Elevated contribution of **kerogen carbon**
- Coincident with previously documented period of high *earthflow* activity that ended shortly before Waimihia eruption
- Cause of high earthflow activity possibly knickpoint migration through susceptible tributaries?
- Also correlates with a stormy period indicated by Lake Tutira record (Page et al., 2010)

Conclusions and future directions

The biogeochemical stratigraphic record on continental margins provides a window into the long term evolution of adjacent landscapes, including the impacts of base-level change, climate, and human perturbation on geomorphic processes. In the Waipaoa system, the stable carbon isotopic composition and especially the ^{14}C age of organic carbon buried on the continental shelf serve as tracers of contributions from deeper and shallower levels in the regolith, and point toward changes in the relative importance of earthflows and shallow landslides to sediment delivery during the Holocene Epoch. In the future, our interpretations can be evaluated along with results from ongoing investigations in the watershed to more fully reconstruct its history.

Although biogeochemical stratigraphic signals of terrestrial environmental change appear to be especially clear in the Waipaoa system, there is reason to believe that a similar approach may be applied other continental margins as well as to lacustrine deposits. In the future, moreover, application of additional geochemical tools for quantifying kerogen and soil contributions to sedimentary organic carbon may facilitate more detailed reconstructions of the Waipaoa margin and elsewhere, and may enable interpretation of stratigraphic records of watershed change beyond the temporal reach of ^{14}C.

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