Organic Molecular Paleohypsometry: A New Approach to Quantifying Paleotopography and Paleorelief

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Stable isotope paleoaltimetry is one of the most commonly used approaches for quantifying the paleoelevation history of an orogen yet this methodology is often limited to arid to semi-arid climates, mountain systems with a clear orographic rainshadow and terrestrial basins. We present a new approach to reconstructing past topography and relief that uses the catchment-integrated signature of organic molecular biomarkers to quantify the hypsometry of fluvially-exported biomass. Because terrestrially-produced biomolecules are synthesized over the full range of global climate conditions and can be preserved in both terrestrial and marine sediments, the geochemistry of fluvially-transported sedimentary biomarkers can provide a means of interrogating the evolution of topography for a range of environments and depositional settings, including those not well suited for a traditional isotope paleoaltimetry approach. We show an example from Taiwan, a rapidly eroding tropical mountain system that is characterized by high rates of biomass production and short organic residence time and discuss key factors that can influence molecular isotope signal production, transport and integration. Data show that in high relief catchments of Taiwan, river sediments can record integration of biomass produced throughout the catchment. Sedimentary biomarker $\delta^{2}H_{n}C_{29}$ in low elevation river deposition sites is generally offset from the $\delta^{2}H_{n}C_{29}$ value observed in local soils and consistent with an isotope composition of organics produced at the catchment mean elevation. We test the effect of distinct molecular production and erosion functions on the expected $\delta^{2}H_{n}C_{29}$ in river sediments and show that elevation-dependent differences in the production and erosion of biomarkers/sediment may yield only modest differences in the catchment-integrated isotopic signal. Relating fluvial biomarker isotope records to quantitative estimates of organic source elevations in other global orogens will likely pose numerous challenges, with a number of variables that influence molecular production and integration in a river system. We provide a discussion of important parameters that influence molecular biomarker isotope signatures in a mountain system and a framework for employing a molecular paleohypsometry approach to quantifying the evolution of other orogenic systems.

Keywords: paleoelevation, paleotopography, stable isotopes, biomarker, catchment integration
INTRODUCTION

The development of large orogens can produce fundamental shifts in global physical and chemical fluxes, atmospheric dynamics, biologic change, and even long-term changes in the redox state of the mantle (Kutzbach et al., 1989; Ruddiman and Kutzbach, 1989; Ramstein et al., 1997; Ruddiman, 2013). Records of the paleoelevation history of an orogen or the evolution of orogenic relief are critical for quantifying the feedbacks among climate, erosion and tectonics, yet challenging to produce. As a result, developing reliable records of paleotopography remains one of the grand challenges in the Earth sciences (National Academies of Sciences, Engineering, and Medicine et al., 2020).

Over the past 20 years, numerous approaches have been developed to quantify changes in the topography of an orogen (Axelrod, 1997; Forest et al., 1999; Garzione et al., 2000; Poage and Chamberlain, 2001; Poage and Chamberlain, 2002; Sahagian et al., 2002; Ghosh et al., 2006; Rowley, 2006/8; Clark, 2007; Rowley and Garzione, 2007; Sahagian and Proussevitch, 2007; Hren et al., 2010). Yet, there continues to be a fundamental information gap with regard to approaches for quantifying topographic change for numerous types of orogens. In particular, current methodologies are commonly limited to application in systems that are characterized by simple orographic rainshadows and a semi-arid to arid climate, terrestrial foreland basin systems, and temperate to cool terrestrial settings with mild to moderate chemical weathering rates. There remain few paleotopography reconstruction approaches that are successful for wet, tropical mountain belts with complex climatology and moisture sourcing, or systems with predominantly marine deposition.

Here we discuss a new approach to quantifying the paleohypsometry of an orogen using the stable isotope composition of organic molecular biomarkers that are produced within a catchment and exported via river networks. This approach is similar to the time-tested methods of cosmogenic isotope determination of catchment erosion rate (Bierman, 1994; Bierman and Steig, 1996; Granger et al., 1996; Heimsath et al., 2001).

Specifically, in an evolving orogen, organic biomass may be produced throughout a catchment. As an orogen and associated catchments evolve, distinct elevation and precipitation isotope and temperature patterns emerge for all points in the catchment. Biomolecules produced by plants or microorganisms at each point in the landscape can record the signature of precipitation isotopes or temperature at the point of production. These molecules are incorporated into soils, bound to clay particles and mobilized throughout a catchment. The geochemical signature of fluvial sediments sampled along the length of a river profile should therefore reflect changes in the source areas of contributing sediment. If the molecular production function and catchment-wide biomass integration can be characterized, the geochemical record preserved in exported and buried sediments can be used to derive a catchment-specific signature of topography and relief through time.

This method focuses on geochemical signatures preserved in material exported from an orogen through river networks. While there are a host of process-specific relationships to resolve for different climate and erosion regimes, the potential power of this approach is that it greatly expands the possible range of sediments that quantitatively capture orogenic events and provides a template for producing measures of catchment hypsometry through time.

Stable Isotope Paleoaltimetry

There are a number of approaches that have been developed to constrain paleotopography (e.g., Kohn, 2018 and references therein). These generally rely on environmental variables that are related to elevation such as temperature (Quade et al., 2013; Quade et al., 2007), pressure (Sahagian and Maus, 1994; Sahagian et al., 2002; Sahagian and Proussevitch, 2007), plant physiology (Wolfe et al., 1997; Forest et al., 1999), or water isotopes (Garzione et al., 2000; Poage and Chamberlain, 2001; Poage and Chamberlain, 2002; Rowley and Garzione, 2007; Hren et al., 2009). Over the past several decades, stable isotope paleoaltimetry has become one of the most commonly utilized paleoelevation techniques (e.g., Huntington et al., 2015; Wheeler et al., 2016; Fan et al., 2017; Tang et al., 2017; Bershaw et al., 2019; Li et al., 2019; Zhuang et al., 2019). This is due in part, to the abundance of materials that preserve the isotopic signature of ambient water such as carbonates and clays (Chamberlain and Poage, 2000; Sjoström et al., 2006; Mulch and Chamberlain, 2007; Mulch et al., 2007), volcanic glasses (Cassell et al., 2009; Bershaw et al., 2019; Colwyn et al., 2019; Colwyn and Hren, 2019), fossils (Kohn et al., 2002), and leaf waxes (Polisnar et al., 2009; Hren et al., 2010; Anderson et al., 2015; Zhuang et al., 2019).

Application of stable isotope-based approaches has provided fundamental insight into how Cordilleran orogens evolve (Fan et al., 2017; Feng et al., 2013; Kent-Corson et al., 2006; Andreas Mulch and Chamberlain, 2007), long-timescale changes in the elevation of orogenic plateaus (Dettman et al., 2003; Ghosh et al., 2006; Molnar et al., 2006; Rowley and Currie, 2006; Hoke et al., 2014; Currie et al., 2016), even the role of tectonic change on biological diversification (Phillips et al., 2013).

Stable isotope paleoaltimetry is founded on the principle that as a moist airmass encounters a topographic barrier, it can undergo lifting, cooling and rainout (Rowley et al., 2001; Rowley and Garzione, 2007; Rowley, 2007). Oxygen and hydrogen fractionation of the rainwater results from the strong temperature-dependence of isotopic partitioning between vapor and liquid or solid phases. Condensation across an orogen progressively removes the “heavy” isotope species producing a characteristic Rayleigh distillation pattern in precipitation that is often described as the isotopic “altitude effect” (Dansgaard, 1964; Gonfiantini et al., 2001) (Figure 1).

While frequently applied as a geochemical technique, there are several key requirements for isotope paleoaltimetry to reliably record changes to topography: 1) changes in surface topography must impart a predictable change in the isotopic composition of ambient water and/or local temperature (i.e., signal generation); 2) proxy materials that form in equilibrium with ambient waters (i.e., clays, glasses, carbonates, or organic matter) must record these changes (signal recording); and 3) proxy records of this change must be preserved in sedimentary environments in
proximity to the area of evolving topography (signal preservation).

In large accretionary collision zones, sediment is commonly preserved in foreland basin systems - elongate regions of sediment accommodation that form in response to geodynamic processes related to subduction (e.g., DeCelles and Giles, 1996). As orogens evolve, sediment deposition sites can vary from deep marine to fluvial and lacustrine deposition in a range of accommodation spaces. Thus, the sedimentary record of orogenesis spans a range of sediment composition and depositional settings. However, records of paleotopography frequently derive from only the terrestrial sediments associated with orogenesis. The most commonly utilized methodology for paleotopography reconstruction, stable isotope paleoaltimetry, is generally not applicable to marine sediments.

In many terrestrial continental environments such as the western North American interior, the Andes or Tibetan Plateau, prevailing wind directions and the orientation of the orogens produce large “orographic rainshadows” and a clear isotopic shift in precipitation that can be preserved in materials deposited within basin sediments close to the orogen. Conventional stable isotope paleoaltimetry generally assumes an airmass travels over an orogen, imparting a clear “elevation” signature on precipitation isotopes (Figure 1). Indeed, most paleoelevation studies utilize materials preserved in basin sediments within an orographic rainshadow. For example, virtually all records of the paleotopography of the Tibetan Plateau are generated from sediments deposited in basins now on the Plateau itself (Rowley et al., 2001; Molnar et al., 2006; Rowley and Currie, 2006; Rowley, 2006/8; Polissar et al., 2009; Xu et al., 2010; Quade et al., 2011; Staish et al., 2014; Huntington et al., 2015; Currie et al., 2016; Tang et al., 2017; Li et al., 2019), with few studies from the Himalayan front (e.g., Hoke et al., 2014; Grujic et al., 2018).

While most paleotopography approaches require an orographic and isotopic rainshadow, in reality, variables such as atmospheric stability and wind-speed influence the path an airmass travels (e.g., Roe, 2005; Galewsky, 2009; Lechler and Galewsky, 2013). As orogens reach critical elevations, airmasses can travel laterally along a barrier rather than over, producing heterogeneous patterns of isotopes of precipitation in the leeward side of a range (Roe, 2005; Galewsky, 2009; Lechler and Galewsky, 2013; Wheeler et al., 2016). Similarly, changes to thermal heating of the landscape can alter moisture transport and isotope fractionation patterns (Poulsen et al., 2010; Insel et al., 2012; Insel et al., 2013; Botsyun et al., 2019). This can produce highly spatially heterogeneous geochemical signatures of topography. As a result, uplift of an orogen may not always produce clear isotopic signatures of elevation within an orographic rainshadow (e.g., Hren et al., 2009; Insel et al., 2010; Insel et al., 2012; Feng et al., 2013; Insel et al., 2013; Botsyun et al., 2016; Botsyun et al., 2019; Shen and Poulsen, 2019). A prime example of this process is observed in the Himalaya and Tibetan Plateau. Here, water isotope records show a large precipitation isotope gradient on the front of the Himalayan orogen, yet large-scale enrichment of water isotope values with progressive distance into the continental interior (Garzione et al., 2000; Hren et al., 2009; Jay; Quade et al., 2011; Bershaw et al., 2012; Yang et al., 2012; Yang et al., 2012). The isotopic shift that results from progressive mixing of multiple moisture sources combined with increased evaporation in the high elevation, arid landscape of the Tibetan plateau, can dwarf the isotopic signature that is related to elevation and observed on the range front or in close proximity to the orogen.

In contrast to the complex isotopic patterns observed in the leeward side of large orogens, particularly with increasing distance from an orographic barrier, along the range front of virtually all orogens on the globe, isotopes of precipitation generally show a clear and consistent relationship between elevation and water $\delta^{18}O$ or $\delta^2H$ and temperature. This geochemical signature can exhibit greater noise at lower elevations (less than 1 km) where local climatic and
Organic Molecular Biomarkers and Paleoelevation

Terrestrial plants produce a variety of compounds within and on their leaves to minimize water loss and provide protection from predation (Holloway, 1969; Barthlott and Neinhuis, 1997). These molecules are produced in abundance and can be preserved over long timescales with minimal or no isotopic alteration (Schimmelmann et al., 1999; Schimmelmann et al., 2006; Yang and Huang, 2003/3). Plants utilize ambient water during biosynthesis and incorporate the isotopic signature of that water into biomolecules. The chemistry of these molecular compounds records water isotopes modified by factors such as evapotranspiration and carbon assimilation rates (e.g., Ehleringer et al., 1990; Chikaraishi and Naraoka, 2003/6; Chikaraishi et al., 2004; Sachse et al., 2004; Sachse et al., 2006; Hou et al., 2008; Sachse et al., 2012). Compound-specific D/H fractionation in plant molecules is primarily dependent on water isotope composition, the biosynthetic pathway (Hayes, 1993) and stomatal water loss in response to water and CO₂ limitation, but integrated soil biomarkers commonly show consistent D/H fractionation in warm/temperate and moist environments (e.g., Sachse et al., 2012; Tipple and Pagani, 2013; Wang et al., 2017). In temperate and tropical environments, soil n-alkane δ²H is correlated with precipitation δ²H due to ecosystem level homogeneities of the vegetation (e.g. Jia et al., 2008; Tipple and Pagani, 2013; Tipple and Pagani 2013; Bai et al., 2015; Zhuang et al., 2015; Liu et al., 2016; Vogts et al., 2016; Bai et al., 2017; Wang et al., 2017; Liu and An 2019). For example, a study of precipitation isotopes and plant wax δ²H along an elevation gradient of nearly 4 km on the SE margin of the Tibetan plateau shows a strong correlation between ambient water isotopes and n-alkane δ²H over a range of elevations (Wang et al., 2017). In addition, the magnitude of change in n-alkane δ²H observed on the SE Tibetan Plateau margin mirrors that observed in other regional studies from the SE Asian region (Jia et al., 2008; Bai et al., 2015). Some studies suggest that the relationship between plant wax δ²H and ambient water may vary as a function of climate and/or elevation in some circumstances, however this remains a subject of debate with recent studies showing no climatic effect on apparent fractionation (Struck et al., 2020), and is similar to questions surrounding uncertainties in water of formation for authigenic minerals and glasses that are commonly used for paleoelevation reconstruction. Plant waxes, including long-carbon chain normal alkanes, can thus provide a geochemical record of ambient water δ²H with similar or less uncertainty than other commonly used paleoprecipitation isotope proxies such as soil carbonates, clays, or volcanic glass. In addition, the molecules that are produced by plants and some terrestrial microorganisms, can be uniquely identifiable from molecules produced by marine organisms, meaning they can be identified and isolated from marine sediments.

Organic Molecular Hypsometry: Catchment Integration of Water and Sediment

The δ¹⁸O and δ²H of stream waters record the precipitation and precipitation isotope-weighted hypsometry of the upstream catchment (e.g., Hren et al., 2009; Rowley et al., 2001; Rowley...
and Garzione, 2007). For example, along the Himalayan front, the δ¹⁸O or δ²H of river water from low sample elevations reflects isotopically depleted values that are consistent with precipitation-weighted elevation (Hren et al., 2009). Thus, the isotopic signature of water at any point on a river will generally reflect the isotopic composition of the precipitation-weighted elevation of the upstream area (Figure 2). Conceptually, this principle is quite simple and river water isotope signatures should reflect the distribution of water isotopes throughout the catchment weighted by the contributions from different portions of the basin. Indeed, more than 25 years ago, Norris and others (1996) argued that isotopic records of the Eocene Green River lakes provided clear indication of a high elevation paleo-Uinta Mountain range (Norris et al., 1996).

Annual precipitation δ²H typically varies by ~15–30‰ per km of elevation in tropical to temperate settings (e.g., Poage and Chamberlain, 2001). The relationship between precipitation isotopes and elevation is most consistent in close proximity to an orogen and tends to increase in noise when the scale of the study area exceeds the scale of the processes that generate the geochemical signal. In large catchments, the isotopic composition of precipitation can vary by more than 100‰ in δ²H from headwaters to river mouth (Figure 2), and the isotopic composition of water at any point along the river (which integrates the entire upstream area) can be quite distinct from the composition of precipitation falling on that point of the landscape. As one moves up a river profile, local elevation increases and catchment size decreases, and the offset between the local elevation of a point on a river and the mean elevation of the upstream area decreases to zero (Figure 2). As these come closer together, precipitation-weighted δ²H becomes identical to ambient precipitation δ²H.

Like water, fluvially-transported organic biomarkers can record the hypsometry of a catchment through their isotopic composition (where δHbiomarker varies in relation to elevation-dependent variations in source water δ²H) or in molecules that reflect the temperature of formation at a specific location in the catchment. To first order, plant waxes record the hydrogen isotope composition of water used during growth and show a similar Δδ²Halkane with elevation as precipitation (e.g., Jia et al., 2008; Bai et al., 2015; Zhuang et al., 2015; Nieto-Moreno et al., 2016; Wang et al., 2017). There are a number of factors that can influence the apparent fractionation between plant waxes and ambient water, including plant-specific differences in evapotranspiration and biosynthesis (e.g., Sachse et al., 2012), and some data suggests potential changes in apparent fractionation with elevation (Bai et al., 2017). However, other data suggests no clear correlation between climate and apparent fractionation (Struck et al., 2020) and numerous studies of biomarkers in soils show a generally consistent fractionation between water and wax (Jia et al., 2008; Tipple and Pagani 2013; Bai et al., 2015; Zhuang et al., 2015; Liu et al., 2016; Vogts et al., 2016; Bai et al., 2017; Wang et al., 2017; Liu and An 2019). Here we present new organic molecular biomarker and water isotope data from soils and rivers of Taiwan to test whether organic biomarker isotopes can reflect catchment integrated signatures of catchment hypsometry.

### Taiwan: A Model System for Studying Catchment Integration and Biomarker Records

The island of Taiwan marks the active boundary of the Eurasian and Philippine Sea plates (Teng, 1990) and hosts some of the highest rates of convergence, exhumation (Yu and Chow, 1997; Dadson et al., 2003; Lee et al., 2015), erosion (Hovius et al., 2000; Dadson et al., 2003; Schaller et al., 2005; Siame et al., 2011/14; Derrieux et al., 2014), and precipitation on the globe. The nearly 400 km long orogenic belt is a product of the oblique collision of the north-trending Luzon Arc and the northeast-trending passive margin of southeast China and is commonly used as a model for an active accretionary wedge (Ho, 1986; Y.-H.; Lee et al., 2006;
Taiwan is also provided as an example of an orogenic system that is in a topographic steady state (Suppe et al., 1981; Willett and Brandon, 2002; Stolar et al., 2007), where the flux of material to the base and front are balanced by the removal of material through physical and chemical erosion (Suppe et al., 1981; Deffontaines et al., 1994; Willett and Brandon, 2002). As a potential steady state orogen, Taiwan serves as an example for understanding the links and feedbacks among tectonics, climate, and erosion (Roe et al., 2006). However, to date, there is no known methodology to constrain the elevation history of orogens such as Taiwan due to the lack of an orographic rainshadow, extremely rapid erosion with minimal onshore terrestrial sediment storage, and the lack of datable carbonates, clays or glasses that could preserve a record of isotopic change due to uplift. As such, it is an ideal location to test a new approach to constraining paleotopographic change.

Taiwan does not have an orographic rainshadow (with high precipitation and moisture sourced from both the east and west), however it is characterized by large temperature and precipitation isotope gradients with elevation. We sampled thirty-three stream waters (Table 1) and twelve modern soils (Table 2) across Taiwan from 0 to 3,500 m to examine the modern relationship between δ²Hn-alkane, elevation, and precipitation δ²H (Figure 3). In addition, we collected sixteen river sediments (Table 3) at sites adjacent to soil collection localities to assess catchment integration signatures within the organic molecular biomarker pool. Soils were collected from locations in close proximity to the river channel, but well above any modern floodplain to avoid contributions from the modern river, and therefore are assumed to reflect only “local” biomarker production for this study. Fluvial sediments were collected from within the channel in an attempt to capture an integrated sediment signature. For each water and river sediment sample, we used ArcGIS to quantify the histogram of the contributing catchment and key parameters such as max/ min/mean catchment elevation. Thus, water and sediment samples are characterized by both a “local” and “catchment mean” elevation that reflects the elevation the samples were collected at and the mean elevation of all areas potentially contributing to the sample collection point. Soil samples are considered “local” and may only be represented as a single sample elevation for the purposes of this work.

For biomarker extraction and analysis, samples were freeze-dried and approximately 150 g of sediment extracted via Soxhlet apparatus using a 400 ml mixture of dichloromethane:methanol (2:1, v:v). Organics were separated by polarity using silica gel column chromatography with hexane, methylene chloride and methanol. The nonpolar hexane fraction (S1) containing n-alkanes were further purified by urea adduction and silver nitrate (AgNO₃) chromatography to separate branched and cyclic alkanes. The distribution of normal alkanes was quantified using a Thermo-Scientific Trace GC Ultra equipped with a flame ionization detector (FID-GC-FID), using a BP-5 column (30 m × 0.25 mm i.d., 0.25 µm film thickness) with helium as the carrier gas at a constant flow rate of 1.5 ml/min. n-alkane δ²H was analyzed for peaks of sufficient abundance using a GC-Isolink coupled to a Thermo-Scientific MAT 253 isotope ratio mass spectrometer (IRMS) using a BP-5 column (30 m × 0.25 mm i.d., 0.25 µm film thickness). The temperature program was set at 50°C for 1 min, ramped to 180°C at 12°C/min, then ramped to 320°C at 4°C/min and held isothermally for 4 min. During the interval of measurement, standards were analyzed every 4-5 four samples across a range of concentrations to correct for size and scale effects. Repeat analyses throughout the run and for a range of standard concentrations yield an external precision of <5‰ for δ²H. All values are expressed in standard delta notation relative to VSMOW. The δ²H of waters was analyzed by the Stable Isotope Laboratory at Louisiana State University and reported relative to VSMOW. Precision is <2‰ for δ²H.

Water samples span the drainage divide and annual precipitation exceeds several m/yr over the study area. All areas

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FIGURE 3 | (A) Sample location of water, soil, and sediment samples used in this study. (B) δ²H of river waters (plotted as sample elevation and as catchments mean elevation). Gray arrow represents the deviation between the δ²H of waters at a sample elevation and the expected δ²H of local precipitation. Black arrow shows the deviation between the elevation of a sample vs. the elevation of the contributing watershed.
are also subject to extreme convection events, different seasonal monsoonal precipitation and typhoons. Given the high relief present in the Taiwan orogen, there is significant contribution from high elevation upstream areas to any given point in the river network. Given the extreme climate variability in Taiwan, one might predict that relationships between isotopes of precipitation and elevation would be highly variable between E and W sides and any elevation-dependent signatures could be muted by the large convective rainfall events. River waters represent a time-integrated groundwater signal. When river waters are plotted as a function of area-weighted elevation (the mean elevation of all portions of the catchment that contribute water to a specific sampling point on the river), the data reveal a classic elevation-dependent Rayleigh distillation pattern. Our data show that waters from the north to the south and collected over multiple years produce a well-defined isotope-elevation relationship (∼18‰ per 1,000 m) (Figures 3A,B) when plotted as a function of catchment mean elevation. We suggest that river waters provide the best estimate of the time-integrated water isotopes incorporated into plants in Taiwan during biosynthesis. This is likely due to the fact that large rainfall events in Taiwan are associated with significant overland flow from the steep slopes of the high relief catchments. Thus, soil water and amount-weighted precipitation δ2H may not be the same. Thus, we focus on river water isotope data which provide a clear expectation for an elevation-dependent isotopic signal within molecular biomarkers produced across the Taiwan landscape.

Soil-derived long-carbon chain n-alkanes show a similar pattern to water δ2H, in support of our emphasis on river water data, and are suggestive of a consistent relationship between δ2H-n-alkane and elevation (Figure 4). This pattern is not surprising, given the high degree of primary productivity at nearly all elevations across Taiwan and C3-dominated forests across nearly all elevations of the subtropical study area. The modern biomarker isotope lase is on the order of ∼21‰ for δ18O-n-C29, with a slightly lower rate for n-C31 and higher for n-C27. Thus, the isotopic lase observed in plant biomarkers closely tracks that of river waters. This likely results from the subtropical climate, long-growing season, high precipitation, and angiosperm-dominated forests at all elevations. Thus, we can confidently argue that to first order, plant wax δ2H records variations in the geochemical signature of precipitation that is a function of elevation and observed in countless other orogenic systems.

The isotope and molecular geochemistry of biomolecules produced throughout a catchment reflect the conditions at the location and time of biosynthesis. The pattern of precipitation isotopes that is observed within a catchment is thus reflected in the isotopic composition of organic biomarkers that are produced throughout that catchment. One might reasonably expect that organics produced at points throughout a catchment would reflect the pattern of water isotopes on the landscape in the form of an organic molecular isoscape. To illustrate this, we show the digital elevation map of the Mugu basin of eastern Taiwan (Figure 5A), with the expected biomarker δ18O-C29 overlain as a colormap (Figure 5B). The “expected” biomarker δ18O-n-C29 shown in Figure 5B is based on modern measured Taiwan soils from varied elevations (this study) using a simple linear isotope-elevation lapse for illustration purposes. At sea level, we assume a local soil δ18O-C29 of ∼150‰ (equal to our most isotopically enriched, low elevation soil value), and a decrease of ∼20‰ per kilometer of elevation, which lies between the measured lapse rate for river waters (18‰) and soils (∼21‰).

As plants shed leaves and surface molecules are ablated throughout the catchment, molecular biomarkers can be integrated into soils and bound to clay minerals. Erosion of soils and downslope movement of biomass can then produce a mixed organic molecular isotopic signature in river sediments that reflects the degree of integration of biomolecules sourced throughout the catchment (Figure 5A). Indeed, work in the Himalaya (e.g., Galy et al., 2011) and recent work in the Gaoping River system of Southeast Taiwan (Chang et al., 2021) shows evidence for downslope transport of organics and indicate that proximity to high relief, steep topography exerts considerable control over the degree of sediment and organic molecular integration in fluvial sediments. One of the great challenges of interpreting fluvial biomarker records is how sediments and organics integrate as they move from source to sink.

Taiwan catchments are generally steep and high relief, often spanning more than 3 km of elevation. Water samples collected at any point in a river reflect all the processes that occur upstream of the sample point. The high topography and steep Taiwan orogen means that the mean elevations of large Taiwan catchments are generally significantly higher (>1 km) than the elevation of the river mouth. Modern Taiwan river water data (this study) shows a significant offset between the isotopic composition of water sampled at a point in a river and the expected composition of precipitation isotopes that might fall at the elevation of the river water sample site (Figure 3). The offset between the expected δ2H composition of precipitation for a given elevation and measured river water δ2H at that elevation can be up to 30‰. This difference is greatest at low elevations, where the offset between the site elevation and the hypsometric mean elevation of the upstream area is largest.

Modern water δ2H and soil-derived n-alkane δ2H data can be used to predict the magnitude of isotopic offset that would result from catchment integration of sediments and molecular biomarkers. Data show that in a Taiwan catchment with
3.5 km of relief such as the Mugu basin (Figure 5), soil n-alkane δ2H should vary from ~150‰ at low elevation to as negative as ~225‰ at elevations in excess of 3 km (Figures 4, 5). Erosion and basin integration of this material will bias the isotopic signature of sediments deposited in floodplains and low elevation sites. If the expected change in n-alkane δ2H in plants and soils as a function of elevation is known (signal generation) and one can estimate the contribution of biomolecules from each point in the landscape (a molecular production and erosion function), it is possible to calculate the expected δ2Hn-alkane of an integrated sedimentary flux. For example, based on modern Taiwan soil n-alkane δ2H data from varied elevations, the δ2H of n-alkanes deposited at the river mouth within a hypothetical catchment with relief of >3 km and a mean elevation of ~1.25 km, should be ~25‰ more negative than the ambient vegetation growing at that elevation (Figures 5A,B), if all areas of the catchment contribute equally to the biomarker flux and the catchment is characterized by a constant apparent fractionation between ambient water and biomarker δ2H and no loss (oxidation) of n-alkanes during transit. In practice, the question is whether or not the organic molecular signal preserved in fluvial sediments is biased to specific elevations or portions of a catchment, much as lithology, relief and landslide frequency might bias cosmogenic isotope signatures of catchment average erosion rates in non-equilibrium landscapes (e.g., Willenbring et al., 2013).

To test this conceptual model of catchment integration of biomarkers, we measured the offset between modern soil-derived n-alkane δ2Hn-C29 and those preserved in fluvial sediments at similar elevations along the river profile. The expectation is that for a given point along a river profile, local soils should show δ2Hn-C29 values consistent with local elevation whereas samples collected from within the river system should reflect integration of materials sourced from both local and upstream areas. Our data show that the hydrogen isotope signature of n-alkanes preserved in modern river sediments are strongly controlled by the hypsometry of the source catchment (Figure 6). Specifically, we plot the δ2Hn-C29 in soils adjacent to river systems as a function of their sample elevation. This is compared to the δ2Hn-C29 in sediments within the river channel, which should reflect some degree of sediment/organic contributions from upstream contributing areas (Figure 6A). The hydrogen isotope signature of fluvially-transported n-alkanes sampled at low elevation deposition sites (i.e., floodplains) are commonly depleted by tens of per mil relative to low elevation soils (Figure 6A). At higher elevations within the catchment (areas of sediment generation rather than sediment sink), there is no observable offset between soil δ2Hn-C29 (local signal) and sediment δ2Hn-C29. What this means is that not surprisingly, low elevation fluvial sediments preserve a geochemical signature of upstream contributions of organic matter and that this signature can be quite significant. The isotopic shift associated with this downslope transport of organic matter is shown by the grey arrow (Figure 6A) which indicates more negative fluvial sedimentary δ2Hn-C29 relative to local soils at the same sample elevation. For example, river sediments collected at a local elevation of ~500 m may yield a δ2Hn-C29 value of ~180‰, which is 20‰ more negative than one might expect for local soils at that elevation. We can examine what the magnitude of the observed offset between soil and fluvial sediment δ2Hn-C29 means by considering a scenario where all portions of the landscape contribute equally to the biomarker flux exported in river sediments. If the biomarker δ2H data from river sediments are plotted as a function of contributing upstream hypsometry (area-weighted elevation), soil and river alkane δ2Hn-C29 data reconcile and fall along the same profile. This qualitative agreement strongly suggests that exported sediments reflect the hypsometry of organic matter within the catchment and means that if all areas of the upstream catchment equally contribute to this river sediment, we might expect that the mean elevation the sedimentary organic matter is sourced from is actually 1–1.5 km higher than the elevation of the sample point along the river. Thus, the geochemical signal of river sediments records information about catchment integration and source elevation. For Taiwan, the δ2Hn-C29 of fluvially-
transported organics is consistent with the integrated isotopic signature of organic matter produced throughout the catchment (i.e., δC29 of organics produced at the catchment mean elevation).

In general, there is a solid basis for the expectation that fluvially-transported biomarkers might represent a catchment mean isotopic signature in Taiwan. First, river water isotopes show a clear isotope-elevation relationship when considered in the context of catchment integrated signals (area-weighted contributions). To first order, catchment integration of water should behave similarly to integration of other components of the system (sediment, organic matter). Second, Taiwan’s subtropical/tropical climate results in a high degree of biomass production over nearly the entire elevation range of the orogen. All portions of Taiwan catchments contribute to biomarker production, though we recognize that climatic and biologic factors may impose variations in biomarker production rates with elevation. Third, the Taiwan landscape is characterized by extremely high rates of exhumation and erosion (associated with the frequent earthquakes, numerous annual typhoons, and high precipitation rates) and rapid turnover of the soil carbon pool. Hilton et al. (2008) suggests that up to 77% of non-fossil carbon may be exported via large events on the decadal timescale and 14C ages of fluvial biomarkers in Taiwan rivers yield ages on the order of hundreds of years old (Eglington et al., 2021). Rapid export of organics is readily replaced by new vegetation due to the high temperature and abundant precipitation over nearly all elevations within the tropical setting. Thus, there is relatively short carbon residence time in soils and sediments within the Taiwan orogen. Fourth, n-alkane δH are not significantly affected by degradation effects that may occur during transport or storage (Zech et al., 2011; Brittingham et al., 2017).

One consideration when measuring biomarker integration signatures is the potential contribution of legacy carbon that can bias the contributions of fluvially-exported leaf waxes. In Taiwan, much of the exposed and rapidly eroding sediments present in the orogen have undergone metamorphism at temperatures in excess of several hundred degrees. This heating results in a breakdown of long-carbon chain normal alkanes that tends to degrade many of the compounds analyzed for organic molecular reconstructions. As a result, legacy carbon is not a significant complication in a setting such as this. Indeed, modern bedrock samples from the slate belt of Taiwan show minimal to no long-carbon chain n-alkanes that would potentially bias the modern isotopic signature of organic molecules. This is not the case in all locations of the western foreland, where Plio-Pleistocene sediments are being uplifted and eroded and contain measurable long-chain normal alkanes. However, ancient sediments there are generally characterized by low abundances of target biomarkers, so while they are likely to be a potential contaminant of concern, legacy contributions are minor compared to active input from primary production in the warm and wet tropical climate.

**Applying Organic Molecular Paleohypsometry**

In recent years, multiple studies have observed downstream transport of organic biomarkers sourced from higher elevations. This includes both plant-derived biomolecules such as n-alkanes and fatty acids, as well as soil-derived compounds commonly utilized to reconstruct past temperature. (e.g., Galy et al., 2011; Ponton et al., 2014; Feakins et al., 2016; Hoffmann et al., 2016; Feakins et al., 2018; Usman et al., 2018; Zhuang et al., 2016; Feakins et al., 2018; Usman et al., 2018; Zhuang et al., 2018).
Studies from a range of landscapes show downslope transport of biomarkers can bias geochemical signatures preserved in low elevation sites yet interpreting these data may be complicated. For example, storm and mass wasting events are shown to produce greater mobilization of materials from the steep proportions of a catchment (Wang et al., 2020). While organic molecular paleohypsometry has the potential to provide a means of quantifying changes in the elevation distribution of biomass within an orogen, reliable application of such an approach to ancient sediments requires constraints on several variables. In particular, how does catchment geometry and climate influence the degree of contribution of biomass from across a catchment? Is the contribution of biomolecules uniform or weighted to specific elevation ranges within a catchment? In the Taiwan example shown above, we used the assumption that all areas of the landscape contributed equally to the biomolecule flux. Is this a reasonable assumption? How do changes to climate that are associated with the evolution of an orogen influence the contribution of biomarkers from different portions of a catchment?

Application of an organic molecular paleohypsometry approach requires a number of assumptions to relate measured n-alkane δ²H to catchment/molecular hypsometry. To examine how sensitive resultant paleohypsometry interpretations are to assumptions for molecular production and integration, we modeled three scenarios of biomarker production, erosion and integration for a hypothetical catchment (Figure 7; Supplemental file). We use a synthetic catchment histogram (area-elevation distribution) and chose three elevation-dependent functions for production and sediment erosion, and display these in elevation frequency plots (Figure 7), where the bar length is proportional to the area-elevation contribution within the hypothetical catchment. The goal of this sensitivity test is to ask the question, how do elevation-dependent differences in the production or erosion of molecular biomarkers affect the integrated signature of materials mobilized through a catchment and deposited in the river mouth. These tests include an assumption of 1) constant biomarker production and sediment erosion at all elevations within a catchment; 2) A decrease in biomarker production by 50% from sea level to 3,000 m and constant sediment erosion for all elevations in the catchment; and 3) constant biomarker production at all elevations in the tropical catchment but a doubling of erosion rates/contribution as a function of elevation from 0 to 3,000 m. These scenarios represent some of the endmember conditions that shape the isotopic signature of catchment integration but are based on observed patterns of organic biomass production or sediment erosion observed in the real world. We include two additional scenarios (shown in Supplementary Scenario) where 4) organic production decreases exponentially as a function of elevation by 75% from 0 to 2000 m and almost 90% by 3,000 m and 5) erosion increases exponentially as a function of elevation with more than 8 times the erosion rate at 3,000 m as at sea level, and biomass production decreases by 50% from 0 to 3,000 m.

Differences in production or erosion as a function of elevation will produce a difference in the area-weighted elevation of source materials (biomarkers). For example, if biomarkers are produced and eroded evenly throughout a catchment, mass balance dictates that the mean source elevation of biomarkers exported to the river mouth is equal to the catchment mean elevation. For a constant isotope-elevation lapse rate, the δ²H of exported biomarkers is therefore equal to the δ²H of biomarkers produced at the mean elevation. Factors that bias the production or erosion of biomarkers to higher or lower elevations in a catchment would then shift the mean biomarker source elevation higher or lower. To test how different assumptions for biomarker production and sediment erosion as a function of elevation might affect the δ²H of river sediments and biomarkers transported through the river system and deposited at a river mouth (reflecting the integrated signature of production and erosion throughout a catchment), we use modern Taiwan soil δ²H data and assume that soils formed at sea level are characterized by a δ²H of ~150‰, and those formed at elevation are modified by a biomarker δ²H lapse of 20‰ per km elevation in the catchment, similar to the pattern observed in surface waters.

For the different endmember conditions of production/erosion we modeled, there is a distinct pattern of biomarker contribution from different elevations to the overall riverine flux. These produce distinct histograms (Supplementary Scenarios S1–3 shown in Figure 7) with the bar length representing the overall biomarker contribution to the fluvial load from each elevation bin. Each of these scenarios uses the same elevation histogram (the same catchment) but produces distinct mean-
biomass contribution elevations (the abundance-weighted elevation of all organic matter contributing to the fluvial signal at the river mouth) and biomarker $\delta^{2}H_{nC29}$ associated with that mean-biomass value. The calculated $\delta^{2}H_{nC29}$ of each scenario can be thought of as the isotopic composition that one would expect to measure in sediments collected at the river mouth for the hypothetical catchment with the associated production/erosion functions. What this shows is that differences in production/erosion of biomarkers over the range of elevations in a catchment can bias the exported geochemical signal to higher or lower portions of a catchment. Yet, for each of the three different production/erosion functions, the calculated $\delta^{2}H_{nC29}$ values for the sediments deposited at the river mouth are relatively consistent, ranging from $-173$ to $-179$ (Figure 7). In the context of isotope-elevation lapse rates, this translates to $\sim 300$ m elevation difference. What this sensitivity test means is that for these three scenarios of varied molecular production and erosion as a function of elevation, we might expect that fluvial sedimentary biomarkers deposited at the river mouth are $23-29\%$ more negative in $\delta^{2}H$ than soils formed in the ambient environment at the sediment deposition site, with mean organic matter contribution elevations of $1,257-1,548$ m for the three scenarios. These values closely align with the true area-weighted mean elevation of the catchment of $1,396$ m. Thus, regardless of our assumptions of the production/erosion function, the measured $\delta^{2}H_{nC29}$ value of organics sampled at the river mouth closely approximate the $\delta^{2}H_{nC29}$ value of organics one would predict to form at and represent the catchment mean elevation. This quantitative examination is generally consistent with the qualitative agreement shown in Figure 6B.

Sensitivity test results suggest that in the context of evolving topography through time, a range of changes to primary production or erosion over time could occur without dramatically influencing the overall relationship between catchment hypsometry and exported isotope signature. If true, then sedimentary records of biomarker $\delta^{2}H_{nC29}$ could reliably record changes in catchment hypsometry through time, even though there remain considerable uncertainties in molecular production and erosion. We caution however, that other changes such as factors that could produce a bimodal distribution of biomarker export as a function of elevation, or climatic effects that result in significant decrease in organic production with elevation, could in fact exert significant changes to the magnitude of offset between the elevation of sediment deposition site, and the elevation predicted based on fluvial biomarker $\delta^{2}H_{nC29}$. For example, if organic biomarker production decreased by $50\%$ from sea level to $1$ km and by $75\%$ at $2$ km elevation (Supplementary Scenarios S4), the mean source elevation of fluvial sediments sampled at sea level would be $1,004$ m, $\sim 400$ m below the true catchment mean elevation. Sediments sampled here would be expected to have a $\delta^{2}H_{nC29}$ of $\sim 168\%$. Such a scenario is not realistic for a setting such as Taiwan as data from tropical settings indicates a decrease in primary productivity on the order of $50\%$ between $0$ and $3,000$ m elevation (e.g., Malhi et al., 2017). Likewise, if erosion increased exponentially with elevation and organic production decreased by $50\%$ from $0$ to $3,000$ m (Supplementary Scenarios S5), the mean source elevation of organics would be $1,720$ m and sediments sampled at the river mouth would be expected to have a $\delta^{2}H_{nC29}$ of $\sim 182\%$. This scenario produces a source elevation $\sim 300$ m higher than the catchment mean. These examples illustrate how differences in production or erosion could bias to the elevation distribution and isotopic composition of contributing organics. Importantly however, all scenarios produce values within several hundred meters of the catchment mean elevation.

New data from Taiwan demonstrates the potential utility of fluvially-exported molecular biomarker isotopes to quantify the hypsometry of a catchment and we provide qualitative and quantitative arguments to suggest these data are consistent with a catchment mean elevation signature in a rapidly eroding tropical landscape. However, as a tool for long-term topographic reconstruction, organic molecular paleohypsometry faces similar constraints to the application of cosmogenic isotopes to quantify catchment average erosion rates (after Dosseto and Schaller, 2016). Specifically, what is the molecular production function? Is there temporal variability in the storage in the weathering profile? How does hillslope transport change over time? What are the timescales of river transport and temporary storage in river alluvium? Further refinement of this approach requires greater examination of the above and other factors. Here we provide a summary of several key steps in utilizing a molecular paleohypsometry approach to constrain changes to topography through time or the development of catchment relief.

(1) Molecular production function: The first consideration for application of a molecular paleohypsometry approach is the determination of a molecular production function. For each pixel of a catchment, how many molecules of the biomarker of interest are produced? Is this function uniform, is it biased as a function of elevation? How does climate influence this function? We show one potential example of a molecular production function in Figures 5A,B that is based on the modern soil $\delta^{2}H_{nC29}$ and assumes even production throughout the catchment. In reality, primary productivity of terrestrial biomass is generally a function of temperature and water availability (Amthor and Baldocchi, 2001). Studies from tropical forests of Peru show a nearly halving of gross and net primary productivity from sea level to $3,000$ m elevation (Malhi et al., 2017). The decrease in primary productivity with elevation could lead to a biomarker production function that is nonlinear with elevation. Strong primary productivity differences could result in substantially greater molecular inputs at lower elevations relative to higher elevation sites. This scenario is obvious for locations with a treeline–above this elevation, molecular inputs would effectively be zero. Likewise, because primary productivity is known to scale with temperature and precipitation, the production function for specific biomolecules may vary as a function of current or paleo climatic conditions.

(2) Decay function: What is the rate of molecular degradation and is there a relationship to transit time? Malhi et al. (2017) show a halving of primary production over a $3$ km gradient but also a general increase in carbon residence time with elevation, with longer residence time in higher elevation,
TABLE 1 | River water samples and basin parameters.

| Name     | Sample Date | δ²H(water) | Longitude (dec. deg.) | Latitude (dec. deg.) | DEM Elevation | Drainage Area (km²) | Basin Elevation |
|----------|-------------|------------|-----------------------|----------------------|---------------|---------------------|-----------------|
|          |             |            |                       |                      |               |                     |                 |
| OT13-01  | 2013        | –65        | 120.951               | 23.789               | 376           | 16.7               | 1622            |
| OT13-02  | 2013        | –57        | 120.987               | 23.801               | 595           | 2.2                | 1238            |
| OT13-03  | 2013        | –77        | 121.014               | 23.785               | 474           | 689.7              | 2152            |
| OT13-04  | 2013        | –69        | 121.012               | 23.787               | 449           | 794.3              | 1873            |
| OT13-05  | 2013        | –78        | 120.925               | 23.549               | 1015          | 50.3               | 2250            |
| OT13-06  | 2013        | –82        | 120.926               | 23.551               | 1002          | 33.3               | 2284            |
| OT13-07  | 2013        | –72        | 120.891               | 23.567               | 770           | 91.0               | 1740            |
| OT13-08  | 2013        | –73        | 120.850               | 23.697               | 479           | 366.2              | 1713            |
| OT13-09  | 2013        | –63        | 121.041               | 23.782               | 909           | 0.4                | 1247            |
| OT13-10  | 2013        | –82        | 121.073               | 23.761               | 1374          | 0.9                | 1848            |
| OT13-11  | 2013        | –87        | 121.174               | 23.764               | 2165          | 0.9                | 2462            |
| OT13-12  | 2013        | –76        | 121.179               | 23.785               | 2236          | 3.3                | 2633            |
| OT13-13  | 2013        | –86        | 121.185               | 23.796               | 2208          | 5.3                | 2633            |
| OT13-14  | 2013        | –87        | 121.177               | 23.807               | 1939          | 38.2               | 2563            |
| OT13-15  | 2013        | –85        | 121.182               | 23.790               | 2210          | 0.5                | 2546            |
| OT13-19  | 2013        | –84        | 121.204               | 23.765               | 2687          | 0.1                | 2712            |
| OT14-02  | 2014        | –82        | 120.806               | 22.753               | 579           | 115.7              | 1590            |
| OT14-03  | 2014        | –78        | 120.817               | 22.759               | 629           | 39.5               | 1594            |
| OT14-04  | 2014        | –80        | 120.836               | 22.747               | 972           | 20.4               | 1670            |
| OT14-05  | 2014        | –70        | 120.837               | 22.746               | 982           | 2.3                | 1398            |
| OT14-06  | 2014        | –80        | 120.883               | 22.731               | 1966          | 0.7                | 2092            |
| OT14-07a | 2014        | –75        | 120.886               | 22.737               | 2013          | 1.7                | 2092            |
| OT14-08  | 2014        | –77        | 120.900               | 22.714               | 1759          | 2.1                | 1966            |
| OT14-09  | 2014        | –77        | 120.815               | 22.756               | 616           | 1.3                | 1211            |
| OT14-19  | 2014        | –74        | 120.789               | 22.737               | 491           | 8.7                | 1453            |
| OT-15-1  | 2015        | –41        | 120.727               | 24.016               | 132           | 3.0                | 326             |
| OT-15-2  | 2015        | –50        | 120.874               | 23.984               | 329           | 3.2                | 548             |
| OT-15-3  | 2015        | –65        | 121.111               | 24.006               | 827           | 3.4                | 1224            |
| OT-15-7  | 2015        | –86        | 121.326               | 24.186               | 2429          | 0.3                | 2672            |
| OT-15-9  | 2015        | –94        | 121.353               | 24.184               | 2332          | 0.4                | 2732            |

(Continued on following page)
cooler conditions. If changes in primary production as a function of elevation are offset by changes in degradation, it could yield a uniform effective production function across elevation ranges in an orogen.

(3) Erosion function: Organic biomarkers make their way into river sediments through a combination of ablation from leaves, transport in surface or groundwater and soil erosion. Soil erosion rates commonly scale with slope

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**TABLE 1** | (Continued) River water samples and basin parameters.

| Name         | Sample Date | δH(water) | Longitude (dec. deg.) | Latitude (dec. deg.) | DEM Elevation | Drainage Area (km²) | Elevation Mean (m) | Elevation Maximum (m) | Elevation Minimum (m) | Basin Relief (m) |
|--------------|-------------|-----------|-----------------------|----------------------|---------------|---------------------|---------------------|----------------------|---------------------|-----------------|
| OT-15-10A    | 2015        | −86       | 121.385               | 24.193               | 2028          | 1.5                 | 2575                | 2016                 | 3052                | 1036            |
| OT-15-10B    | 2015        | −92       | 121.385               | 24.193               | 2028          | 5.3                 | 2714                | 2025                 | 3336                | 1311            |
| OT-15-11     | 2015        | −55       | 121.571               | 24.169               | 342           | 0.4                 | 839                 | 359                  | 1315                | 956             |
| OT-15-12     | 2015        | −34       | 121.594               | 23.853               | 7             | 6.9                 | 296                 | 19                   | 585                 | 566             |

**TABLE 2** | Modern soil samples and n-alkane hydrogen isotopes.

| Sample        | Latitude | Longitude | Sample Elevation | n | δ²H(C27) | δ²H(C29) | δ²H(C31) | δ²H(C27-31) | ACL |
|---------------|----------|-----------|------------------|---|----------|----------|----------|-------------|-----|
| OT-15-1       | 24.016   | 120.727   | 132              | 2 | −145     | −157     | −167     | −157        | 28.5|
| 19TW-LW19 A   | 24.171   | 121.590   | 144              | 2 | −158     | −162     | −176     | −176        | 30.0|
| OT-15-13      | 22.913   | 121.119   | 217              | 2 | −167     | −162     | −165     | −165        | 1035|
| MT-TW-07b     | 120.781  | 24.069    | 224              | 1 | −145     | −150     | −154     | −151        | 9.0 |
| OT-15-2       | 23.984   | 120.874   | 329              | 2 | −167     | −169     | −162     | −164        | 29.4|
| OT-15-11      | 24.169   | 121.571   | 342              | 4 | −169     | −164     | −161     | −162        | 30.5|
| OT-15-3       | 24.006   | 121.111   | 827              | 2 | −171     | −168     | −157     | −159        | 30.4|
| OT-15-4       | 24.096   | 121.178   | 2095             | 4 | −187     | −193     | −186     | −189        | 30.0|
| OT-15-7       | 24.186   | 121.326   | 2429             | 4 | −186     | −191     | −184     | −187        | 28.8|
| OT-15-8       | 24.181   | 121.308   | 2660             | 3 | −206     | −204     | −196     | −200        | 29.9|
| OT-15-6       | 24.164   | 121.288   | 2976             | 5 | −249     | −230     | −223     | −231        | 29.8|
| OT-15-5       | 24.135   | 121.281   | 3415             | 4 | −242     | −229     | −226     | −231        | 29.2|

**TABLE 3** | Modern Taiwan river sediment n-alkane δ²H, sample elevation, and basin mean elevation.

| Sample        | Latitude | Longitude | Sample Elevation | Catchment Mean Elevation | δ²H(C27) | δ²H(C29) | δ²H(C31) | δ²H(C27-31) |
|---------------|----------|-----------|------------------|--------------------------|----------|----------|----------|-------------|
| OT-15-3       | 23.785   | 121.014   | 474              | 2151                     | −181     | −175     | −178     | −178        |
| WT-11-12      | 121.049  | 23.158    | 778              | 1397                     | −167     | −184     | −174     | −179        |
| WT-11-10      | 121.018  | 23.185    | 782              | 2107                     | −168     | −177     | −175     | −175        |
| WH02          | 120.928  | 22.729    | 788              | 1516                     | −182     | −170     | −174     | −174        |
| OT-14-09      | 120.9    | 22.714    | 1759             | 1956                     | −183     | −183     | −183     | −183        |
| WT-14-07A     | 120.883  | 22.731    | 1966             | 2029                     | −193     | −185     | −187     | −187        |
| OT-14-08      | 120.886  | 22.737    | 2013             | 2091                     | −166     | −184     | −176     | −178        |
| WT-11-4       | 121.024  | 23.327    | 2681             | 3005                     | −228     | −220     | −217     | −220        |
| WT-11-02      | 121.026  | 23.328    | 2693             | 2998                     | −217     | −211     | −207     | −210        |
| WT-11-03      | 121.025  | 23.327    | 2709             | 3039                     | −210     | −216     | −205     | −207        |
| WT-11-01      | 121.025  | 23.328    | 2709             | 3007                     | −210     | −209     | −207     | −209        |
| WT-11-07      | 121.03   | 23.286    | 3091             | 3228                     | −218     | −214     | −209     | −213        |
| WT-11-6       | 121.042  | 23.293    | 3136             | 3332                     | −217     | −210     | −209     | −211        |
| WT-11-05      | 121.054  | 23.293    | 3031             | 3201                     | −215     | −207     | −213     | −214        |
| 19TW-LW16-Sed | 121.495  | 24.182    | 443              | 1600                     | −198     | −174     | −165     | −179        |

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Detrital Contribution: Ancient sediments, and in particular, clay-bearing sediments, can contain a significant reservoir of molecular compounds identical to modern plant or microbially-produced biomarkers. Detrital inputs of molecular components are generally of minimal significance in igneous terrain, however of greater concern during stages of orogenesis where there may be significant thin skin deformation and erosion of foreland sediments.

Local and integrated sampling sites: For quantification of paleorelief, reconstructions must incorporate records of low elevation local (in situ) water isotopes as well as catchment-integrated signals or models that can approximate both. An example may be a system that is dominated by local inputs for the bulk of time, punctuated by sporadic mass wasting or erosive events. A second example could be a scenario characterized by beds of paleobotanical remains in low elevation floodplain sites (intact fossil leaf materials) in combination with sediment-bound leaf waxes. This is due to the fact that leaf transport studies show that intact leaves preserved in sedimentary sequences generally indicate short transport distances on the order of 100s of meters or less prior to deposition. Longer transport distances are commonly associated with greater degradation and breakage of intact leaves. In contrast, fine-grained sediments that contain leaf waxes bound to mineral (clay) surfaces, may be readily transported long distances. Thus comparison of waxes from intact leaf mats relative to fine grained sediments, may provide one measure of catchment relief.

Elevation-dependent isotope and/or temperature relationships and constant or known fractionations between ambient water and molecular biomarkers. In order to reliably apply an organic molecular paleohypsometry approach, there must be a consistent elevation-dependent geochemical signature and a means of quantifying or constraining the relationship between that signature and organic biomarkers (for plant wax δ2H,n-C29 this is the apparent fractionation). This relates to the factors that control signal generation.

In total, determination of catchment paleohypsometry requires attention to the key factors identified above. In addition, in order to determine a catchment-wide organic molecular hypsometry, one must assume that: 1) The production of molecular biomarkers is at steady-state at the catchment scale; and 2) Each eroding area of the catchment contributes plant- or microbial-derived biomarkers to the river sediment in proportion to the above defined production, erosion and degradation functions. In practice, it is likely that different climatic/tectonic/erosive regimes will be characterized by distinct relationships between the geochemical signature of organic matter integration and catchment hypsometry. Thus, the relationships observed in Taiwan may not readily translate to every global orogen. In addition, we note that there is a distinct difference between hypsometry and topography and comment that organic molecular hypsometry provides insight into the elevation distribution of source organics in a catchment—it does not specifically record the maximum elevation of an orogen. However, the approach presented above provides a framework for interrogation of fluvially-exported sediments as a record of the topographic evolution of an orogen and the catchments that drain a landscape.

CONCLUSION

We discuss a new approach to investigating the topographic evolution of an orogen using the isotopic signature of plant waxes preserved in fluvial deposits. Modern plant biomarker and water isotope data from Taiwan show that the δ2H,n-C18 value of fluvially-transported leaf waxes reflects the hypsometry of organic matter produced throughout a catchment. The isotopic composition of exported waxes is generally consistent with the δ2H,n-C18 value observed at the catchment mean elevation. As a result, the δ2H,n-C18 of detrital organics in fluvially-transported sediments can theoretically provide a record of catchment hypsometry through time. Models for different catchment molecular production and erosion functions show that differences in these factors can shape the relationship between the isotopic signature of fluvially-exported leaf waxes and catchment morphology, yet in our test case the effect of these varied functions is on the order of only several per mil and several hundred meters for highly distinct boundary conditions. Application of this methodology in other orogens will require further investigation of the controls on biomarker integration. Despite this, data presented here demonstrates the potential utility of organic molecular paleohypsometry as a new tool for interrogating the evolution of global orogens.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

MH conceived the idea, collected and analyzed samples, and wrote the article. WO contributed to field sampling, data analysis and writing the article.

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SUPPLEMENTARY MATERIAL

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