Earth and Planetary Science Letters 452 (2016) 238–246

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Biospheric and petrogenic organic carbon flux along southeast Alaska

Xingqian Cui [a,*], Thomas S. Bianchi [a], John M. Jaeger [a], Richard W. Smith [b]

[a] Department of Geological Sciences, University of Florida, Gainesville, FL, USA
[b] Global Aquatic Research LLC, 6276 Ridge Rd., Sodus, NY 14551, USA

ARTICLE INFO

Article history:
Received 4 March 2016
Received in revised form 27 July 2016
Accepted 1 August 2016
Available online 20 August 2016
Editor: D. Vance

Keywords:
carbon cycle
fjords
southeast Alaska
petrogenic OC
glaciers

ABSTRACT

Holocene fjords store ca. 11–12% of the total organic carbon (OC) buried in marine sediments with fjords along southeast (SE) Alaska possibly storing half of this OC (Smith et al., 2015). However, the respective burial of biospheric (OC_{bio}) and petrogenic OC (OC_{petro}) remains poorly constrained, particularly across glaciated versus non-glaciated systems. Here, we use surface sediment samples to quantify the sources and burial of sedimentary OC along SE Alaska fjord-coastal systems, and conduct a latitudinal comparison across a suite of fjords and river-coastal systems with distinctive OC sources. Our results for SE Alaska show that surface sediments in northern fjords (north of Icy Strait) with headwater glaciers are dominated by OC_{petro}, in contrast to marine and terrestrially-derived fresh OC in non-glaciated southern fjords. Along the continental shelf of the Gulf of Alaska, terrestrial OC is exported from rivers. Using end-member mixing models, we determine that glaciated fjords have significantly higher burial rates of OC_{petro} ($\sim 1.1 \times 10^3$ g OC m^{-2} yr^{-1}) than non-glaciated fjords and other coastal systems, making SE Alaska potentially the largest sink of OC_{petro} in North America. In contrast, non-glaciated fjords in SE Alaska are effective in burying marine OC ($OC_{bio\text{-}mari}$) (13–82 g OC m^{-2} yr^{-1}). Globally, OC in fjord sediments are comprised of a mixture of OC_{petro} and fresh OC_{bio}, in contrast to the pre-aged OC from floodplain river-coastal systems. We find that there may be a general latitudinal trend in the role of fjords in processing OC, where high-latitude temperate glacial fjords (e.g., Yakutat Bay, SE Alaska) rebury OC_{petro} and non-glacial mid-latitude fjords (e.g., Doubtful Sound, Fiordland) sequester CO_2 from phytoplankton and/or temperate forests. Overall, we propose that fjords are effective in sequestering OC_{bio} and re-burying OC_{petro}. Based on our study, we hypothesize that climate change will have a semi-predictable impact on fjords' OC cycling in the near future.

1. Introduction

Over geological timescales, atmospheric CO_2 drawdown can be achieved in part through the net burial of biospheric OC (OC_{bio}) in sedimentary basins (e.g., Berner, 2004). OC_{bio} consists of carbon that is fixed via photosynthesis in terrestrial ($OC_{bio\text{-}terr}$) and marine environments ($OC_{bio\text{-}mari}$). Petrogenic OC, or OC stored in rocks (OC_{petro}), represents the largest global pool of OC and interacts with the modern active carbon cycle through rock uplift and weathering (Hedges, 1992). While some fraction of OC_{petro} can be degraded by microbes during transport and re-burial, allowing components of OC_{petro} to contribute to atmospheric CO_2 production (Berner, 2004; Galy et al., 2015; Petsch et al., 2001), much of it escapes oxidation and is re-buried in marine sediments, having relatively minimal effects on the modern C cycle (Berner, 2004; Galy et al., 2015). Overall, the burial of OC_{bio} and oxidation of OC_{petro} are important processes influencing atmospheric CO_2 over geological timescales (Mackenzie and Lerman, 2006).

Coastal sediments are major carbon depo-centers that account for as much as 90% of Holocene OC burial in the global ocean (Berner, 1982; Burdige, 2005; Hedges, 1992). In particular, fjords have been recognized as "hotspots" of carbon burial (Nuwer and Keil, 2005), with more recent estimates suggesting fjord surface area-normalized OC burial rates are at least five times greater than other marine systems and one hundred times greater than the entire ocean average (Smith et al., 2015). More specifically, fjords accumulate only ~5% of total sediment input from the continents and yet account for 11–12% ($\sim 17\text{–}20 \times 10^{12}$ g OC yr^{-1}) of the total OC buried in marine sediments. This implies that they represent a potentially important CO_2 sink over glacial/interglacial timescales.

Fjords occur over a wide range of latitudes (40°–80°) and are consequently subjected to a broad spectrum of climatic and land-ocean processes. For example, in high latitudes, glacial erosion contributes to significant input of OC_{petro} to fjords (Syvitski et al., 1987; Walinsky et al., 2009). Moreover, glacial retreat and ex-

* Corresponding author. Fax: +1 352 392 9294.
E-mail address: cuixingqian@ufl.edu (X. Cui).

http://dx.doi.org/10.1016/j.epsl.2016.08.002
0012-821X/

pansion of vegetation at lower latitudes can result in a change from OC_{petro}-dominated export to one more comprised of OC_{bio}. Fjords from southeast (SE) Alaska, British Columbia and Fiordland, New Zealand reveal latitudinal gradients in concentrations and accumulation rates of sedimentary OC from glacier- to vegetation-dominated watersheds (e.g., Cui et al., 2016; Hinojosa et al., 2014; Hood et al., 2009; Smith et al., 2015; Smittenberg et al., 2004; Walinsky et al., 2009). We believe that Holocene fjords provide natural laboratories for the examination of global gradients in the fate of OC_{petro} vs. OC_{bio}.

While past work has explored the sedimentary dynamics between glaciers and fjords (e.g., Jaeger et al., 1998; Syvitski et al., 1987; Ullrich et al., 2009), linkages between biochemical processes and carbon storage in fjord sediments have received less attention (Hood and Scott, 2008; Hood et al., 2009; Walinsky et al., 2009). Specifically, SE Alaskan fjords are believed to have the highest OC accumulation rates (Hallet et al., 1996; Walinsky et al., 2009) among global fjords (12 to 265 $g\,OC\,m^{-2}\,yr^{-1}$), with this region possibly accounting for as much half of the total global OC burial in fjords (Smith et al., 2015). Yet, less is known about the potential burial and export of OC_{petro} and OC_{bio} from within SE Alaskan fjords to the open marine environment. While the relationship between glacial versus non-glacial watersheds and sedimentary OC properties in SE Alaskan fjords has been examined (Walinsky et al., 2009), details on the fate of changing OC_{petro} inputs are still lacking.

In this study, we posit that SE Alaska re-buries a significant amount of OC_{petro} through bedrock erosion but also represents a significant modern-day CO_2 sink by burying OC_{bio}. In addition, SE Alaska shows distinct sedimentary OC differences between vegetated and glaciated watersheds. Building on the previous work in fjords of SE Alaska (e.g., Hood et al., 2009; Walinsky et al., 2009), British Columbia (Smittenberg et al., 2004) and New Zealand (Cui et al., 2016; Hinojosa et al., 2014; Smith et al., 2015), we conduct a multi-tracer comparison of sedimentary OC composition in surface sediments from these regions (with the addition of radiocarbon measurements in SE Alaska) to obtain a more global perspective on 1) differences in how fjords bury carbon, 2) the potential effects of climate change on carbon cycling in fjords, and 3) the potential role of fjords in the global sequestration of CO_2.

2. Site description, sampling, and methods

2.1. Site description

SE Alaska covers the coastal region from Prince William Sound to the SE Panhandle, with latitudinal ranges between 61°N and 54°N. SE Alaskan fjords span a range in watershed characteristics from tidewater glacial in the northern Gulf of Alaska (GOA) to glacier-free and well-vegetated in the southern Panhandle. Relative to Icy Strait (58°N), northern areas are largely covered by glaciers, while the southern panhandle has a significant amount of bedrock exposure with variable vegetation cover following early Holocene glacial retreat. The bedrock geology of SE Alaska is dominated by accreted tectonic terranes. Coastal watersheds are composed of the Chugach, Yakutat, and Alexander terranes (Plafker et al., 1989). The watersheds in this study contain mostly marine and marginal marine sedimentary rock of the Chugach/Yakutat terranes, with some contribution of Alexander terrane (schist, marble, greenstone, graywacke, phyllite, and argillite; Winkler et al., 2000) from the Hubbard Glacier in Disenchantment Bay.

2.2. Sampling

Eight sampling locations cover a range from glaciated to vegetated watersheds (Fig. 1). More specifically, multi-core samples are from sites EW0408 76 (multi-core MC 2), 73 (MC 2), and 68 (MC 2) in/near Yakutat Bay (north), and sites 32 (MC 8), 36 (MC 3), and 39 (MC 4) in/near Sitka Sound (south). These two transects represent the inner-to-outer reaches of fjords within distinct watersheds that are currently glaciated in the north (Yakutat) or non-glaciated in the south, which is partially-covered by vegetation and exposed bedrock. In addition, southern sites 43 (MC 4) and 19 (MC 2) are within the relatively small Deep and Crawfish Inlets, respectively, which are both highly vegetated. We use previously published sediment accumulation rates at each site (Ullrich et al., 2009; Walinsky et al., 2009) except for station 73, where a revised ^{210}Pb geochronology is established (Table S5; Fig. S3).

2.3. Methods

Bulk sediment total organic carbon (%OC), total nitrogen (N), C/N ratios, stable carbon isotopes ($\delta^{13}C$) are measured after removal of inorganic carbon with acid fumigation, according to the method of Harris et al. (2001). Samples for OC radiocarbon analysis are combusted and converted into graphite using the zinc reduction method (Xu et al., 2007). Radiocarbon analyses are made using an Accelerated Mass Spectrometry (AMS) at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) laboratory, using the general radiocarbon methods described by McNichol et al. (1992). Radiocarbon results are reported as ages, $\Delta^{14}C$ values and fraction modern (F_{mod}) values. F_{mod} values are based on $\Delta^{14}C$ values using the equation $F_{mod} = (\Delta^{14}C/1000 + 1)/[e^{(-\lambda^*(\text{collection year}-1950))}]$ (see supplemental data). Biomarker analyses, which included lignin phenols, fatty acids, and glycerol dialkyl glycerol tetraethers (GDGTs), are measured according to the methods of Feng et al. (2013), Goñi and Hedges (1992), and Hopmans et al. (2004), with details provided in the supplemental data.

Eight lignin phenols, normalized to OC (Λ_8 in mg 100 mg OC^{-1}), are used to trace OC contributions from vascular plants (Goñi et al., 1998). The compound 3,5-dihydroxybenzoic acid (3,5-Bd), forms largely in soils by bacteria from the breakdown of plant-derived materials (Houel et al., 2006), is used as a soil tracer. The ratio of 3,5-Bd/vanillyl phenols (3,5-Bd/V) is used as a proxy of relative soil OC versus vascular plant contributions (Houel et al., 2006). The ratio of vanillic acid to vanillin ($(Ad/Al)_V$) is used as an index for lignin oxidative degradation. Branched/isoprenoid tetraether (BIT) is used to indicate soil OC inputs relative to marine primary production (Hopmans et al., 2004). Fatty acids are another group of biomarkers for tracing a diversity of OC sources (Bianchi and Canuel, 2011; Waterson and Canuel, 2008). For example, short-chain fatty acids (SCFAs; C_{12-18}) are considered to have a diversity of OC sources, including terrestrial plants, marine algae, and microbes. In contrast, the even-numbered long-chain fatty acids (LCFAs; C_{24-30}), a major component of leaf waxes, are produced exclusively by terrestrial sources (Feng et al., 2013). The ratios of terrestrial to aquatic fatty acids (TAR_{FA}; $C_{24+26+28}/C_{12+14+16}$) have been widely used to indicate relative terrestrial OC inputs (Waterson and Canuel, 2008).

A ternary mixing model is applied to determine the background OC_{petro} in sediments by assuming a constant OC_{petro} background level in fjord sediments (see supplemental data) (Galy et al., 2008; Leithold et al., 2006). The OC buried in these fjord sediments is comprised of a mixture of OC_{petro} and non-rock-derived OC_{bio}, which consists of $OC_{bio\text{-}mari}$ and $OC_{bio\text{-}terr}$. Then the radiocarbon composition of the bulk OC can be expressed as follows:

$$F_{mod} \times \%OC = F_{mod\text{-}bio} \times \%OC_{bio} + F_{mod\text{-}petro} \times \%OC_{petro} \quad (1)$$

where, F_{mod}, $F_{mod\text{-}bio}$ and $F_{mod\text{-}petro}$ are the radiocarbon compositions of the bulk OC, OC_{bio} and OC_{petro} in sediments. %OC, $\%OC_{bio}$,