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## $\delta^{44/40}$ Ca variability in shallow water carbonates and the impact of submarine groundwater discharge on Ca-cycling in marine environments

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## Abstract

Shallow water carbonates from Florida Bay, the Florida Reef Tract, and a Mexican Caribbean fringing reef at Punta Maroma were studied to determine the range of Ca-isotope variation among a cohort of modern carbonate producers and to look for local-scale Ca-cycling effects. The total range of Ca-isotope fractionation is 0.4% at Punta Maroma, yielding an allochem-weighted average  $\delta^{44/40}$ Ca value of -1.12% consistent with bulk sediment from the lagoon with a value of -1.09%. These values are virtually identical to bulk carbonate sediments from the Florida Reef Tract (-1.11%) and from one location in Florida Bay (-1.09%) near a tidal inlet in the Florida Keys. No evidence was found for the  $\sim 0.6\%$  fractionation between calcite and aragonite which has been observed in laboratory precipitation experiments. Combining these results with carbonate production modes and  $\delta^{44/40}$ Ca values for pelagic carbonates taken from the literature, we calculate a weighted average value of  $-1.12 \pm 0.11\%$  ( $2\sigma$ ) for the global-scale Ca-output flux into carbonate sediments. The  $\delta^{44/40}$ Ca value of the input Ca-flux from rivers and hydrothermal fluids is  $-1.01 \pm 0.04\%$  ( $2\sigma_{mean}$ ), calculated from literature data that have been corrected for inter-laboratory bias. Assuming that the ocean Ca cycle is in steady state, we calculate a  $\delta^{44/40}$ Ca value of  $-1.23 \pm 0.23\%$  ( $2\sigma$ ) for submarine groundwater discharge (SGD) on a global scale. The SGD Ca-flux rivals river flows and mid-ocean ridge hydrothermal vent inputs as a source of Ca to the oceans. It has the potential to differ significantly in its isotopic value from these traditional Ca-inputs in the geological past, and to cause small changes in the  $\delta^{44/40}$ Ca value of oceans through time.

In the innermost water circulation restricted region of northeastern Florida Bay, sediments and waters exhibit a  $0.7_{00}^{\circ}$  gradient in  $\delta^{44/40}$ Ca values decreasing towards the Florida Everglades. This lowering of  $\delta^{44/40}$ Ca is predominantly caused by local-scale Ca-inputs from SGD, which has a high Ca concentration (450 mg/L) and low  $\delta^{44/40}$ Ca value ( $-0.96_{00}^{\circ}$ ). Mixing calculations show that Ca inputs from SGD and surface water runoff from the Florida Everglades contribute between 8% and 60% of the dissolved Ca to the studied waters with salinities between 30 and 14, respectively. Similar degrees of circulation restriction between epeiric seas and oceans in the geological past may have also led to overprinting of sedimentary carbonate  $\delta^{44/40}$ Ca values in nearshore regions of epeiric seas due to local-scale cycling of seawater through coastal carbonate aquifers. Local Ca-cycling effects may explain some of the scatter in  $\delta^{44/40}$ Ca values present in the Ca-isotope evolution curve of Phanerozoic oceans.

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## **1. INTRODUCTION**

Calcium isotopes have the potential to track changes in the ocean Ca-cycle through time using  $\delta^{44/40}$ Ca values recorded in sedimentary carbonate successions. A portion of the work performed, thus far, has focused on reconstructions of ocean Ca-cycling over the past 30 million years using downcore records of  $\delta^{44/40}$ Ca variations in foraminifera (Heuser et al., 2005; Sime et al., 2007), sedimentary barite (Griffith et al., 2008) and bulk nannofossil ooze (De La Rocha and DePaolo, 2000: Fantle and DePaolo, 2005: Fantle, 2010). The reconstructed trends were evaluated using inverse modeling techniques with the aim of deducing changes in ocean Ca concentrations through time. The modeling highlights the sensitivity of the calculated Ca concentrations to the values of certain input variables that also might have changed through time (Sime et al., 2007; Fantle, 2010). Chief among them are the  $\delta^{44/40}$ Ca value of the global-scale input Ca-flux to the oceans and the fractionation factor associated with the global-scale output Ca-flux into carbonate sediments. Shallow water settings, which contribute 47% of net carbonate production today (Milliman, 1993; Milliman and Droxler, 1996), represent a significant gap in our knowledge of the workings of the ocean Ca-cycle. Filling this gap could lead to improved estimates of the  $\delta^{44/40}$ Ca values of the input and output Ca-fluxes mentioned above, as well as more informed evaluation of the tectonic, biotic and climatic changes that might have been required to alter the isotopic signatures of these fluxes in the past.

Shallow-water settings also serve as modern analogs for carbonate production in ancient epeiric seas. Another reason to study them is to look for local Ca-cycling effects that may have operated in their much larger geological counterparts. At the present day, marginal marine environments are the most likely places to find local Ca-cycling effects due to the restricted degree of water circulation with the open ocean. But in the geological past, continental submergence was more widespread than it is today, and vast distances separated the oceans from the interior regions of the epeiric seas. Consequently, water circulation restriction may have affected larger areas, and, because carbonate sediment production was largely confined to these seas prior to the evolution of pelagic calcifying organisms in the Mesozoic (Berger and Winterer, 1974; Riding, 1993), local Ca-cycling phenomena may be widespread in the shallow water carbonate record (Holmden, 2009). For example, some of the scatter observed in the putative record of calcium isotope variation in Phanerozoic oceans (Farkas et al., 2007), much of which is reconstructed from analyses of brachiopod shells collected from the deposits of epeiric seas, may be due to local Ca-cycling effects. A similar claim has been made for carbon isotope records reconstructed from epeiric sea carbonate successions (Patterson and Walter, 1994; Holmden et al., 1998; Immenhauser et al., 2003; Panchuk et al., 2005, 2006; Melchin and Holmden, 2006; Fanton and Holmden, 2007; Immenhauser et al., 2008; Swart, 2008; LaPorte et al., 2009).

In this paper we present  $\delta^{44/40}$ Ca values of carbonate sediments and waters representing two contrasting deposi-



Fig. 1. Regional-scale map of the Gulf of Mexico showing the locations of the two study areas: Punta Maroma, Mexico, situated along the coast of the Yucatan Peninsula, and Florida Bay in southern Florida.

tional settings at the present day (Fig. 1). The first is a reef environment located off the northeast coast of the Yucatan Peninsula, Mexico, where the reef and lagoon are well mixed with open ocean waters of the Caribbean Sea. The second is Florida Bay, an estuarine lagoon located at the southern tip of the Florida shelf, where the shelf waters are restricted from mixing with waters of the Atlantic Ocean and Gulf of Mexico. We use these data, along with literature data on the riverine and hydrothermal Ca-fluxes to the oceans, to calculate the  $\delta^{44/40}$ Ca value of submarine groundwater discharge on a global scale, which has been identified in ocean Ca budgets as a large input Ca-flux to the oceans (Milliman, 1993). We also provide an updated budget for the ocean Ca-cycle that includes submarine groundwater discharge, and takes into account inter-laboratory biases in reported Ca-isotope analyses of the major Ca-fluxes to and from the oceans. And we comment on the disparity between secular reconstructions of seawater Ca-isotope changes over the past 30 million years based on analyses of sedimentary barite, bulk nannofossil ooze and foraminifera, in light of our analyses of shallow water carbonates and the role played by submarine groundwater discharge, a component of the continental weathering flux of Ca to the oceans and potential driver of ocean Ca-cycle secular changes.

### 2. DEPOSITIONAL SETTINGS

## 2.1. Punta Maroma reef

The reef at Punta Maroma is located less than 1 km from shore in the state of Quintana Roo, Mexico, about 16 km north of Playa del Carmen. The study reef (Fig. 2) is part of the larger fringing-reef system that spans much of the coastline of the Yucatan Peninsula. A shallow lagoon of  $\sim$ 4 m depth separates the reef from the beach. Behind the beach is a  $\sim$ 2 km patch of sand, shrub, and grass that abuts a shoreline-parallel ridge of Pleistocene limestone. Highway 307 runs along this ridge.



Fig. 2. Local-scale map of the study reef and lagoon at Punta Maroma, Mexico, showing the sample collection area.

Water in the lagoon is well mixed by over-the-reef currents resulting from wave set-up during periods of normal wave activity (average wave height =  $0.8 \pm 0.4$  m,  $1\sigma$ ). As a result, the turnover time of water in the lagoon is less than 3 h (cf. Coronado et al., 2007). The salinity and temperature of the lagoon, therefore, closely correspond to the sea surface of the open ocean.

#### 2.2. Florida Bay, Florida Reef Tract and Florida Everglades

Florida Bay (Fig. 3) is a seasonally hypersaline estuarine lagoon located at the southernmost tip of the submerged Florida shelf (Wanless and Tagett, 1989). It is roughly triangular in shape with barriers that limit circulation with open marine waters. To the east and south, the nearly continuous exposure of Pleistocene limestone composing the Florida Keys keeps surface Atlantic waters of the Florida Reef Tract out of Florida Bay, with the exception of a few tidal passes. To the west, a series of shallow mudbanks limits circulation with the Gulf of Mexico. To the north, Florida Bay is bounded by mangrove wetlands of the Florida Everglades. Florida Bay is partitioned into a series of shallow basins or 'lakes' delineated by mudbank deposits. Waters are typically <3 m deep, and it is common to find areas that have been scoured of sediment to reveal the underlying Pleistocene limestone bedrock. Outcrop exposures of limestone are common in the coastal region of northern Florida Bay, as well as in the wetlands of the Florida Everglades.

South Florida has a tropical monsoon-type climate (Trewartha, 1954; Price et al., 2008) that greatly affects spatial and temporal patterns of salinity in Florida Bay (Nuttle et al., 2000; Swart and Price, 2002; Kelble et al., 2007). In northeastern Florida Bay, the focus of this study, salinity gradients expand across the Bay during the wet season (May–October) and contract towards the Everglades during the dry season (November–April; Fig. 3). Fresh water enters the Bay through creeks that cut through the Buttonwood Embankment, such as Trout Creek (Hittle et al., 2001; Langevin et al., 2004). It is estimated that only ~10% of the freshwater input to Florida Bay is from Everglades runoff in the northeast region (Nuttle et al., 2000), with the remainder coming from precipitation, and a potentially large component of brackish groundwater that seeps into the Bay from the seabed (Corbett et al., 1999; Corbett et al., 2000; Langevin et al., 2004; Swain et al., 2004; Swarzenski et al., 2009).

#### 2.2.1. Hydrogeology of the Florida Everglades

The Surficial Aquifer System occupies the uppermost 50-82 m of Miocene to Holocene age sedimentary deposits beneath southern Florida, comprising highly permeable pelletoidal lime packstone, grainstone, and sandstone (Perkins, 1977; Fish and Stewart, 1991). It is unconfined at the top and hydraulically continuous between the Everglades and Florida Bay. In the upper part of the aquifer, fresh and brackish waters flow north to south across the Everglades, driven by a gently sloping topographical gradient of ~9 m relief over a distance of 65 km, measured from the northern boundary of Everglades National Park to the Florida Bay coastline. The elevation change of the water table over the same distance is  $\sim 2.5$  m (Fig. 2, in Price and Swart, 2006). Seawater seeps into the lower part of the Surficial Aquifer System due to buoyancy and tidal forces (Langevin et al., 2004). The area affected has been mapped by an airborne geophysical surveying technique (Fig. 3), which revealed brackish groundwater extending 8-30 km inland from the Florida Bay coastline (Fitterman and Deszcz-Pan, 1998). These brackish waters are circulated back to the sea along with the topographically driven flow of fresh water (Fig. 4). Using a 2-D model simulating surface and groundwater flow in the Everglades, Langevin et al. (2004) predicted a large zone of groundwater discharge in the coastal region of northeastern Florida Bay (Fig. 3).

Groundwater seepage from the seabed is referred to as submarine groundwater discharge (SGD) (Burnett et al., 2006) (Fig. 4). The definition does not distinguish between seepages of dilute groundwater, brackish water or seawater. The reason is due to the emphasis that is placed on SGD as a source for dissolved metals and nutrients to coastal seas distinct from surface runoff (Moore, 1999, 2010). Brackish



Fig. 3. Local-scale map of Florida Bay and the Florida Reef Tract showing the locations of sampling Stations 1–6. Salinity contours are reproduced from a salinity map published by the Southeast Environmental Research Center, Water Quality Monitoring Network in Florida Bay (http://serc.fiu.edu/wqmnetwork/). The salinity distribution reflects conditions in January 2001. Sampling was performed in early March 2001. The salinities at the time of sampling are listed in Table 3 and are higher by about 5 parts per thousand in most locations compared to the salinities recorded in January. Surface water samples were collected for this study. A mass of saline groundwater extends 5–30 km northward of the Florida Bay shoreline beneath the Florida Everglades. The 30–20 ohm resistivity contour marks the northernmost extent of seawater penetration beneath the Florida Everglades (Fitterman and Deszcz-Pan, 1998). The area of northeastern Florida Bay affected by submarine groundwater discharge, predicted from the hydrogeological modeling study of Langevin et al. (2004), is also shown.

groundwater in the Everglades has lower pH ( $\sim 6.72 \pm 0.2$ , n = 14) than surface waters ( $\sim 7.3 \pm 0.2$ , n = 9), and 'excess Ca' over Na of about five times the amount predicted from seawater-freshwater mixing. Brackish Everglades groundwater is also lower in dissolved oxygen (odors of H<sub>2</sub>S were reported by Price et al., 2006), higher in alkalinity than surface ocean waters, and is generally higher in biological nutrients such as nitrate and phosphate (Corbett et al., 1999; Price et al., 2006). It was suggested by Price et al. (2006) that the 'excess Ca' effect, which originates from dissolution of carbonate aquifer materials, might serve as a tracer of SGD into Florida Bay. In this study we show that SGD may be traced using Ca isotopes, and that groundwater contributions to Florida Bay may be quantified using material balance equations.

## 3. SAMPLING AND ANALYTICAL METHODS

Carbonate-producing organisms were collected, *in situ*, from the reef at Punta Maroma, as well as a grab sample

of skeletal sand and gravel from the lagoon (Fig. 2). A water sample was also collected from the lagoon. The carbonate samples were rinsed of sea salts using deionized water, dried in an oven, and then powdered using an agate mortar and pestle.

Five samples of water, and five samples of underlying carbonate sediment were collected from Florida Bay during the dry season in early March 2001 (Fig. 3). The sampling transect started in the south at an ocean inlet near Tavernier in the Florida Keys (Station 2), traversing northwards to Trout Creek, Joe Bay, and the lower reaches of a creek draining the southern margin of the mangrove fringe (Station 6) of the Florida Everglades (Fig. 3). The sediment at Station 2 was skeletal sand. The sediments at Stations 3, 4 and 5 were predominantly carbonate mud. A carbonate sample was created from the peat sample at Station 6 by combining fragments of ten different mollusk shells collected from the peat. In addition to the Florida Bay samples, one sample of seawater and skeletal carbonate sand was collected on the Atlantic side of the Florida Reef Tract

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Fig. 4. Schematic diagram showing seawater penetration of coastal aquifers, a wedge of brackish waters formed by subsurface mixing with fresh groundwater, and the area of the seabed where brackish groundwater seeps into coastal waters, called submarine groundwater discharge (SGD). The slope of the water table beneath the Florida Everglades is much shallower than shown in the diagram, allowing seawater to penetrate up to 30 km inland (Fitterman and Deszcz-Pan, 1998). Figure modified after Price et al. (2006).

(Station 1). Water samples were filtered using 0.45  $\mu$ m acid cleaned FEP cup filters. The carbonate sediment samples were drained of seawater before drying and powdering.

The Ca-isotope analyses were performed in the Saskatchewan Isotope Laboratory with a <sup>43</sup>Ca<sup>-42</sup>Ca double spike using a thermal ionization mass spectrometer (Thermo Fisher Triton) following methods described in Holmden and Bélanger (2010). Aliquots of Ca were purified from matrix elements prior to mass spectrometry using MP50 cation exchange resin in gravity flow columns. Routine monitoring of the K beams demonstrated that no correction was needed for <sup>40</sup>K interference on <sup>40</sup>Ca. The <sup>44</sup>Ca/<sup>40</sup>Ca analyses are reported in the standard delta notation as  $\delta^{44/40}Ca$ (= <sup>44</sup>Ca/<sup>40</sup>Ca<sub>sample</sub>/<sup>44</sup>Ca/<sup>40</sup>Ca ratio relative to the stan-(%<sub>oo</sub>) deviations in the <sup>44</sup>Ca/<sup>40</sup>Ca ratio relative to the standard, which is natural seawater. We find no difference in  $\delta^{44/40}$ Ca values among the three aliquots of seawater (Caribbean, Atlantic and Pacific) measured in our laboratory at the  $\pm 0.07\%$  level of precision ( $2\sigma$ ).

Calcium isotope data reported in the literature as  $\delta^{44/40}$ Ca may be converted to  $\delta^{44/40}$ Ca using Eqs. (1) and (2):

$${}^{4}\text{Ca}/{}^{40}\text{Ca} = \frac{{}^{44}\text{Ca}/{}^{42}\text{Ca}}{\beta}$$
(1)

$$\beta = \frac{\ln\left(\frac{m_{44}}{m_{42}}\right)}{\ln\left(\frac{m_{44}}{m_{40}}\right)} = 0.488\tag{2}$$

Here  $m_{40}$ ,  $m_{42}$ , and  $m_{44}$  are the atomic masses of the Ca isotopes. A kinetic isotope mass fractionation law is used because Ca-isotope fractionation in the mass spectrometer, as well as in nature, is governed mostly by kinetic rather than equilibrium isotope fractionation (Russell and Papanastassiou, 1978; Lemarchand et al., 2004; Fantle and DePaolo, 2007; Jacobson and Holmden, 2008).

The precisions reported for Ca-isotope measurements have been improving in recent years to the point where inter-laboratory biases need to be considered. In Table 1 we list per mil differences between seawater and SRM 915a ( $\Delta_{915a-seawater}$ ) reported in the literature, finding a total range of ~0.2‰. Our value for  $\Delta_{915a-seawater}$  is –  $1.81 \pm 0.08\%$  ( $2\sigma$ ), which is at the low end of the range of reported values. It is lower than our previously reported value of -1.86% (Holmden and Bélanger, 2010).

Selected literature data presented and discussed in this paper are corrected for inter-laboratory bias using the appropriate value for  $\Delta_{915a-seawater}$  (Table 1). We only correct the data showing the largest offsets with data produced in the Saskatchewan Isotope Laboratory because the correction is another source of uncertainty. For example, one or more of the above reference materials may have been measured less often in some laboratories compared to

Table 1 Survey of  $\Delta_{915a-seawater}$  values reported in the literature.

References	$\delta^{44/42}$ Ca			δ <sup>44/40</sup> Ca		
	$\Delta_{915a-seawate}$	r		$\Delta_{915a-seawater}$		
		Uncertai	nty		Uncertain	nty
Wieser et al. (2004)	-0.88	0.11	$2\sigma$	-1.80		
Schmitt et al. (2009)	-0.88			-1.80	0.20	$2\sigma$
This paper	-0.88			-1.81	0.08	$2\sigma$
Amini et al. (2009)	-0.89			-1.82	0.20	$2\sigma$
Farkas et al. (2007)	-0.91			-1.86	0.20	$2\sigma$
Amini et al. (2007)	-0.91			-1.86	0.04	$2\sigma_{\rm mean}$
Holmden and Bélanger (2010)	-0.91			-1.86	0.07	$2\sigma$
Huang et al. (2010)	-0.91			-1.86	0.12	$2\sigma$
Huesuer et al. (2005)	- <u>0.92</u>			-1.88		
Gussone et al. (2007)	-0.92			-1.88	0.12	$2\sigma_{\text{mean}}$
Hippler et al. (2003)1	-0.94			-1.88	0.04	$2\sigma_{\rm mean}$
Schmitt and Stille (2003)	-0.92			-1.88	0.20	$2\sigma$
Tipper et al. (2010)	-0.93	0.06	$2\sigma_{\rm mean}$	- <u>1.91</u>		
Hindshaw et al. (2011)	-0.95	0.03	$2\sigma_{\rm mean}$	- <u>1.95</u>		
Sime et al. (2005)	-0.99	0.14	$2\sigma$	-2.03		
Fantle and DePaolo (2005) and Fantle (2010)	-1.00			-2.04	0.10	$2\sigma$

Note: underlined ratios were calculated using 0.488, the slope of the kinetic isotope fractionation relation (Eq. (1)).

others, leading to potentially inaccurate estimations of  $\Delta_{915a-seawater}$ . This was the case in the Saskatchewan Isotope Laboratory, where the 915a standard was measured less often than seawater and an internal CaF<sub>2</sub> standard. Typically, literature values reported as  $\delta^{44/40}$ Ca on the 915a scale are converted to the seawater scale by subtracting the value for  $\Delta_{915a-seawater}$  determined by the laboratory that produced the data. If a further correction is made for inter-laboratory bias, then it is indicated in the text.

Major element analyses were performed using an ICP-AES instrument at the Saskatchewan Research Council Analytical Laboratories in Saskatoon, with a reproducibility of  $\pm 5\%$  (2 $\sigma$ ). Salinity was measured in the laboratory with a refractometer calibrated using mixtures of deionized water and the IAPSO salinity standard between 0 and 35. Salinities higher than 35 were determined using the slope determined from the linear relationship.

### 4. RESULTS AND DISCUSSION

#### 4.1. Fractionation of Ca isotopes in shallow water carbonates

The  $\delta^{44/40}$ Ca value of seawater on the lagoon side of the Punta Maroma reef is 0‰. It is indistinguishable from Atlantic and Pacific seawater routinely measured in the Saskatchewan Isotope Laboratory with an external precision of  $\pm 0.07\%$  ( $2\sigma$ ).

The  $\delta^{44/40}$ Ca values of the *in situ*-collected, biologicallyproduced, carbonates are listed in Table 2, along with the mineralogy from Bathhurst (1975). The average value for two red algae is  $-0.86 \pm 0.07\%$  ( $2\sigma$ ), six corals yielded  $-1.07 \pm 0.07\%$  ( $2\sigma$ ), and five green algae yielded  $-1.20 \pm 0.10\%$  ( $2\sigma$ ). All Ca-isotope data are reported relative to seawater. The weighted grand mean is -1.12%based on mass fractions of allochems in Punta Maroma beach sand (Medina, 2008). This compares well with the  $\delta^{44/40}$ Ca value of a bulk sediment sample collected from the lagoon, yielding -1.09%. The temperature of seawater in the lagoon was not measured during sampling, but it is typically 24–25 °C in February (Merino and Otero, 1991), which is the month when the fieldwork was conducted.

 $δ^{44/40}$ Ca values for water and surface sediment grabsamples from Florida Bay and the Florida Keys are listed in Table 3. Station 1, located on the Atlantic side of the Florida Keys, yielded a  $δ^{44/40}$ Ca<sub>water</sub> value of 0.01‰ and a  $δ^{44/40}$ Ca<sub>carb</sub> value of -1.11‰. The salinity at the time of sampling was 40.1. Station 2, located near a tidal inlet on the Florida Bay side of the Florida Keys, yielded a  $δ^{44/40}$ Ca<sub>water</sub> value of 0.00‰ and  $δ^{44/40}$ Ca<sub>carb</sub> value of -1.09‰. The salinity at this station was 36.3. Combining these results yields an average  $δ^{44/40}$ Ca value of -1.10‰for bulk sediment production, which is virtually identical to the value determined at Punta Maroma, Mexico of -1.09‰. Archival sea–surface temperature data from nearby monitoring stations recorded 25 ± 2 °C for both localities at the time of sampling (http://serc.fiu.edu/wqm network/SFWMD-CD/Pages/FB.htm).

Combining  $\delta^{44/40}$ Ca measurements of bulk carbonate sediment from the Florida Keys (Stations 1 and 2) with

the  $\delta^{44/40}$ Ca value for bulk carbonate sediment from Punta Maroma lagoon yields  $-1.10 \pm 0.03\%$  (2 $\sigma$ ).

## 4.1.1. Global-scale Ca-isotope fractionation factor for ocean carbonate production

Pelagic carbonates are dominated by coccolithophorids and foraminifera, with each taxon contributing  $\sim 50\%$  of the production (Broecker and Clark, 2009). Recognizing that  $\delta^{44/40}$ Ca values of coccolithophorids are dependent on temperature, and that they have a wide latitudinal range in the Earth's oceans, we adopt 17 °C for the global average sea surface temperature, and calculate a global average  $\delta^{44/}$  $^{40}$ Ca value of  $-1.22 \pm 0.10\%$  (2 $\sigma$ ) for coccolith calcite using the paleotemperature equation for E. huxleyi (Gussone et al., 2006). Applying the same temperature to foraminiferal calcite using the paleotemperature equation for O. Universa (Gussone et al., 2005) yields a lower value of  $-1.07 \pm 0.05\%$  (2 $\sigma$ ). In another study, twelve species of foraminifera collected from Atlantic waters covering a wide range of latitudes and sea surface temperatures yielded  $-1.30 \pm 0.05\%$  ( $2\sigma_{\text{mean}}$ , n = 61) (Sime et al., 2005). Taken at face value, it is significantly lower than -1.07% – the value calculated using the paleotemperature equation. However, after correcting for inter-laboratory bias (Table 1), it is in better agreement, yielding -1.08%(=-1.30-0.22%). Assigning equal weight to the production flux of foraminifera and coccolithophorids (Broecker and Clark, 2009), a flux weighted average  $\delta^{44/40}$ Ca value of  $-1.15 \pm 0.11\%$  (2 $\sigma$ ) is calculated for the pelagic carbonate sink at the present day. This compares reasonably well to the average value of  $-1.06 \pm 0.05\%$  ( $2\sigma_{mean}$ ) for six deep-sea carbonate ooze samples (<0.5 million years of age) from two cores taken from Deep Sea Drilling Project holes 590B (Fantle and DePaolo, 2005) and 807A (Fantle and DePaolo, 2007), after correction for inter-laboratory bias (=-1.29 - 0.23%) (Table 1).

Using estimates in Milliman (1993) for carbonate-sediment mass accumulation fluxes between pelagic (53%) and shallow water settings (47%), we calculate a value of  $-1.12 \pm 0.11\%$  ( $2\sigma$ ) for the  $\delta^{44/40}$ Ca value of the CaCO<sub>3</sub> sink on a global scale, which is also the global-scale fractionation factor ( $\Delta_{sed}$ ). If the ocean Ca-cycle is assumed to be in steady state, then the benchmark value for the weathering flux input of Ca to the oceans is also -1.12%  $\pm 0.11\%$  ( $2\sigma$ ).

# 4.1.2. Global-scale $\delta^{44/40}$ Ca value for submarine groundwater discharge

Traditionally, rivers and mid-ocean ridge hydrothermal vents have been the most often considered input sources of Ca to the oceans. Tipper et al. (2010) reported new and expanded Ca-isotope data ( $\delta^{44/42}$ Ca) for dissolved Ca in rivers worldwide, yielding a discharge-weighted average  $\delta^{44/40}$ Ca value of  $-1.13 \pm 0.16\%$  ( $2\sigma$ ) (=0.38/0.488–1.91), which is close to the value of -1.07% measured by Schmitt and Stille (2003). Correcting for bias relative to the Saskatchewan Isotope Laboratory yields, respectively, -1.03% and -1.00%. Mid-ocean ridge hydrothermal vents deliver Ca to the oceans with an average  $\delta^{44/40}$ Ca value of  $-0.95 \pm 0.07\%$  ( $2\sigma$ ) (Amini et al., 2008). Assuming

Table 2 Carbonate  $\delta^{44/40}$ Ca values from the reef and lagoon at Punta Maroma, Mexico.

Samples	$\delta^{44/40}$ Ca (‰ sw)	$\delta^{44/40}$ Ca (‰ 915a)	Mineralogy <sup>a</sup>
Red algae			
Amphiroa tribulus	-0.81	1.00	HMC
Porolithon pachydermum	-0.91	0.90	HMC
$\Delta_{ m sed}$	-0.86	0.95	
$2\sigma$	0.07	0.07	
Green algae			
Halimeda opuntia	-1.22	0.59	Aragonite
Rhipocephalus phoenix	-1.24	0.57	Aragonite
Udotea flabellum	-1.20	0.61	Aragonite
Halimeda tuna	-1.22	0.59	Aragonite
Halimeda incrassata	-1.11	0.70	Aragonite
$\Delta_{ m sed}$	-1.20	0.61	
$2\sigma$	0.10	0.10	
Coral			
Dendrogyra cylindricus	-1.05	0.76	Aragonite
Monastrea annularis	-1.06	0.75	Aragonite
Colpophylia natans	-1.14	0.67	Aragonite
Porites furcata	-1.05	0.76	Aragonite
Porites astreoides	-1.08	0.73	Aragonite
Millepora complanata	-1.02	0.79	Aragonite
$\Delta_{ m sed}$	-1.07	0.74	
$2\sigma$	0.08	0.08	
Other			
Planktic foram	-1.09	0.72	Calcite
Echinoid spine	-1.12	0.69	HMC
Bulk sediment (lagoon)	-1.09	0.72	Mixed
Beach sediment fractions <sup>b</sup>			Weight fraction
Green algae	-1.20	0.61	0.4
Corals	-1.07	0.74	0.1
Foraminifera	-1.09	0.72	0.1
Red algae and echinoderms <sup>c</sup>	-0.99	0.82	0.1
Micritic and lithic bioclasts and molluscs	-1.09	0.72	0.3
Grand weighted average $\Delta_{sed}$	-1.12	0.69	

<sup>a</sup> Common mineralogy from the literature (HMC = High Mg calcite).

<sup>b</sup> Classification of allochems and fractions is based on a study of Punta Maroma beach sand (Medina, 2008).

 $^{\rm c}~\delta^{44/40} Ca$  is the average value for samples measured in this study.

Table 3  $\delta^{44/40}Ca$  data from Florida Bay waters and carbonate sediments.

Samples	Sediments		$2\sigma$	п	Waters 2		$2\sigma$ n	п	$\Delta_{\rm sed}$	Na (mg/L)	Ca	Na/Ca	Salinity
	δ <sup>44/40</sup> Ca (‰ sw)	δ <sup>44/40</sup> Ca (‰ 915a)			δ <sup>44/40</sup> Ca (‰ sw)	δ <sup>44/40</sup> Ca (‰ 915a)				(IIIg/L)	(IIIg/L)	(1101/1101)	
FB 1	-1.11	0.70	0.05	2	0.01	1.82			-1.12	12,200	450	47.2	40.1
FB 2	-1.09	0.72			0.00	1.81			-1.09	11,200	423	46.1	35.9
							$rac{\Delta_{ m sed}}{2\sigma}$	$-1.10 \\ 0.04$					
FB 3	-1.07	0.74			-0.09	1.72	0.02	2	-0.98	8970	343	45.6	30.1
FB 4	-1.40	0.41	0.00	2	-0.12	1.69	0.05	2	-1.29	7330	312	40.9	25.1
FB 5	-1.55	0.26			-0.39	1.42			-1.16	6240	334	32.6	22.0
FB 6	-1.99	-0.18			-0.69	1.12	0.02	2	-1.30	4070	378	18.8	14.0

that 80% of the Ca-flux to the oceans is delivered by rivers and 20% by hydrothermal fluids (Milliman, 1993; Milliman

and Droxler, 1996), the  $\delta^{44/40}Ca$  value of the combined riverine and hydrothermal Ca-flux is calculated to be

 $-1.01 \pm 0.04_{00}^{\prime\prime}$  ( $2\sigma_{mean}$ ). The propagated uncertainty is based on the  $2\sigma_{mean}$  values for 22 large rivers reported by Tipper et al. (2010), yielding  $\pm 0.034$  (=  $\pm 0.16/\sqrt{22}$ ), and 16 hydrothermal fluids measured by Amini et al. (2008), yielding  $\pm 0.02_{00}^{\prime\prime}$  (=  $\pm 0.07/\sqrt{16}$ ).

It has been known for some time that the output Ca-flux into carbonate sediments exceeds the input Ca-flux from rivers and hydrothermal fluids, and that a large Ca-flux from submarine groundwater discharge is needed to balance the ocean Ca budget (Garrels and Mackenzie, 1971; Wilkinson and Algeo, 1989; Milliman, 1993; Milliman and Droxler, 1996). Referring to the ocean Ca budget of Milliman and Droxler (1996), the size of the input Ca-flux from SGD could, in fact, rival the contributions from riverine and hydrothermal Ca sources. Using these Ca-fluxes (listed in Table 4), the  $\delta^{44/40}$ Ca value of the SGD Ca-flux to the oceans may be calculated from isotope mass balance considerations. At steady state, the global output Ca-flux into carbonate sediments (Fsed) equals the global input Ca-flux from rivers (F<sub>r</sub>), hydrothermal vents (F<sub>h</sub>) and groundwater ( $F_{gw}$ ), as described by Eq. (3):

$$F_{sed} = F_r + F_h + F_{gw} \tag{3}$$

Eq. (4) is the corresponding isotope mass balance equation:

$$F_{sed}\delta_{sed} = F_r\delta_r + F_h\delta_h + F_{gw}\delta_{gw}$$
<sup>(4)</sup>

In these equations,  $\delta^{44/40}$ Ca values for Ca fluxes  $F_r$ ,  $F_h$  and  $F_{gw}$  are denoted  $\delta_r$ ,  $\delta_h$  and  $\delta_{gw}$ . If the ocean Ca-cycle is in steady state, then the  $\delta^{44/40}$ Ca value of the total input Ca-flux from all sources of weathering ( $\delta_w^T$ ) must equal the total output Ca-flux into all types of carbonate sediments ( $\delta_w^T = \delta_{sed}$ ).

Solving Eq. (4) for  $\delta_{gw}$ , and plugging in the values for the parameters listed in Table 4, yields  $-1.23 \pm 0.23\%_{oo}$  $(2\sigma)$  for the global scale input Ca-flux from SGD. This value is not statistically different from the combined (weighted average) value for the other two input Ca-fluxes,  $\delta_r$  and  $\delta_h$  $(-1.01 \pm 0.04 \ 2\sigma_{mean})$ . To obtain a more precise result, the present-day global-scale output Ca-flux into carbonate sediments needs to be known with greater precision, as this uncertainty contributes greatly to the propagated uncertainty in  $\delta_{gw}$ . More work in this area will also help to determine whether the limited dataset on shallow water

Table 4 Simplified modern ocean Ca budget

Simplified modern ocean Ca budget.								
Budget	Ca Flux <sup>a</sup> (Tmol/y)	Input mass (fraction) <sup>b</sup>	δ <sup>44/40</sup> Ca (	‰ sw)	δ <sup>44/40</sup> Ca (‰ 915a)			
Inputs								
Rivers	13	0.4	-1.03	$\pm 0.03 \ (2\sigma_{\text{mean}})$	0.78			
Hydrothermal vents	3	0.1	-0.95	$\pm 0.02 \ (2\sigma_{\text{mean}})$	0.86			
Ground water <sup>c,d</sup>	16	0.5	-1.23	$\pm 0.23~(2\sigma)$	0.59			
Output								
CaCO <sub>3</sub> sediment	32		-1.12	$\pm 0.11$ (2 $\sigma$ )	0.69			

<sup>a</sup> Milliman (1993).

<sup>b</sup> Calculated relative to the output Ca flux of 32 Tmol/y.

<sup>c</sup> Input mass fraction calculated by difference (=32-13-3).

<sup>d</sup> Ground water  $\delta^{44/40}$ Ca value calculated using Eq. (4) from the text.



Fig. 5. The  $\delta^{44/40}$ Ca values for the major Ca reservoirs and fluxes of the modern ocean Ca-cycle. The range in  $\delta^{44/40}$ Ca values for silicate rocks is from Amini et al. (2009). The range in  $\delta^{44/40}$ Ca values for carbonate rocks is from Farkas et al. (2007). The  $\delta^{44/40}$ Ca value for the river input Ca-flux is from Tipper et al. (2010). The  $\delta^{44/40}$ Ca value for the pelagic carbonate deposition flux was calculated in section 4.1.1. The globalscale  $\delta^{44/40}$ Ca value for the SGD Ca-flux was calculated in section 4.1.2., assuming that the ocean Ca cycle is in steady state. The  $\delta^{44/40}$ Ca value for the shallow water carbonate deposition flux is from this study, as is the estimate of the global-scale fractionation factor for marine carbonate deposition ( $\Delta_{sed}$ ). Selected literature values have been corrected for inter-laboratory bias as indicated in the text.

carbonates presented in this study is truly representative of shallow water carbonate production on a global scale. The isotopic budget of the modern ocean Ca-cycle with SGD is summarized in Fig. 5.

#### 3.2. Local-scale Ca-cycling effects in Florida Bay

 $\delta^{44/40}$ Ca values of Florida Bay waters decrease from 0.0% to -0.69% in the direction of the Florida Everglades (Stations 2–6, Fig. 3). Salinity decreases from 35.9 to 14.0 over the same distance (Fig. 6a). Carbonate sediment  $\delta^{44/40}$ Ca values decrease from -1.09 to -1.99%, strongly correlating with the  $\delta^{44/40}$ Ca values of the overlying waters ( $r^2 = 0.93$ , figure not shown). Most of the decline in  $\delta^{44/40}$ Ca values occurs in the coastal zone of northeastern Florida Bay and along the southern mangrove fringe of the Florida Everglades (Fig. 3).

A plot of dissolved Na and Ca vs. salinity (Fig. 6b) shows that Na is conservative over the entire range of water samples collected. In contrast, Ca exhibits increasingly non-conservative behavior with closer sampling proximity to the Florida Everglades. The change occurs at a salinity of  $\sim 25$ , near Station 4. Here the initial trend of decreasing Ca with decreasing salinity changes to a trend of increasing Ca with decreasing salinity – an indication that nearshore waters have 'excess Ca' – more Ca than predicted by seawater–freshwater mixing.

Florida Bay waters define a strong linear trend on a plot of  $\delta^{44/40}$ Ca vs. Na/Ca (Fig. 6c). The linear relationship is evidence for mixing between two sources of Ca with differing  $\delta^{44/40}$ Ca values and Na/Ca ratios. The two most likely sources of Ca are seawater, with a Na/Ca  $\approx$  47 and a  $\delta^{44/}$ <sup>40</sup>Ca value of 0%, and weathered carbonate, with a Na/ Ca  $\approx$  0 and a  $\delta^{44/40}$ Ca value of -1.16% (the coordinates of the y-intercept). The carbonate-weathering signature falls within the range of  $\delta^{44/40}$ Ca values for modern shallow water carbonates (-0.81% to -1.22%) measured in this study.

Additional insight into the mechanism by which excess Ca is delivered to the coastal waters of Florida Bay comes from plotting Florida Bay waters on a  $\delta^{44/40}$ Ca vs. Ca diagram (Fig. 7) and comparing the distribution to the hypothetical trend of seawater–freshwater mixing given by Eq. (5):

$$\delta_{\rm mix}^{\rm Ca} = \frac{C_{\rm sw}^{\rm Ca} C_{\rm fw}^{\rm Ca} \left( \delta_{\rm fw}^{\rm Ca} - \delta_{\rm sw}^{\rm Ca} \right)}{C_{\rm mix}^{\rm Ca} \left( C_{\rm sw}^{\rm Ca} - C_{\rm fw}^{\rm Ca} \right)} + \frac{C_{\rm sw}^{\rm Ca} \delta_{\rm sw}^{\rm Ca} - C_{\rm fw}^{\rm Ca} \delta_{\rm fw}^{\rm Ca}}{C_{\rm sw}^{\rm Ca} - C_{\rm fw}^{\rm Ca}} \tag{5}$$

In this equation, concentrations are represented by  $C_i^{Ca}$  for components (i), which include freshwater (fw), seawater (sw) and brackish water (mix). Calcium isotope values are represented by  $\delta_i$ . Data from the Atlantic side of the Florida Keys (Station 1) are used for the seawater end-member, and literature data are used to define the average Ca concentration of freshwater from the Everglades (76  $\pm$  20 ppm) (Price and Swart, 2006). We assume that the corresponding  $\delta^{44/40}$ Ca value for Everglades freshwater is  $-1.16\%_{oo}$ , the value deduced for the carbonate weathering end-member using the mixing line in Fig. 6c. The water samples collected from the coastal region of northeastern Florida Bay (Stations 3–6) plot below the seawater–fresh-

water mixing curve due to the excess Ca supplied by carbonate weathering. This finding is reminiscent of the excess Ca reported in Florida Everglades groundwater by Price et al. (2006), suggesting that brackish groundwater is being discharged from the seabed in the vicinity of Stations 3–6, consistent with predictions based on hydrogeological modeling (Langevin et al., 2004) (Fig. 3).

Although we did not measure  $\delta^{44/40}$ Ca in brackish groundwater from the Everglades, we estimate its value using literature data (Cl = 130 mM and Ca = 13.5 mM in Fig. 8 from Price et al. (2006)), and the assumption that Na and Cl are conservative. We first calculate the mass of seawater contained in Everglades brackish groundwater using a Na balance Eq. (6):

$$C_{gw}^{Na}M_{gw} = C_{sw}^{Na}M_{sw} + C_{fw}^{Na}M_{fw}$$

$$\tag{6}$$

The components of the system (i) are seawater (sw), freshwater (fw) and groundwater (gw); M is the mass of component i, and  $C_i^{Na}$  is the concentration of Na in component i. Next, we construct a Ca balance equation (Eq. (7)) that is similar to the Na balance equation, except that there is an additional term for the mass of Ca released from subsurface weathering of carbonate aquifer material  $(m_{carb}^{Ca})$ :

$$C_{gw}^{Ca}M_{gw} = C_{sw}^{Ca}M_{sw} + C_{fw}^{Ca}M_{fw} + m_{carb}^{Ca}$$

$$\tag{7}$$

Eq. (8) is the isotope mass balance equation corresponding to Eq. (7):

$$\delta_{gw}^{Ca} C_{gw}^{Ca} M_{gw} = \delta_{sw}^{Ca} C_{sw}^{Ca} M_{sw} + \delta_{fw}^{Ca} C_{fw}^{Ca} M_{fw} + \delta_{carb}^{Ca} m_{carb}^{Ca}$$
(8)

Combining Eqs. (6)–(8), an expression is derived for the  $\delta^{44/40}$ Ca value of Everglades brackish groundwater ( $\delta_{gw}^{Ca}$ ) (Eq. (9)):

$$\begin{split} \delta_{gw}^{Ca} &= \left( \frac{C_{gw}^{Na} - C_{fw}^{Na}}{C_{sw}^{Na} - C_{fw}^{Na}} \right) \frac{C_{sw}^{Ca}}{C_{gw}^{Ca}} (\delta_{sw}^{Ca} - \delta_{carb}^{Ca}) \\ &+ \left( \frac{C_{gw}^{Na} - C_{sw}^{Na}}{C_{fw}^{Na} - C_{sw}^{Na}} \right) \frac{C_{fw}^{Ca}}{C_{gw}^{Ca}} (\delta_{fw}^{Ca} - \delta_{carb}^{Ca}) + \delta_{carb}^{Ca} \end{split}$$
(9)

The calculation requires that  $\delta^{44/40}$ Ca values for *fresh* Florida Everglades surface water ( $\delta_{fw}^{Ca}$ ) and subsurface limestone bedrock ( $\delta_{carb}^{Ca}$ ) are known. We take both values to be  $-1.16_{00}^{00}$  because it is presumed that weathering of exposed limestone will supply the bulk of the dissolved Ca in Florida Everglades surface water. Further manipulations of Eqs. (6) and (7) and the water mass balance equation ( $M_{gw} = M_{sw} + M_{fw}$ ) yields Eq. (10),

$$f_{Ca}^{carb} = \frac{m_{carb}^{Ca}}{C_{gw}^{Ca}M_{gw}} = 1 - \left[\frac{C_{sw}^{Ca}}{C_{gw}^{Ca}} \left(\frac{C_{gw}^{Na} - C_{fw}^{Na}}{C_{sw}^{Na}C_{fw}^{Na}}\right) + \frac{C_{fw}^{Ca}}{C_{gw}^{Ca}} \left(\frac{C_{gw}^{Na} - C_{sw}^{Na}}{C_{fw}^{Na} - C_{sw}^{Na}}\right)\right]$$
(10)

which is used to calculate the fraction of carbonate derived Ca in Everglades brackish groundwater, for which we obtain a value of 0.72. If the Ca contribution from Everglades freshwater is included, as well, then the mass fraction of carbonate derived Ca increases to 0.82. The remaining Ca is from seawater. The calculated average salinity for Everglades brackish groundwater is 7.4, if the salinity of seawater infiltrating southern Florida's coastal aquifers is 35; or 8.4 if the salinity is closer to 40 (Table 5).



Fig. 6. (a) Covariant trends between salinity and  $\delta^{44/40}$ Ca values for waters and sediments of northeastern Florida Bay. The decrease in  $\delta^{44/40}$ Ca with decreasing salinity is most pronounced in the coastal region and southern mangrove fringe of the Florida Everglades. The water sample data reflect a snapshot of  $\delta^{44/40}$ Ca variation in early March 2001. The surface sediment grab samples reflect a time-integrated pattern of  $\delta^{44/40}$ Ca variation. (b) A plot of Na and Ca concentrations in Florida Bay waters *vs.* salinity. Sodium shows conservative mixing behavior. Calcium shows increasingly non-conservative behavior with decreasing salinity and closer sampling proximity to the Everglades. (c) A plot of  $\delta^{44/40}$ Ca *vs.* Na/Ca displays a strongly covariant trend suggestive of mixing between two components: (1) seawater, and (2) submarine groundwater discharge. The  $\delta^{44/40}$ Ca value for Everglades groundwater is  $-0.96_{00}^{\circ}$  (calculated in section 4.2 using Cl and Ca concentration data on Everglades brackish groundwater reported in Price et al. (2006)). Note that the regression line does not include the groundwater datum. The y-intercept of  $-1.16_{00}^{\circ}$  is interpreted to represent the average  $\delta^{44/40}$ Ca value for the subsurface aquifer material through which the brackish waters have flowed.

Next, we determine the impact of submarine groundwater discharge on Florida Bay waters. Everglades brackish groundwater plots in the bottom right-hand corner of the  $\delta^{44/40}$ Ca vs. Ca diagram (Fig. 7). If we assume that the excess Ca in Florida Bay waters comes from submarine groundwater discharge (SGD), then a new set of mixing curves can be constructed using an equation similar to Eq. (5) that models the  $\delta^{44/40}$ Ca and Ca concentration of



Fig. 7. A graphical representation of a mixing model used to calculate the mass fraction of groundwater and groundwater derived Ca in Florida Bay waters. The non-conservative behavior of Ca and  $\delta^{44/40}\text{Ca}$  in Florida Bay waters is shown relative to the expected relationship for conservative mixing between seawater and Everglades surface water. Water samples from the coastal region of Florida Bay and the southern mangrove fringe of the Florida Everglades have higher Ca concentrations and lower  $\delta^{44/}$ <sup>40</sup>Ca values, and thus fall below the seawater-freshwater mixing curve. Brackish groundwater from the Everglades plots in the lower right hand corner of the diagram. A second set of mixing curves is drawn between Everglades brackish groundwater and several points on the seawater-freshwater mixing curve, with the only constraint being that the groundwater mixing curves must pass through the measured Florida Bay water samples. These curves are used to calculate water and Ca fractions contributed by submarine groundwater discharge in the near shore region of northeastern Florida Bay (see Table 5 and sample locations in Fig. 3). The percentage of Ca derived from groundwater is indicated for Stations 4-6. The number in parentheses is the salinity.

Florida Bay waters (FBW) as mixtures of two sources: (1) submarine groundwater discharge (gw), and (2) brackish surface waters (sw-fw-mix). The latter is calculated as hypothetical mixtures of freshwater from the Everglades and seawater from the surrounding oceans. The mass fraction of calcium contributed to Florida Bay waters by SGD  $(f_{ow}^{Ca})$  is calculated using Eq. (11):

$$f_{gw}^{Ca} = \frac{\delta_{FBW}^{Ca} - \delta_{sw-fw-mix}^{Ca}}{\delta_{gw}^{Ca} - \delta_{sw-fw-mix}^{Ca}}$$
(11)

Table 5

Posults of mixing calculations performed on Florida Pay water

The waters from stations closest to the Everglades show the biggest SGD-Ca fractions: 0.31 at Station 5, rising to 0.64 at Station 6. Further away from the Everglades, less Ca is contributed by SGD, and Florida Bay waters plot closer to the hypothetical seawater-freshwater mixing curve. The contribution of Everglades brackish groundwater to Florida Bay waters may be calculated using Eq. (12):

$$\begin{split} \mathbf{f}_{gw} &= \frac{\mathbf{M}_{gw}}{\mathbf{M}_{gw} + \mathbf{M}_{sw-fw-mix}} \\ &= \frac{\mathbf{C}_{sw-fw-mix}^{Ca} \left( \delta_{sw-fw-mix}^{Ca} - \delta_{FBW}^{Ca} \right)}{\mathbf{C}_{gw}^{Ca} \left( \delta_{FBW}^{Ca} - \delta_{gw}^{Ca} \right) + \mathbf{C}_{sw-fw-mix}^{Ca} \left( \delta_{sw-fw-mix}^{Ca} - \delta_{FBW}^{Ca} \right)} \end{split} \tag{12}$$

As expected, the waters from stations closest to the Everglades show the biggest fractional contributions: 0.19 at Station 5 and 0.43 at Station 6.

The results obtained from the above mixing model calculations are listed in Table 5 along with the values used for the mixing end-members. Included in Table 5 are the results of another apportionment calculation using Eq. (13). This calculation determines the total fraction of Ca  $(f_w^{Ca})$ in Florida Bay waters contributed by all sources of CaCO<sub>3</sub> weathering.

$$f_{w}^{Ca} = \frac{\delta_{FBW}^{Ca} - \delta_{sw}^{Ca}}{\delta_{w}^{Ca} - \delta_{sw}^{Ca}}$$
(13)

It does not require knowledge of the mechanism by which weathered Ca is delivered to Florida Bay, just knowledge of the  $\delta^{44/40}$ Ca value of the weathered Ca source ( $\delta_w^{Ca}$ ). The expectation is that  $f_w^{Ca}$  will be greater than  $f_{gw}^{Ca}$ , as the latter does not include Ca inputs from Everglades runoff, or diagenetic sources of Ca from carbonate sediment dissolution (Patterson and Walter, 1994). Examination of the results in Table 5 shows that on the whole, the model-based calculations of  $f_{gw}^{Ca}$  are comparable to  $f_{w}^{Ca}$ , thus lending support to the basic structure of the model and the dominance of SGD as a pathway in the transmission of the carbonate weathering flux signature to Florida Bay's coastal waters.

A quantitative analysis of the uncertainty can be determined for  $f_w^{Ca}$  with greater reliability than  $f_{gw}^{Ca}$  because the former does not depend on knowing the  $\delta^{44/44}$ Ca value

Results of mixing calculations	s performed on Florid	da Bay waters.				
Sample	$\delta^{44/40}$ Ca (‰ sw)	δ <sup>44/40</sup> Ca (‰ 915a)	Na (mg/L)	Ca (mg/L)	Na/Ca (mol/mol)	Salinity
Mixing end-members						
Seawater	0.01	1.82	12,200	450	47.2	40.1
Everglades						
Surface water	-1.16	0.65	34	76	0.78	0.11
High-Ca ground water (gw)	-0.96	0.85	2568	541	8.27	8.4
			gw fraction in in FB waters		<i>CaCO</i> <sub>3</sub> weathering fraction	
Florida Bay (FB)			$f_{gw}$	$f_{gw}^{Ca}$	$f_{\rm w}^{\rm Ca}$	
FB 1	0.01	1.82	_	_	_	
FB 2	0.00	1.81	_	_	_	
FB 3	-0.09	1.72	0.01	0.02	0.08	
FB 4	-0.12	1.69	0.01	0.02	0.11	
FB 5	-0.39	1.42	0.19	0.31	0.34	
FB 6	-0.69	1.12	0.43	0.64	0.60	

and Ca concentration of SGD. Moreover, the uncertainty in  $f_w^{Ca}$  is minimized by the goodness-of-fit of the linear regression on the plot of  $\delta^{44/44}$ Ca vs. Na/Ca in Fig. 6c  $(r^2=0.99)$ , which lends confidence to the two-component mixing model. Accordingly, we need only consider the reliability of the end-member uncertainties in order to calculate an uncertainty for  $f_w^{Ca}$ . Because seawater has a fixed value globally, the largest source of uncertainty reflects the degree of confidence that we have in the value of -1.16% used to characterize the carbonate end-member, which we determined from the y-intercept of the mixing line in Fig. 6c. If we shift the carbonate end-member along the regression line to -1.10%, then the calculated values for  $f_w^{Ca}$  would be 5% higher than the values listed in Table 5.

In summary, the impact of carbonate weathering increases in the shoreward direction in northeastern Florida Bay between stations 3 and 6, covering a distance of ~10 km. These results are consistent with hydrogeological modeling performed by Langevin et al. (2004), showing that stations 4, 5 and 6 are situated in a major groundwater discharge area with simulated groundwater flow rates that increase towards the southern margin of the Everglades. This is the direction of the decreasing trend in  $\delta^{44/40}$ Ca values of Florida Bay waters and bulk carbonate sediments.

#### 4.3. The role of SGD in the global Ca-cycle

It has been proposed that the  $\delta^{44/40}$ Ca value of the global-scale input Ca-flux to the oceans ( $\delta_w^T$ ) has changed over the past 30 million years (Griffith et al., 2008; Fantle, 2010). The hypothesized changes are quite large, ranging between ~0.3‰ and 0.5‰ over periods as short as 5 million years. Although no mechanisms were offered to support the plausibility of the hypothesis, the authors concede that sufficient leverage may not exist in the isotopic makeup of the continental rock reservoir to support changes of this magnitude in the given time frame (Schmitt and Stille, 2003; Sime et al., 2007; Griffith et al., 2008; Fantle, 2010). The possibility that the global-scale input Ca-flux to the oceans from SGD may rival the combined riverine and hydrothermal Ca fluxes brings new information to bear on the question of secular changes in  $\delta_w^T$ .

In contrast to rivers, which drain the vast interiors of the continents, the  $\delta^{44/40}$ Ca value of the SGD Ca-flux is controlled by a much smaller set of rocks that surround the margins of the continents. Silicate and carbonate rocks are included in this grouping, but only the carbonates can play a significant role in changing  $\delta_w^{T}$ . This conclusion is based on a study of radiogenic <sup>40</sup>Ca in marine carbonates showing no appreciable enrichment of this isotope in the oceans over geological time. The implication is that the ocean Ca-cycle is dominated by weathering of sedimentary carbonates and mantle-derived silicate rocks of basaltic composition (Caro et al., 2010). The latter exhibit such a narrow range of  $\delta^{44/40}$ Ca values, however, that it must be the carbonate rocks that control secular changes in  $\delta_w^{\rm T}$ . For example, seven analyses of rocks of basaltic to andesitic composition, reported by Amini et al. (2009), exhibit a total range of variation of just 0.16% at the 95% level of confidence, and an average  $\delta^{44/40}Ca$  value of -1.06%. Moreover, the isotopic signature of the mid-ocean ridge hydrothermal Ca-flux  $(-0.95 \pm 0.02\%, 2\sigma_{mean})$  may be buffered against changes over time by isotope exchange reactions between seawater and the continuously forming oceanic crust.

Carbonates, on the other hand, record a much wider range in  $\delta^{44/40}$ Ca values of  $\sim 0.7\%$  (Farkas et al., 2007), and are easily weathered. In fact, apportionment studies have shown that 90% of the calcium in rivers is traceable to carbonate weathering on a global scale (Gaillardet et al., 1999). Consistent with this finding. Tipper et al. (2010) reported that  $\delta^{44/40}$ Ca values for large rivers overlapped the values found in Phanerozoic marine carbonate rocks (Farkas et al., 2007), supporting our contention that only carbonate weathering needs to be considered when evaluating changes in  $\delta_w^T$  in the geological past. However, the  $\delta^{44/40}$ Ca value of the carbonate rock reservoir changes rather slowly, at the rate of  $\sim 0.1\%$ /100 Ma (Fig. 8 in Farkas et al., 2007), too slow to cause modeled changes of 0.3-0.5% in  $\delta_w^T$  over short time-scales of just 3–5 million-years (Griffith et al., 2008; Fantle, 2010). This leads us to consider an alternative but related hypothesis, one that involves weathering of coastal marine carbonate successions by SGD in low latitudes.

As a source of water to the oceans. SGD rivals river flows. This is the conclusion of Moore et al. (2008) who used a <sup>228</sup>Ra tracer technique to study SGD in the Atlantic Ocean basin, bracketing the contribution between 80% and 160% of the river water inputs. Most of the SGD revealed by this technique is recycled seawater. Given that Ca concentrations are typically higher in groundwater (e.g., Hanshaw and Back, 1980) and marine sediment pore water (e.g., Fantle and DePaolo, 2007) than river water (e.g., Schmitt and Stille, 2003), the Ca-flux contributed by SGD could easily exceed the Ca-flux from rivers on a global scale. A case in point is the exposed carbonate shelf of the Yucatan Peninsula. Meteoric water sinks freely into the underlying karstified carbonate bedrock before entering the oceans as SGD (Hanshaw and Back, 1980) with a Ca concentration that is 10-fold higher than the median value for global rivers (Schmitt and Stille, 2003). Using data provided by Hanshaw and Back (1980), we calculate the SGD Ca-flux from the Yucatan Peninsula to be half as large as the Ca-flux from Columbia River (a typical medium sized large river) which drains a continental area that is 10 times larger than the Yucatan, and carries a water flux that is 24 times larger (Columbia River data from Tipper et al., 2010). Weathered Ca-fluxes from places like the Yucatan Peninsula, and other coastlines where carbonates were deposited during previous high stands of sea level (Blanchon et al., 2009), have not been tabulated in global estimates of Cafluxes to the oceans.

Although the global-scale SGD Ca-flux appears to be large enough to impact the Ca concentration of seawater, the question remains: is there sufficient isotopic leverage in this weathered source of Ca to change the  $\delta^{44/40}$ Ca value of the oceans over geological time? Consider the middle Miocene as a case in point. Pelagic carbonate records suggest that the  $\delta^{44/40}$ Ca value of seawater was ~0.4‰ lower than today (De la Rocha and DePaolo, 2000; Heuser et al.,

2005; Fantle and DePaolo, 2005; Sime et al., 2007; Griffith et al., 2008; Fantle, 2010). Assuming that bulk-carbonate fractionation factors did not change, then shallow water carbonates deposited during the middle Miocene would have formed with  $\delta^{44/40}$ Ca values of about -1.5%. It follows that a subsequent lowering of sea level would expose these carbonates to subsurface weathering by groundwater, which may in turn cause a lowering of  $\delta_w^{T}$ . By contrast, the average  $\delta^{44/40}$ Ca value for the riverine and hydrothermal Ca-fluxes would likely remain the same as today  $(-1.01 \pm 0.04\%_{o}, 2\sigma_{mean})$ . Therefore, due to mixing effects, the decrease in  $\delta_w^T$  would be expected to be less than the decrease in shallow water carbonate  $\delta^{44/40}$ Ca values. For example, lowering the  $\delta^{44/40}$ Ca of SGD from the present day value of -1.23% to the middle Miocene value of -1.50% would lower  $\delta_w^T$  by ~0.15\% from -1.12% to -1.26% (Eq. (4)), if all other input Ca-fluxes and their isotopic compositions remained the same. But even this amount of change is on the high side of what is reasonable, as it assumes that a large proportion of the SGD Ca-flux to the oceans, worldwide, stems from the weathering of coastal marine carbonate successions deposited in low latitudes. In other words, mixing effects with the SGD Ca-inputs from higher latitudes are not considered in the calculation. The SGD Ca weathering flux hypothesis provides a mechanism that supports the suggestion by Fantle (2010) that changes in  $\delta_w^{T}$  might broadly track secular changes in seawater  $\delta^{44/40}$ Ca. We caution, however, that the secular variation in  $\delta_w^T$  was likely smaller than indicated in his model. In addition, any hypothesized SGD-driven changes in  $\delta_{\omega}^{T}$  would be expected to correlate with sea level changes.

The SGD Ca weathering flux hypothesis is tentative; its validation or invalidation must await a more thorough examination of secular records of  $\delta^{44/40}$ Ca variation in coastal marine carbonate successions. But even by this mechanism the changes in  $\delta_w^T$  are much smaller than the  $\sim 0.3-0.5\%$  changes proposed in models of ocean Ca cycling over the past 30 million years (Griffith et al., 2008; Fantle, 2010). We therefore conclude that the barite and bulk nannofossil ooze records cannot be entirely accurate records of secular changes in seawater  $\delta^{44/40}$ Ca values over the past 30 million years, particularly in the light of the foraminiferal reconstructions (Heuser et al., 2005; Sime et al., 2007) which show secular changes that are less dramatic, and modeled Ca concentration changes in the oceans that are much less dependent on large hypothesized changes in  $\delta_{w}^{T}$ . Although it has been suggested that secular changes in bulk carbonate fractionation factors between shallow and pelagic depositional modes might help to explain the discrepancies (Fantle, 2010), the differences proposed in the geological past are large (>1%), and contrast the very small differences found at the present day (<0.1%). A similar caution extends to the suggestion that the basic structure of the Ca isotope record of Phanerozoic oceans is explained by oscillating calcite and aragonite seas (Farkas et al., 2007), as we have found no evidence for a strong mineralogical control governing the pattern of Ca isotope fractionation among the major carbonate producers at the present day.

# 4.4. The role of SGD as a factor influencing local Ca-cycling in ancient epeiric seas

There is a growing body of work documenting local carbon cycling effects in epeiric seas, both in the geological past (Beauchamp et al., 1987; Holmden et al., 1998; Finney et al., 1999; Immenhauser et al., 2003; Kaljo et al., 2004; Gischler and Lomando, 2005; Panchuk et al., 2005, 2006; Melchin and Holmden, 2006; Fanton and Holmden, 2007; Immenhauser et al., 2008; Swart, 2008; LaPorte et al., 2009) and at the present day (Patterson and Walter, 1994; Swart and Eberli, 2005). Recently, it was reported that a  $\delta^{44/40}$ Ca study of Ordovician carbonates in the Williston Basin suggested the presence of local Ca-cycling effects in epeiric sea carbonates (Holmden, 2009). The finding of a  $\delta^{44/40}$ Ca gradient in the sediments and waters of Florida Bay strengthens and expands this claim.

Submarine groundwater discharge may be capable of sustaining platform gradients in seawater  $\delta^{44/40}$ Ca values in ancient epeiric seas. Over the course of geological time, shallow seas expanded and contracted countless times over vast areas of previously deposited marine carbonates. Shorelines were typically hundreds of kilometers from the open ocean, and seawater circulation was greatly restricted due to the distances, the shallowness of the waters, and potential barriers to circulation such as mud banks and other carbonate buildups. Like southern Florida, an exceedingly shallow relief characterized the coastal regions of the epeiric seas. Carbonate aquifers were likely hydraulically continuous beneath coastal areas, and seawater likely penetrated these aquifers, flowing inland for tens of kilometers in the subsurface. The greater the length of coastline, the greater was the area for seawater-freshwater mixing in subterranean estuaries. Carbonate aquifers were dissolved and isotopically light calcium flowed out of the seabed into the coastal waters forming shore-to-basin gradients in seawater  $\delta^{44/40}$ Ca values, aided by the sluggish circulation of seawater between the interior regions of the epeiric seas and the open ocean. Other factors may have been important as well. Rainfall recharges coastal aquifers and drives the topographical flow of freshwater towards the sea where mixing with Ca-enriched groundwater occurs in the subsurface. An important role is therefore played by climate. Microbial metabolism and oxidation of organic matter lowers groundwater pH, enabling the carbonate aquifer to dissolve (Jacobson and Wu, 2009). Although vascular plants did not evolve until the late Devonian, bryophytes, fungi and bacteria are known to have colonized terrestrial environments in earlier times (Yapp and Poths, 1993; Wellman et al., 2003). Microbial respiration of organic matter may have supplied the aqueous CO<sub>2</sub> needed to drive the dissolution of subsurface carbonates in the coastal regions of the epeiric seas long before the evolution of land plants.

From the local Ca-cycling perspective, SGD presents a Ca weathering flux that is more evenly distributed along the coastline than the point source delivery of weathered Ca by rivers, which are also lower in Ca concentration than groundwater. Considering further that the salinity of SGD may be similar to seawater, or at least brackish rather than fresh, SGD will contribute much less than rivers to salinity reduction in epeiric seas. Therefore, attempts to identify carbonate deposits affected by SGD on the basis of faunal associations affected by salinity must bear this caution in mind. For example, if many of the brachiopods that were used to reconstruct the Ca-isotope record of Phanerozoic oceans (Farkas et al., 2007) were collected from shallow water deposits affected by local Ca-cycling effects in epeiric seas, then the seawater evolution curve may be biased towards lower  $\delta^{44/40}$ Ca values.

## 5. CONCLUSIONS AND IMPLICATIONS

The vast majority of marine carbonate rocks preserved in the sedimentary rock record were deposited in shallow water settings. As isotope investigations into the Earth's ancient Ca-cycle increase, these ancient carbonate successions will be targeted for reconstructing changes in ocean Ca-cycling through time, with the aim of providing information on Earth's changing climate, ocean circulation, and tectonics (e.g., Payne et al., 2010). Reconstructing ocean secular trends using  $\delta^{44/40}$ Ca values recorded in shallow water carbonates, however, is not without pitfalls. In a modern example, we have shown that enhanced subsurface weathering of carbonate rocks by groundwater, and the delivery of isotopically light Ca by SGD, prevents the ocean  $\delta^{44/40}$ Ca signature from being recorded in the near shore region of Florida Bay – a phenomenon that most likely extends to Ca-cycling in ancient epeiric seas as well. Because SGD can be brackish, the decrease in salinity is also much less than would normally be expected if meteoric waters were mixing with seawater. For this reason, it may be difficult to recognize carbonate deposits affected by SGD in the sedimentary rock record and to avoid sampling these deposits when isotopically tracing the ocean Ca-cycle through time.

Reconstructions of past-ocean Ca-cycling using genuine ocean sediments will not have to contend with the integrity of the  $\delta^{44/40} Ca$  record insofar as local Ca-cycling effects are concerned. Nevertheless, there is a fair amount of disagreement in the isotopic trends reconstructed over the past 30 million years using different sedimentary materials (Fantle, 2010), highlighted by the different ways in which  $\delta_w^{T}$  is hypothesized to have changed through time. We argued in this paper that the proposed secular changes in  $\delta_w^{\rm T}$  are too large, and occur too quickly, to be explained by any known mechanism that we can think of to produce them, with the possible exception of submarine groundwater discharge. Even by this mechanism, however, changes greater than  $\sim 0.15\%$  over the past 30 million years are unlikely given the current state of knowledge of the workings of the ocean Ca-cycle.

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#### REFERENCES

- Amini M., Eisenhauer A., Böhm F., Fietzke J., Bach W., Garbe-Schonberg D., Rosner M., Bock B., Lackschewitz K. S. and Hauff F. (2008) Calcium isotope (δ<sup>44/40</sup>Ca), fractionation along hydrothermal pathways, Logatchev field (Mid-Atlantic Ridge, 14 degrees 45'N). *Geochim. Cosmochim. Acta* 72, 4107–4122.
- Amini M., Eisenhauer A., Böhm F., Holmden C., Kreissig K., Hauff F. and Jochum K. P. (2009) Calcium isotopes in MPI-DING Reference Glasses, USGS rock powders and various rocks: evidence for Ca isotope fractionation in terrestrial silicates. *Geostand. Newslett.* 33, 231–247.
- Bathhurst R. G. C. (1975) Carbonate Sediments and Their Diagenesis. Developments in Sedimentology 12. Amsterdam, Netherlands: Elsevier Science B.V. 658 p.
- Beauchamp B., Oldershaw A. E. and Krouse H. R. (1987) Upper carboniferous to upper Permian <sup>13</sup>C-enriched primary carbonates in the Sverdrup Basin, Canadian Arctic: comparisons to coeval western North American ocean margins. *Chem. Geol.* 65, 39–413.
- Berger W. H. and Winterer E. L. (1974) Plate stratigraphy and the fluctuating carbonate line. In *Pelagic Sediments: On Land and Under the Sea, Special Publication, Vol. 1* (eds. K. J. Hsq and H. C. Jenkins). International Association of Sedimentologists, Osney Mead, Oxford: Blackwell Scientific.
- Blanchon P., Eisenhauer A., Fietzke J. and Liebetrau V. (2009) Rapid sea-level rise and reef back-stepping at the close of the last interglacial highstand. *Nature* 458, 881–884.
- Broecker W. S. and Clark E. (2009) Ratio of coccolith CaCO<sub>3</sub> to foraminifera CaCO<sub>3</sub> in late Holocene deep sea sediments. *Paleoceanography* 24, PA3205. doi: 10.1029/2009PA001721.
- Burnett W. C., Aggarwal P. K., Aureli A., Bokuniewicz H., Cable J. E., Charette M. A., Kontar E., Krupa S., Kulkarni K. M., Loveless A., Moore W. S., Oberdorfer J. A., Oliveira J., Ozyurt N., Povinec P., Privitera A. M. G., Rajar R., Ramessur R. T., Scholten J., Stieglitz T., Taniguchi M. and Turner J. V. (2006) Quantifying submarine groundwater discharge in the coastal zone via multiple methods. *Sci. Total Environ.* **367**, 498–543.
- Caro G., Papanastassiou D. A. and Wasserburg G. J. (2010) 40K– 40Ca isotopic constraints on the ocean calcium cycle. *Earth Planet. Sci. Lett.* 296, 124–132.
- Corbett D., Chanton J., Burnett W., Dillon K., Rutkowski C. and Fourqurean J. (1999) Patterns of Groundwater Discharge into Florida Bay. *Limnol. Oceanogr.* 44, 1045–1055.
- Corbett D. R., Dillon K., Burnett W. and Chanton J. (2000) Estimating the groundwater contribution into Florida Bay via natural tracers 222Rn and CH4. *Limnol. Oceanogr.* 45, 1546– 1557.
- Coronado C., Candela J., Iglesias-Prieto R., Sheinbaum J., López M. and Ocampo-Torres F. J. (2007) On the circulation in the Puerto Morelos fringing reef lagoon. *Coral Reefs* 26, 149–163.
- De La Rocha C. L. and DePaolo D. J. (2000) Isotopic evidence for variations in the marine calcium cycle over the Cenozoic. *Science* 289, 1176–1178.
- Fantle M. S. and DePaolo D. J. (2005) Variations in the marine Ca cycle over the past 20 million years. *Earth Planet. Sci. Lett.* 237, 102–117.
- Fantle M. S. and DePaolo D. J. (2007) Ca isotopes in carbonate sediment and pore fluid from ODP Site 807A: The  $Ca^{2+}(aq)$ calcite equilibrium fractionation factor and calcite recrystalli-

zation in Pleistocene sediments. Geochim. Cosmochim. Acta 71, 2524–2546.

- Fantle M. S. (2010) Evaluating the Ca isotope proxy. *Am. J. Sci.* **310**, 194–230.
- Fanton K. C. and Holmden C. (2007) Sea level forcing of carbon isotope excursions in epeiric seas: implications for carbon isotope chemostratigraphy. *Can. J. Earth Sci.* 44, 807–818.
- Farkas J., Böhm F., Wallmann K., Blenkinsop J., Eisenhauer A., Geldren R. V., Munnecke A., Voigt S. and Veizer J. (2007) Calcium isotope record of Phanerozoic oceans: Implications for chemical evolution of seawater and its causative mechanisms. *Geochim. Cosmochim. Acta* **71**, 5117–5134.
- Finney S. C., Berry W. B. N., Cooper J. D., Ripperdan R. L., Sweet W. C., Jacobson S. R., Soufiane A., Achab A. and Noble P. J. (1999) Late Ordovician mass extinction: A new perspective from stratigraphic sections in central Nevada. *Geology* 27, 215– 218.
- Fitterman D. V. and Deszcz-Pan M. (1998) Helicopter EM mapping of saltwater intrusion in Everglades National Park, Florida. *Explor. Geophys.* 29, 240–243.
- Fish J. E. and Stewart M. (1991) Hydrogeology of the surficial aquifer system, Dade County, Florida: US Geological Survey Water-Resources Investigation Report 90–4018, 53 p.
- Garrels R. M. and Mackenzie F. T. (1971) Evolution of Sedimentary Rocks. W.W. Norton, New York, 379 p.
- Gaillardet J., Dupre B., Louvat P. and Allegre C. J. (1999) Global silicate weathering and CO<sub>2</sub> consumption rates deduced from the chemistry of large rivers. *Chem. Geol.* **159**, 3–30.
- Gischler E. and Lomando A. J. (2005) Offshore sedimentary facies of a modern carbonate ramp, Kuwait, northwestern Arabian-Persian Gulf. *Facies* 50, 443–462.
- Griffith E. M., Paytan A., Caldeira K., Bullen T. D. and Thomas E. (2008) A Dynamic Marine Calcium Cycle During the Past 28 Million Years. *Science* **322**, 1671–1674.
- Gussone N., Böhm F., Eisenhauer A., Dietzel M., Heuser A., Teichert B. M. A., Reitner J., Worheide G. and Dullo W. C. (2005) Calcium isotope fractionation in calcite and aragonite. *Geochim. Cosmochim. Acta* 69, 4485–4494.
- Gussone N., Langer G., Thoms S., Nehrke G., Eisenhauer A., Riebesell U. and Wefer G. (2006) Cellular calcium pathways and isotope fractionation in *Emiliania huxleyi. Geology* 34, 626– 628.
- Gussone N., Langer G., Geisen M., Steel B. A. and Riebesell U. (2007) Calcium isotope fractionation in coccoliths of cultured *Calcidiscus leptoporus*, *Helicosphaera carteri*, *Syracosphaera pulchra* and *Umbilicosphaera foliosa*. *Earth Planet. Sci. Lett.* 260, 505–515.
- Hanshaw B. B. and Back W. (1980) Chemical mass-wasting of the northern Yucatan Peninsula by groundwater dissolution. *Geology* 8, 222–224.
- Heuser A., Eisenhauer A., Böhm F., Wallmann K., Gussone N., Pearson P.N., Nagler T.F. and Dullo W.C. (2005) Calcium isotope (δ<sup>44/40</sup>Ca) variations of Neogene planktonic foraminifera: *Paleoceanography* **20**, PA2013.
- Hindshaw R. S., Reynolds B. C., Wiederhold J. G., Kretzschmar R. and Bourdon B. (2011) Calcium isotopes in a proglacial weathering environment: Damma glacier, Switzerland. *Geochim. Cosmochim. Acta* **75**, 106–118.
- Hippler D., Schmitt A.-D., Gussone N., Heuser A., Stille P., Eisenhauer A. and Nägler T. F. (2003) Calcium isotopic composition of various reference materials and seawater. *Geostandards* 27, 13–19.
- Hittle C.D., Patino E. and Zucker M. (2001) Freshwater Flow from Estuarine Creeks into Northeastern Florida Bay. US Geological Survey Water-Resources Investigations Report 01– 4164.

- Holmden C., Creaser R. A., Muehlenbachs K., Leslie S. A. and Bergstrom S. M. (1998) Isotopic evidence for geochemical decoupling between ancient epeiric seas and bordering oceans: Implications for secular curves. *Geology* 26, 567–570.
- Holmden C. (2009) Ca isotope study of Ordovician dolomite, limestone, and anhydrite in the Williston Basin: implications for subsurface dolomitization and local Ca-Cycling. *Chem. Geol.* 268, 180–188.
- Holmden C. and Bélanger N. (2010) Ca isotope cycling in a forested ecosystem. *Geochim. Cosmochim. Acta* 74, 995–1015.
- Huang S., Farkaš J. and Jacobsen S. B. (2010) Calcium isotopic fractionation between clinopyroxene and orthopyroxene from mantle peridotites. *Earth Planet. Sci. Lett.* **292**, 337–344.
- Immenhauser A., Della Porta G., Kenter J. A. M. and Bahamonde J. R. (2003) An alternative model for positive shifts in shallowmarine carbonate δ<sup>13</sup>C and δ<sup>18</sup>O. Sedimentology **50**, 953–959.
- Immenhauser A., Holmden C. and Patterson W.P. (2008) Interpreting the carbon-isotope record of ancient shallow epeiric seas: lessons from the Recent. In *Dynamics of Epeiric Seas* (eds. B. R. Pratt and C. Holmden). Geological Association of Canada Special Paper 48. pp. 137–174.
- Jacobson A. D. and Holmden C. (2008) <sup>44</sup>Ca evolution in a carbonate aquifer and its bearing on the equilibrium isotope fractionation factor for calcite. *Earth Planet. Sci. Lett.* **270**, 349–353.
- Jacobson A. D. and Wu L. (2009) Microbial dissolution of calcite at T=28 C and ambient pCO2. *Geochim. Cosmochim. Acta* 73, 2314–2331.
- Kaljo D., Hints L., Martma T., Nõlvak J. and Oraspõld A. (2004) Late Ordovician carbon isotope trend in Estonia, its significance in stratigraphy and environmental analysis. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 210, 165–185.
- Kelble C. R., Johns E. M., Nuttle W. K., Lee T. N., Smith R. H. and Ortner P. B. (2007) Salinity patterns in Florida Bay. *Estuar. Coast. Shelf Sci.* 71, 318–334.
- Langevin C. D., Swain E. D. and Wolfert M. A. (2004) Simulation of integrated surface-water/groundwater flow and salinity for a coastal wetland and adjacent estuary. USGS Open File Report 2004–1097, 30 p.
- LaPorte D. F., Holmden C., Patterson W. P., Loxton J. D., Melchin M. J., Mitchell C. and Finney S. C. (2009) Local and global perspectives on carbon and nitrogen cycling during the Hirnantian Glaciation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 276, 182–195.
- Lemarchand D., Wasserburg G. J. and Papanastassiou D. A. (2004) Rate-controlled calcium isotope fractionation in synthetic calcite. *Geochim. Cosmochim. Acta* 68, 4665–4678.
- Medina A. (2008) Where land meets the sea: Provenance and distribution of carbonate beach sand at Punta Maroma, Yucatan Peninsula, Mexico. M. Sc. Dept. of Geosciences, Univ. of Fribourg, Unpublished.
- Melchin M. J. and Holmden C. (2006) Carbon isotope chemostratigraphy in Arctic Canada. Seal-level forcing of carbonate platform weathering and implications for Hirnantian global correlation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 234, 186–200.
- Merino M. and Otero L. (1991) Atlas Ambiental Costero, Pureto Morelos – Quintana Roo. Ferrandiz SA, México DF 14640, 80 pp.
- Milliman J. D. (1993) Production and accumulation of CaCO<sub>3</sub> in the ocean: budget of a non-steady state. *Global Biogeochem. Cy.* 7, 927–957.
- Milliman J. D. and Droxler A. W. (1996) Neritic and pelagic carbonate sedimentation in the marine environment: ignorance is not bliss. *Geol. Rundsch.* 85, 496–504.
- Moore W. (1999) The subterranean estuary: a reaction zone of ground water and sea water. *Marine Chem.* 65, 111–125.

- Moore W. (2010) The effect of submarine groundwater discharge on the ocean. *Annual Rev. Mar. Sci.* 2, 59–88.
- Moore W. S., Sarmiento J. L. and Key R. M. (2008) Submarine groundwater discharge revealed by <sup>228</sup>Ra distribution in the upper Atlantic Ocean. *Nature* **1**, 309–311.
- Nuttle W. K., Fourqurean J. W., Cosby B. J., Zieman C. and Robblee M. B. (2000) Influence of freshwater supply on salinity in Florida Bay. *Water Res.* 36, 1805–1822.
- Panchuk K. M., Holmden C. and Kump L. R. (2005) Sensitivity of the epeiric sea carbon isotope record to local-scale carbon cycle processes: Tales from the Mohawkian Sea. *Palaeogeogr. Palaeocl. Palaeoecol.* 228, 320–337.
- Panchuk K. M., Holmden C. and Leslie S. A. (2006) Local controls on carbon cycling in the Ordovician Midcontinent region of North America with implications for carbon isotope secular curves. J. Sed. Res. 76, 200–211.
- Patterson W. P. and Walter L. M. (1994) Depletion of C in seawater CO<sub>2</sub> on modern carbonate platforms: significance for the carbon isotope record of carbonates. *Geology* 22, 885–888.
- Payne J. L., Turchyn A. V., Payton A., DePaolo D. J., Lehrmann D. J., Yu M. and Wei J. (2010) Calcium isotope constraints on the end-Permian mass extinction. *PNAS* 107, 8543–8548.
- Perkins R. D. (1977) Pleistocene depositional framework of south Florida. in *Quaternary sedimentation in south Florida-Bahama area* (eds. Enos, Paul, and R. D. Perkins). Geological Society of America Memoir 147, pp. 131–198.
- Price R. M. and Swart P. K. (2006) Geochemical indicators of groundwater recharge in the surficial aquifer system, Everglades National Park, Florida, USA. *Geol. Soc. Am. Spec. Pap.* 404, 15p.
- Price R. M., Swart P. K. and Fourqurean J. W. (2006) Coastal groundwater discharge – an additional source of phosphorous for the oligotrophic wetlands of the Everglades. *Hydrobiology* 569, 23–36.
- Price R. M., Swart P. K. and Willoughby H. E. (2008) Seasonal and spatial variation in the stable isotopic composition ( $\delta^{18}$ O and  $\delta$ D) of precipitation in south Florida. *J. Hydrol.* **358**, 193– 205.
- Riding R. (1993) Phanerozoic patterns of marine CaCO<sub>3</sub> precipitation. *Naturwissenschaften* 80, 513–516.
- Russell W. A. and Papanastassiou D. A. (1978) Ca isotope fractionation in ion-exchange chromatography. *Analyt. Chem.* 50, 1151–1154.
- Schmitt A. D. and Stille P. (2003) The calcium riverine and hydrothermal isotopic fluxes and the oceanic calcium mass balance. *Earth Planet. Sci. Lett.* **213**, 503–518.
- Schmitt A. D., Gangloff S., Cobert F., Lemarchand D., Stille P. and Chabaux F. (2009) High performance automated ion chromatography separation for Ca isotope measurements in geological and biological samples. J. Anal. Atomic. Spec. 24, 1089–1097.

- Sime N. G., De La Rocha C. and Galy A. (2005) Negligible temperature dependence of calcium isotope fractionation in 12 species of planktonic foraminifera. *Earth Planet. Sci. Lett.* 232, 51–66.
- Sime N. G., De La Rocha C. L., Tipper E. T., Tripati A., Galy A. and Bickle M. J. (2007) Interpreting the Ca isotope record of marine biogenic carbonates. *Geochim. Cosmochim. Acta* 71, 3979–3989.
- Swain E. D., Wolfart M. A., Bales J. D. and Goodwin C. R. (2004) Two-dimensional hydrodynamic simulation of surface-water flow and transport to Florida Bay through the southern inland and coastal systems (SICS). US Geological Survey, Water Resources Investigations Report 03–4287.
- Swart P. K. and Price R. M. (2002) Origin of salinity variations in Florida Bay. *Lim. Oceanogr.* 47, 1234–1241.
- Swart P. K. and Eberli G. (2005) The nature of the  $\delta^{13}$ C of periplatform sediments: implications for stratigraphy and the global carbon cycle. *Sed. Geol.* **175**, 115–129.
- Swart P. K. (2008) Global synchronous changes in the carbon isotopic composition of carbonate sediments unrelated to changes in the global carbon cycle. *Proc. Natl. Acad. Sci.* 105, 13741–13745.
- Swarzenski P., Reich C. and Rudnick D. (2009) Examining submarine ground-water discharge into Florida Bay by using 222Rn and continuous resistivity profiling: US Geological Survey Open-File Report 2008-1342, 66 p.
- Tipper E. T., Gaillardet J., Galy A. and Louvat P. (2010) Calcium isotope ratios in the world's largest rivers: a constraint on the maximum imbalance of oceanic calcium fluxes. *Global Biogeochem. Cy.* 24, GB3019, 13p. doi:10.1029/2009GB003574.
- Trewartha G. T. (1954) An Introduction to Climate. McGraw-Hill, New York.
- Wanless H. R. and Tagett M. G. (1989) Origin, growth and evolution of carbonate mudbanks in Florida Bay. *Bull. Mar. Sci.* 44, 454–489.
- Wellman C. H., Osterloff P. L. and Mohiuddin U. (2003) Fragments of the earliest land plants. *Nature* 425, 282–285.
- Wieser M. E., Buhl D., Bouman C. and Schwieters J. (2004) High precision calcium isotope ratio measurements using a magnetic sector multiple collector inductively coupled plasma mass spectrometer. J. Anal. At. Spectrom. 19, 844–851.
- Wilkinson B. H. and Algeo T. (1989) Sedimentary carbonate record of calcium-magnesium cycling. Am. J. Sci. 289, 1158– 1194.
- Yapp C. J. and Poths H. (1993) The carbon isotope geochemistry of goethite (a-FeOOH) in ironstone of the Upper Ordovician Neda Formation, Wisconsin, USA: implications for early Paleozoic continental environments. *Geochim. Cosmochim. Acta* 57, 2599–2611.

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