Supporting Information:

Quantifying biogenic versus detrital carbonates on marine shelf: an isotopic approach

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Materials and Methods:

Samples material

Rivers and PRGL1-4 sediments

Approximatively 5g for bulk river sediment (i.e. from very coarse sand to clay) and 2g for bulk PRGL1-4 sediments grounded in agate mortar, weighed carefully and digested by 40 mL of 5% (v/v) acetic acid 96% for analyses in pre-cleaned 50 mL centrifuge tubes. 12 hours after the 5% acid acetic injection, centrifuge tubes were placed in ultrasonic bath for 30' and left at room temperature during 36h. After 48h of digestion, tubes were centrifuged 5 min/2500 rpm, then supernatants were transferred into pre-cleaned 50 mL centrifuge tube and then evaporated on a hot plate during ~18 hours in order to pre-concentrate the mother solution.

The clear mother solutions were then filtered using 0.45 µm Nalgene® syringe filters and then split for different analyses.

12 mL of mother solution were transferred to pre-cleaned 15 mL tube few hours prior to measurement by ICP-EOS, an aliquot of 3 mL of the mother solution was evaporated into pre-cleaned Savillex® vial, taken up in 1 mL HNO_3 1M for Sr purification.

Analytical methods

Strontium isotopes

TIMS Triton

Strontium was isolated from the matrix by column chromatography using a Sr-Spec resin (Eichrom®) prior to be analysed by TIMS (ThermoFischer TRITON) at the Pôle de Spectrometrie Océan (Brest, France) on static mode. Total procedural blanks were < 200 pg of Sr.

Purified Sr fractions are loaded on single W filaments together with TaF_5 activator.

All measured Sr ratios were normalized to $^{86}Sr/^{88}Sr = 0.1194$. During the course of analysis, Sr isotope compositions of standard solution NBS987 gave $^{87}Sr/^{86}Sr = 0.710259 \pm 7$ (2σ, n=9, recommended value 0.710250).

LA-MC-ICPMS Neptune

Samples for isotopes analyses on pure calcite were washed using a 150 µm sieve. All residues were composed of calcite material (bivalves, shell, foraminifera tests). Calcite material were soaked in 5% H_2O_2 to remove organic matter, and cleaned sonically in methanol to remove fine-grained particles. Clean samples were embedded in epoxy, polished with 1 µm diamond paste for in-situ isotopic measurements.

Strontium isotopes were analysed using a laser ablation technic coupled to MC-ICPMS (ThermoFischer Neptune) at the Pôle de Spectrometrie Océan (Brest, France). Laser ablation condition were 500 Hz, 20µJ pulse energy, the beam spot size of 10µm. Laser ablated material was carried with He gas to a double torch chamber in which the ablated aerosol was mixed with a 2% HNO_3 solution before to be injected into the plasma. These conditions were adjusted to obtain the maximal plasma sensibility and stability. Interferent ^{87}Rb signal was monitored by ^{85}Rb, and

$^{87}Sr/^{86}Sr$ was corrected following Barnett-Johnson et al., 2010 procedure. Finally, NIST 987 $^{87}Sr/^{86}Sr$ ratio were analysed at the beginning and end of each ablation to check the reliability of $^{87}Sr/^{86}Sr$ measurements, and yielded $^{87}Sr/^{86}Sr$ ratio of 0.71021 ± 4 10^{-5} (2σ, n=4).

Major element analyses

Major elements of the carbonate fraction were determined at the Pôle de Spectrometrie Océan (Brest, France) using an ICP-OES (HORIBA Ultima 2). The ICP-OES was calibrated using a limestone reference material solution (CAL-S, MACS-3) digested using the same procedure as the samples (Rongemaille et al., 2011) and diluted to the appropriate concentrations.
CAL-S leachates measurements are in agreement with already published values with a precision better than 5% for all elements.

GIS extraction

Hydrological parameters of areas draining the GoL, including catchments of studied tributaries, were extracted using the Hydrology tools of the Spatial Analyst extension of ArcGiS 10.2, from the SRTM DEM 3 arc-second (http://srtm.csi.cgiar.org/srtmdata/) (Farr et al., 2007). The reference vector maps for carbonates extension on the catchment are the 1:1,000,000 geologic map and 1:1,000,000 lithologic map of France, from the French Geological Survey Institut (BRGM) (Chantraine et al., 1996). We extracted geological data (formation extent and ages) from each catchment using the clip tool of ArcGis software.

Seismic data and flux estimation:

Stratigraphic knowledge of the area relies on previous studies based on seismic and PROMESS drilling data in the Gulf of Lion (Rabineau, 2001; Rabineau et al., 2005, 2006, Bassetti et al., 2008 among others); (SI Fig. 4). Identified units were picked on the shelf within a 2260 km^2 area. The volume of sediments preserved for selected time intervals were first estimated from each thickness map (built over the same area with a same meshgrid) of seismic units and associated ages established by Rabineau et al., 2005, 2006, (SI Fig. 4). Fluxes are then estimated from these volumes. A transformation from time to depth domain was computed using a constant velocity, using 1750 m/s within the sediment from measurements of P-wave velocity in PRGL2-2 in Dennielou, 2006.
We focused on sediment budget within the Sequence 3, in which high-resolution seismic data allowed identifying two units U75 and U80 that respectively correspond to MIS 9 and 8, (SI Fig. S4). Initial sediment budgets obtained from these units were then corrected for in-situ carbonate production (this study) and porosity (using lithologic data from PRGL 1-4 borehole (Bassetti et al., 2008) to obtain ‘true’ terrigenous solid volumes. Using the evolution of pore pressure with depth (Bassetti et al., 2008), and the porosity values measured in PRGL1-4 borehole (Dennielou, 2006), we consider that the correction for porosity (almost stable at ~30% from the surface to 90 mbsf) can be negligible.

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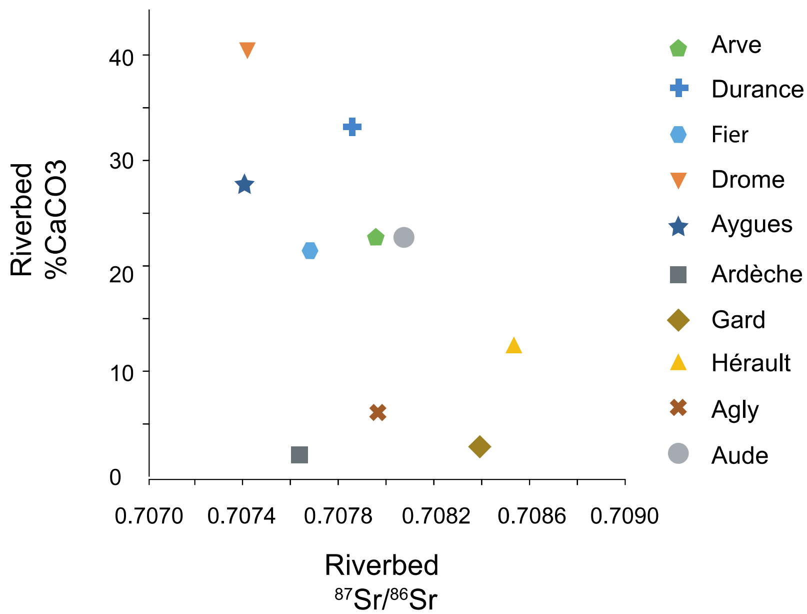

Fig. S1: Riverbed cross plot of $^{87}Sr/^{86}Sr$ versus $\%CaCO_3$.

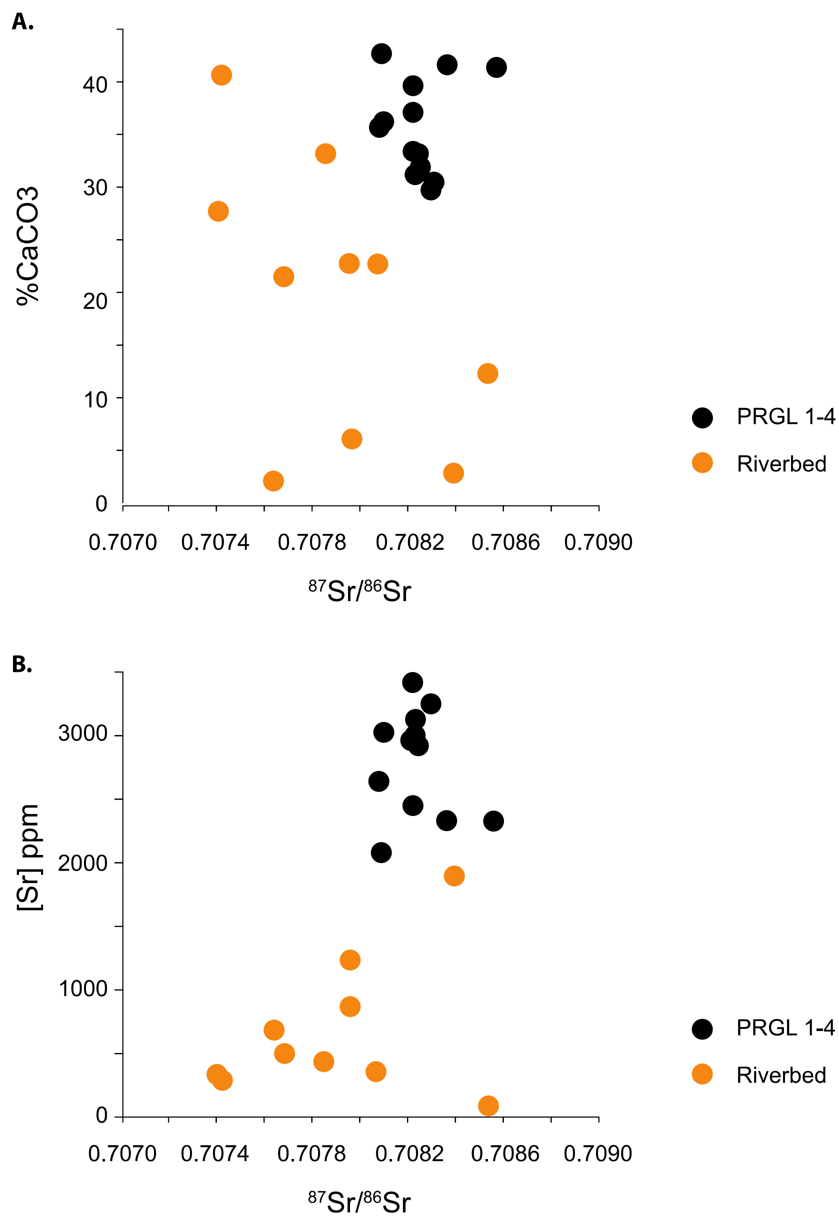

Fig. S2: Cross plot of $^{87}Sr/^{86}Sr$ versus %$CaCO_3$ for PRGL 1-4 (black circles) and riverbed (orange circles) sediments. In both case, no clear trend is observed indicating that the Sr isotopic composition is driven neither by the %CaCO3, nor by [Sr].

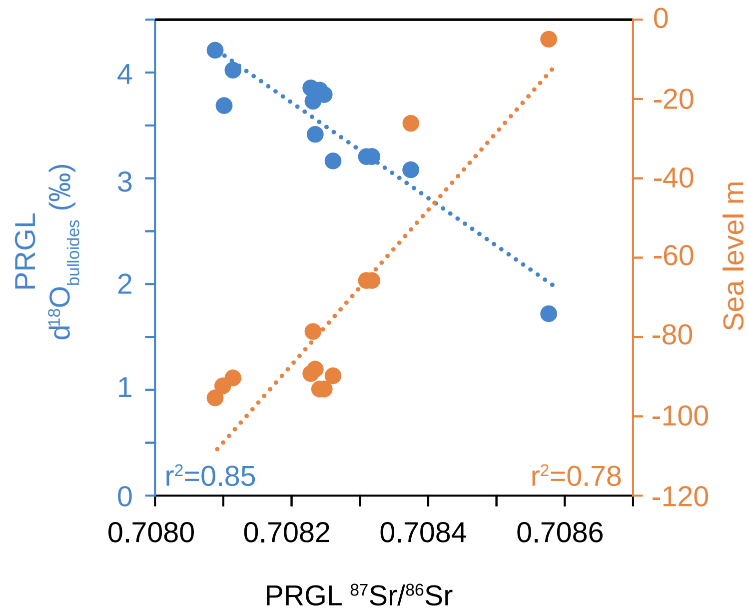

Fig. S3: Crossplot of both $\delta^{18}O_{G.bulloides}$ (this core, Sierro et al., 2009) and Relative Sea Level (coreKL09, Grant et al., 2014) with $^{87}Sr/^{86}Sr$ (this study). Correlation observed with $\delta^{18}O_{G.bulloides}$ (r^2= 0.85) is better than correlation with RSL (r^2= 0.78), probably due to age models discrepancies and/or local effects between the two sites.

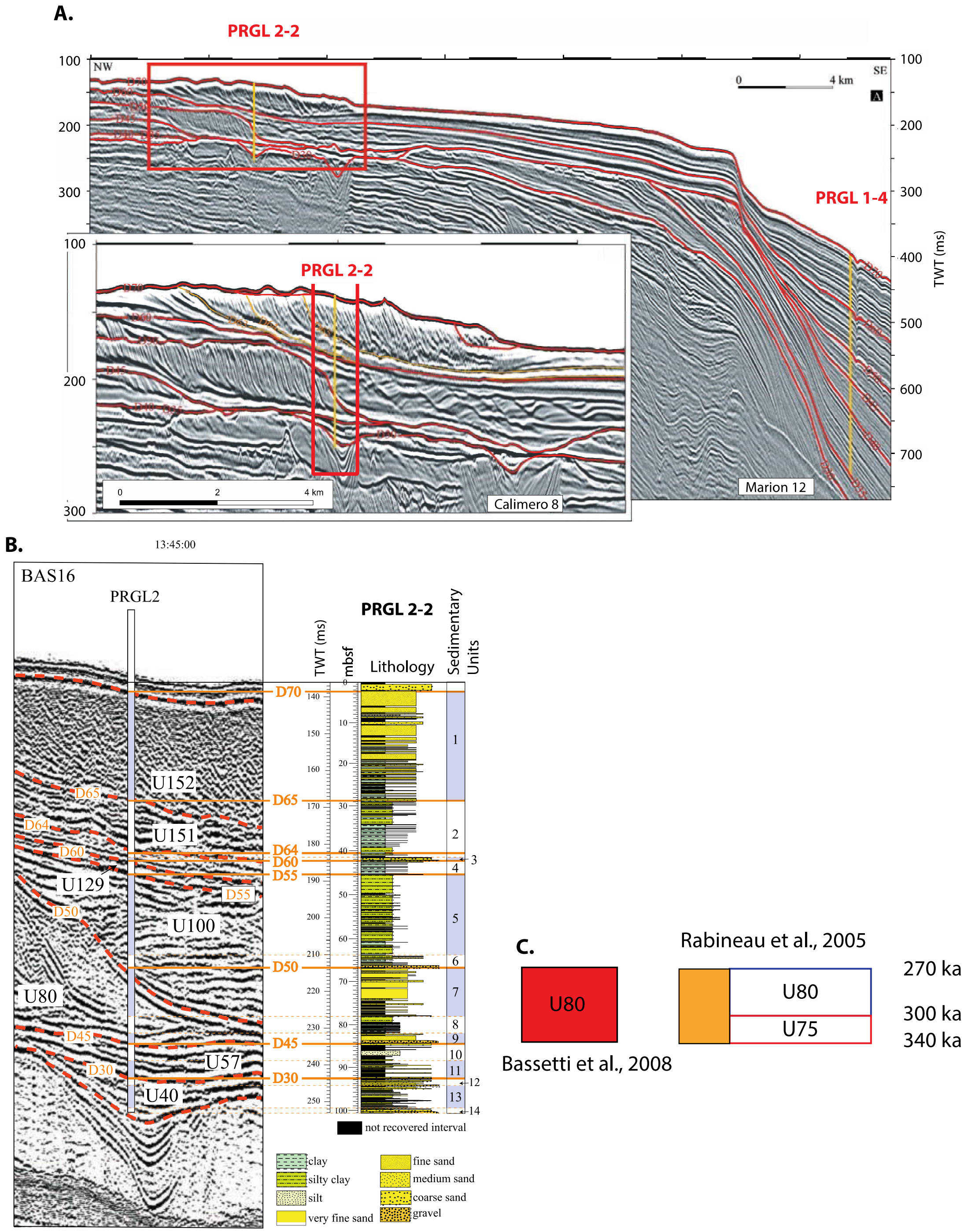

Fig. S4: A. High-resolution seismic profiles crossing PRGL 2-2: (a) shelf-slope seismic line (Marion 12) showing depositional sequences bounded by discontinuities on the shelf that can be followed into correlative conformities on the slope (PRGL1–4 site); (b) close-up view at the position of PRG2-2 (line Calimero8). **B.** Correlation between seismic and lithological data after the conversion of mbsf depths into mstwtt. Sedimentary units 1–14 are detailed in Bassetti et al., 2008. **C.** Units subdivision and ages used in this study from Rabineau et al., 2006.

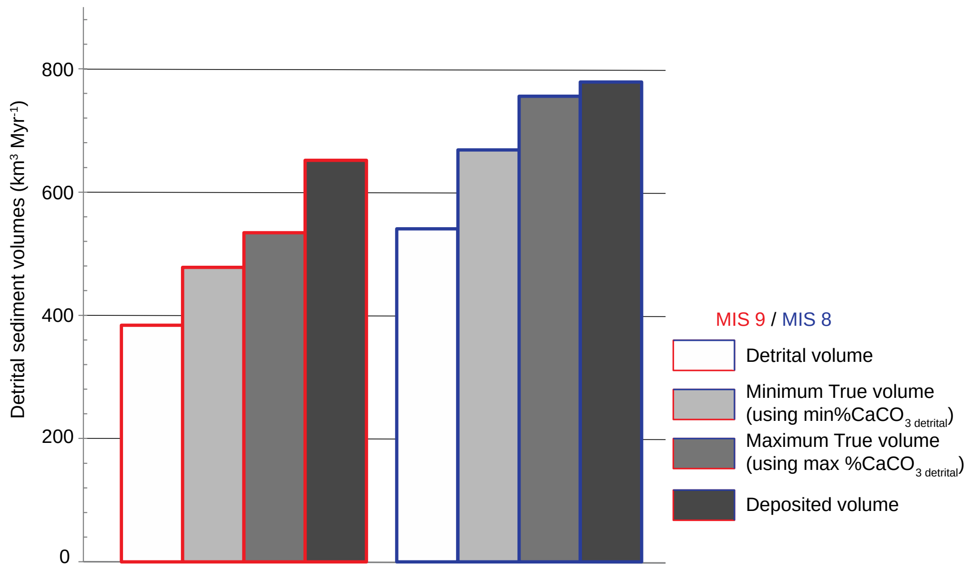

Fig. S5: Quantitative comparison between the detrital sediment volumes ($km^3\ Myr^{-1}$) for MIS 8 (blue envelope) and MIS 9 (red envelope) taking into account various proportion of detrital carbonate (%$CaCO_{3detrital}$).

PRGL 1-4 depth, mbsf	Age, kyr	87Sr/86Sr	CaCO3, %	Sr, ppm	Ca, ppm	Mg, ppm	Al, ppm	Ba, ppm	K, ppm	Na, ppm
Bulk										
72.10	123.83	0.70858	41.1	2162	1054994	29764	1403	130	4122	25764
74.07	132.13	0.70838	41.3	2160	854626	35075	1065	98	2730	21503
81.68	137.66	0.70823	39.4	2278	1049403	47191	1277	110	3749	34852
85.53	140.44	0.70810	42.4	1922	854095	29529	1015	80	2528	23028
88.49	142.59	0.70809	35.3	2447	1098259	32693	2196	158	5557	37810
91.13	144.50	0.70811	35.8	2813	1226483	38468	3298	206	5120	39827
93.25	146.05	0.70823	36.8	2759	1059182	43978	1686	128	3783	31137
95.12	147.03	0.70824	33.2	3186	1226532	51657	2523	155	5852	44310
100.30	149.21	0.70826	31.6	2728	1071100	47909	4488	206	6060	52921
104.88	151.49	0.70825	32.9	2806	993573	43279	2290	181	5140	38386
105.21	151.96	0.70824	31.0	2915	1086069	48838	3037	194	5344	39857
110.05	158.81	0.70831	29.5	3021	1172656	53929	2997	218	6295	49967
River										
Durance		0.70787	32.8	396	143529	832	66	16	30	85
Drome		0.70743	40.3	255	102446	656	47	14	21	59
Aude		0.70809	22.5	313	392075	2788	188	28	48	253
Herault		0.70855	12.0	58	63607	4534	155	26	40	141
Fier		0.70769	21.2	444	253147	1449	104	9	42	129
Arve		0.70797	22.4	803	310609	2078	137	12	58	168
Aygues		0.70741	27.4	295	207734	1111	88	23	23	64
Ardeche		0.70765	2.0	6231	3150068	23299	26984	2366	7984	17132
Gard		0.70841	2.6	1755	3328970	17824	8987	819	3892	12168
Agly		0.70798	5.8	1144	1052816	32556	1233	111	445	1859
Pure calcite										
72.1		0.70921								
88.5		0.70919								

Table S1: Depth, estimated age, and associated geochemical information from PRGL 1-4 samples, riverbeds and pure calcite (LA-MC-ICP-MS).

	Epoch	$^{87}Sr/^{86}Sr$
Data Compilation *	Miocene	0.708724
	Eocene	0.707743
	Cretaceous	0.707406
	Jurassic	0.707199

	Epoch	$^{87}Sr/^{86}Sr$ measured	Debit $m^3\ s^{-1}$ (% total)	$^{87}Sr/^{86}Sr$ river debit	Exposed carbonated lithology m^2 (% total)	$^{87}Sr/^{86}Sr$ exposed carbonated lithologies
Gulf of Lion		**** 0.707906**	**521.73 (100%)**	**0.707931**	**20984955186 (52%)**	**0.707556**
	Miocene				2459555504 (12%)	
	Eocene				3040562322 (14%)	
	Cretaceous				9365839062 (45%)	
	Jurassic				6118998299 (29%)	
Durance		**0.707866**	**188 (36%)**		**8921179008 (67%)**	
	Miocene				1159314618 (13%)	
	Eocene				288609946 (3%)	
	Cretaceous				3828870436 (43%)	
	Jurassic				3644384007 (41%)	
Drome		**0.707434**	**20 (4%)**		**1575731709 (95%)**	
	Miocene				123963387 (7.9%)	
	Eocene				869694 (0.1%)	
	Cretaceous				1052191574 (66.8%)	
	Jurassic				398707053 (25.3%)	
Aude		**0.708085**	**43.6 (8%)**		**3129530139 (60%)**	
	Miocene				292289134 (9%)	
	Eocene				2151569675 (69%)	
	Cretaceous				568503130 (18%)	
	Jurassic				117168200 (4%)	
Herault		**0.708554**	**43.7 (8%)**		**980788820 (37%)**	
	Miocene				275095667 (28%)	
	Eocene				112720675 (11%)	
	Cretaceous				108746232 (11%)	
	Jurassic				484226244 (49%)	
Fier		**0.707694**	**41.2 (8%)**		**1068484782 (78%)**	
	Miocene				174665206 (13%)	
	Eocene				163592902 (3%)	
	Cretaceous				584409221 (43%)	
	Jurassic				145817451 (41%)	
Arve		**0.707971**	**75 (14%)**		**928999991 (45%)**	
	Miocene				0	
	Eocene				112099128 (12%)	
	Cretaceous				411848922 (44%)	
	Jurassic				405051940 (44%)	

Table S2: Average $^{87}Sr/^{86}Sr$ values used in this study for Miocene, Eocene, Cretaceous and Jurassic carbonated lithologies exposed in the Gulf of Lion catchment area from Howard & McArthur, 1997; McArthur & Howarth, 2001data-compilation.

Gulf of Lion and individual watershed exposed carbonated lithologies as function of Age, $^{87}Sr/^{86}Sr$ ratio measured on riverbed samples, individual river debit in m^3s^{-1} (and associated percentage) used to weighted measured $^{87}Sr/^{86}Sr$ river debit; surface of exposed carbonates lithology according to age in m^2 (and % from total surface, and relative to all carbonated exposed surfaces).

UNITS	MARINE ISOTOPIC STAGE	%CaCO3	DEPOSITED VOLUME (km^3/Myr)	DETRITAL FLUXES (km^3/Myr)	%CaCO3$_{detritic}$	TRUE DETRITAL FLUX (km^3/Myr)
U75	9	40	651.6	390.96	30-50	69.15 - 521.28
U80	8	30	778.91	545.24	55-85	73.76 - 743.87

Table S3: Estimates of preserved sediment volumes and associated sediment fluxes from seismic units previously identified in Rabineau et al., 2005, 2006. Mean 'deposited' volume correspond to previously identified volume deposited into the Gulf of Lion; 'Detrital' volume refers to remaining volume after correction of the marine in-situ production by considering 100% of $CaCO_3$ results from the biogenic carbonates; and 'True' volume take into consideration the detrital part of carbonate content from this study (blue).