Supporting Information:

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

V. Pasquier\textsuperscript{1,2}, S. Revillon\textsuperscript{2,3}, E. Leroux\textsuperscript{4}, S. Molliex\textsuperscript{2,5}, L. Moccochain\textsuperscript{6}, M. Rabineau\textsuperscript{2}

\textsuperscript{1} now at Earth and Planetary Sciences department, Weizmann Institute of Sciences, Rehovot, Israël
\textsuperscript{2} IUEM, UMR CNRS 6538, Laboratoire Géosciences Océan, Université de Bretagne Occidentale, F-29280 Plouzane, France
\textsuperscript{3} SEDISOR, IUEM, Place Nicolas Copernic, F-29280, Plouzane, France
\textsuperscript{4} IFREMER, Laboratoire Géodynamique et enregistrements Sédimentaires, BP70, F-29280 Plouzané, France
\textsuperscript{5} CRPG, UMR 7358, CNRS-Université de Lorraine, 15 rue Notre Dame des Pauvres, F-54501 Vandœuvre-lès-Nancy Cedex, France
\textsuperscript{6} UPMC, Université Pierre et Marie Curie, ISTEP, Institut des Sciences de la Terre de Paris, F-75005, Paris, France

Correspondence and requests for materials should be addressed to V.P.

(virgil.pasquier@weizmann.ac.il).
Materials and Methods:

Samples material

Rivers and PRGL1-4 sediments

Approximately 5g for bulk river sediment (i.e. from very coarse sand to clay) and 2g for bulk PRGL1-4 sediments ground 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 HNO₃ 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 (ThermoFisher 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 TaF₅ activator. All measured Sr ratios were normalized to $^{86}\text{Sr} / ^{88}\text{Sr} = 0.1194$. During the course of analysis, Sr isotope compositions of standard solution NBS987 gave $^{87}\text{Sr} / ^{86}\text{Sr} = 0.710259 \pm 7$ (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% H₂O₂ 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 (ThermoFisher 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% HNO₃ solution before to be injected into the plasma. These conditions were adjusted to obtain the maximal plasma sensibility and stability. Interferent $^{87}\text{Rb}$ signal was monitored by $^{85}\text{Rb}$, and
$^{87}\text{Sr}/^{86}\text{Sr}$ was corrected following Barnett-Johnson et al., 2010 procedure. Finally, NIST 987 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio were analysed at the beginning and end of each ablation to check the reliability of $^{87}\text{Sr}/^{86}\text{Sr}$ measurements, and yielded $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of $0.71021 \pm 4 \times 10^{-5}$ ($2\sigma$, 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.
References:

Barnett-Johnson, R., Teel, D.J., and Casillas, E., 2010, Genetic and otolith isotopic markers identify salmon populations in the Columbia River at broad and fine geographic scales: Environmental Biology of Fishes, v. 89, no. 3-4, p. 533–546, doi: 10.1007/s10641-010-9662-5.

Bassetti, M.A., Berné, S., Jouet, G., Taviani, M., Dennielou, B., Flores, J.A., Gaillot, A., Gelfort, R., Lafuerza, S., Sultan, N., 2008. The 100-ka and rapid sea level changes recorded by prograding shelf sand bodies in the Gulf of Lions (western Mediterranean Sea). Geochem. Geophys. Geosyst. 9, n/a–n/a. doi:10.1029/2007GC001854.

Chantraine J., Autran A., Cavelier C. et al. (1996) - Carte géologique de la France (1.000 000ème). Ed. BRGM.

Farr, T.G., Rosen, P.A., Caro, E., Crippen, R., Duren, R., Hensley, S., Kobrick, M., Paller, M., Rodriguez E., Roth, L., Seal, D., Shaffer, S., Shimada, J., Umland, J., Werner, M., Oskin, M., Burbank, D., Alsdorf, D., 2007. The shuttle radar topography mission. Reviews of geophysics 45(2), RG2004.

Dennielou, B., 2006. Physical properties in Hole PRGL2-2. Institut français de recherche pour l'exploitation de la mer - Centre de Brest, PANGAEA, doi: 10.1594/PANGAEA.465156.

Rabineau, M., 2001. Un modèle géométrique et stratigraphique des séquences de dépôts quaternaires de la plate-forme du Golfe du Lion: enregistrement des cycles glacioeustatiques de 100 000 ans. Thèse de Doctorat, 392.

Rabineau, M., Berné, S., Aslanian, D., Olivet, J.-L., Joseph, P., Guillocheau, F., Bourillet, J.-F., Ledrezen, E., Granjeon, D., 2005. Sedimentary sequences in the Gulf of Lion: A record of 100,000 years climatic cycles. Marine and Petroleum Geology 22, 775–804. doi:10.1016/j.marpetgeo.2005.03.010.

Rabineau, M., Berné, S., Olivet, J.-L., Aslanian, D., Guillocheau, F., Joseph, P., 2006. Paleo sea levels reconsidered from direct observation of paleoshoreline position during Glacial Maxima (for the last 500,000 yr). Earth and Planetary Science Letters 252, 119–137. doi:10.1016/j.epsl.2006.09.033.

Rongemaille E, Bayon G, Pierre C, et al. Rare earth elements in cold seep carbonates from the Niger delta. Chemical Geology. 2011;286(3-4):196-206. doi:10.1016/j.chemgeo.2011.05.001.
Fig. S1: Riverbed cross plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\%\text{CaCO}_3$. 
Fig. S2: Cross plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\%\text{CaCO}_3$ 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 $\%\text{CaCO}_3$, nor by [Sr].
Fig. S3: Crossplot of both $\delta^{18}$O$_{G.bulloides}$ (this core, Sierro et al., 2009) and Relative Sea Level (core KL09, 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 ($r^2 = 0.72$) 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 mbf depths into msstw. Sedimentary units 1–14 are detailed in Bassetti et al., 2008. C. Units subdivision and ages used in this study from Rabineau et al., 2005.
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$_3$detrital).

Table S1: Depth, estimated age, and associated geochemical information from PRGL 1-4 samples, riverbeds and pure calcite (LA-MC-ICP-MS).
## Table S2: Average $^{87}\text{Sr}/^{86}\text{Sr}$ 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, 2001 data-compilation.

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

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).