

Mineralogical and Geochemical Tracers of Terrigenous Transfers

Viviane Bout-roumazeilles

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Université Lille 1

Rapport de synthèse Présenté en vue d'obtenir

L'Habilitation à Diriger des Recherches

Par

Viviane BOUT-ROUMAZEILLES

Mineralogical and Geochemical Tracers of Terrigenous Transfers

Soutenue le 13 septembre 2012, devant le jury composé de:

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MINERALOGICAL AND GEOCHEMICAL TRACERS OF TERRIGENOUS TRANSFERS



Viviane Bout-Roumazeilles

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General introduction

Terrigenous transfers

My main objective is to improve our understanding of the relationships between climate, ocean and atmospheric systems by **constraining continent-ocean particle transfers** over the late Quaternary. Indeed, ocean and atmosphere are dynamical components of the climate responsible for global heat flow distribution. Tracing the past variability of ocean and atmosphere is complex, and most paleoenvironmental studies focus on the record their geochemical/physical signatures. But the ocean and the atmosphere are also responsible for the transport of detrital particles from the continent toward the ocean. Interactions between climate variations and these fluid layers affect the main modes of terrigenous transfer (Figure 1). In this context, the terrigenous fraction of sediments may be used to retrace the past variability of oceanic/atmospheric transfers, complementary with the physical/chemical characterisation.



Figure 1: Source-to-sink terrigenous transfer modes

Clay-size particles can be transported from the continent toward the ocean through **fluvial** systems (*s.l.* including, slope sedimentary transfers) and then redistributed by **oceanic** water masses, or carried *via* **eolian** processes (Figure 1). But deciphering the detrital sedimentary record implies that both **particles provenance** and **geochemical processes** -modifying the initial record through authigenesis or diagenesis- are well constrained. The characterization of the **clay sources** is one crucial point to deal with and constitutes the initial step for any paleoenvironmental study (Biscaye, 1965; Griffin and Goldberg, 1969; Rateev *et al.*, 1969; Gradusov, 1974; Windom, 1976).

Tracking provenance

Clay minerals are widely distributed in the world marine sediments. As they are mainly land-derived, **clay mineral associations** were often used to identify the detrital particles source region (Biscaye, 1965; Griffin *et al.*, 1968). Indeed, the mineralogical nature of sediments depends on the petrographic characteristics of their source areas (*e.g.*, Bout-Roumazeilles *et al.*, 1999; Sionneau *et al.*, 2008). Clay minerals may thus be used to reconstruct changing terrigenous provenance once the main sources are identified and well constrained. The clay mineral fraction provides information on climatic conditions, such as precipitation and runoff patters over the adjacent continents (Chamley, 1989; Montero *et al.*, 2009; 2010), as well as on the dynamics of river inputs (Pinsak and Murray, 1960, Doyle and Sparks, 1980; Gutierrez-Mas *et al.*, 1997).

The geochemical signature (major and trace elements) of marine sediments allows characterizing the main sources and assessing the relative contribution of these sources using mixing models (Martinez *et al.*, 2010, Liu *et al.*, 2010). Moreover some elemental ratios (Ti/Al, Zr/Ti, etc) are used to evidence specific transportation patterns or transfer processes (Haug *et al.*, 2001; Martinez-Ruiz *et al.*, 2003; Kandler *et al.*, 2009). The geochemical characteristics of marine sediments allow checking the dominant detrital signature of

the records. Element concentrations and enrichment factors provide valuable informations on influence of both **authigenic and diagenetic processes** that may severely alter the sedimentary record. The rare-earth element normalized patterns and associated anomalies highlight any specificity of the detrital supply and evidence any authigenic modifications.

Some studies (Chamley, 1989) demonstrated that temporal clay mineral association changes may be due to different physical and chemical weathering conditions on rather long timescale. Indeed, clay mineral composition is sensitive to weathering through mineral/chemical modifications due to the successive removal of mobile elements during hydrolysis. These processes lead to the formation of pedogenic profiles enriched non-mobile elements (Al, Fe, i.e. kaolinite, oxy-hydroxides, etc...). Previous studies (Thiry, 2000; Thiry et al., 1999) evidenced that such processes may significantly alter the clay mineral records (*i.e.* at regional scale) over very long timescale, several order of magnitude above the studied climatic transitions. Establishing combined variations in Sr-Nd-Pb isotope ratios of clays will be proof of changing source provenance rather than weathering conditions. An important characteristic of the continental crust is that different regions are characterised by distinct Sr-Nd-Pb isotope signatures depending on age and thermotectonic evolution (Faure, 1986). This has allowed previous workers to successfully document the changing isotopic signatures and, by implication, source provenance of ice-rafted lithic detritus (IRD) (Revel et al., 1996b; Gwiazda et al., 1996; Winter et al., 1997; Hemming et al., 1998; Grousset et al., 2000) aerosols (Biscaye et al., 1974; Grousset et al., 1988; 1998; Bory et al., 2002; Basile et al., 1997; Krom et al., 1999; Grousset and Biscaye, 2005; Krueger et al., 2008), authigenic material (Abouchami and Goldstein, 1995; O'Nions et al., 1998; Frank et al., 1999; Rutberg et al., 2000; Frank et al., 2002; 2006; van de Flierdt et al., 2007; Piotrowski et al., 2008; Copard et al., 2010) and detrital particles (Revel et al., 1996a, Fagel et al., 1999; Innocent et al., 1997; Fagel et al., 2002; 2004; 2006; Ehrmann et al., 2003; Hemming et al., 2007; Gutjahr et al., 2008; Hillebrand et al., 2009; Skonieczny et al., 2011).

Tracing transfer pathways

Clay mineral sources and **distribution** provide information on the sediment propagation pathways and respective fluvial, eolian and oceanic contributions to sedimentation. Clay minerals can be advected over long distances and settle far away from their source area, being carried by the nepheloid layer (Biscaye and Eittreim, 1977; Jones, 1984). The possibility of clay minerals acting as tracers of oceanic water masses was inferred from the frequent occurrence of abundant clay size material in the water column and several studies used deep-sea clay mineral associations as tracers of source regions and as indicators of water mass fluctuations ((Biscaye, 1965; Chamley, 1975; Kennett, 1982; Petschick *et al.*, 1996; Fagel *et al.*, 1997; Gingele *et al.*, 2001, Boulay *et al.*, 2005; Fagel *et al.*, 2006; Liu *et al.*, 2007; Colin *et al.*, 2010). Clay particles are mainly transported from the continents to the ocean, by **deep-oceanic circulation**, **the atmosphere** (Folger, 1970; Caquineau *et al.*, 1998; 2002; Bout-Roumazeilles *et al.*, 2006; Kandler *et al.*, 2009; Formenti *et al.*, 2011), **the nepheloid layer** (Bout-Roumazeilles *et al.*, 1999) or by surface **oceanic circulation** (Bout-Roumazeilles *et al.*, 1997).

The transfer regime is investigating by coupling the clay mineral and grain-size studies. Indeed, deep marine sediments **grain-size** (mode and sorting), which is primarily driven by sedimentary processes, reflects the transportation conditions (Ehrmann *et al.*, 2007; Montero *et al.*, 2009; Sionneau *et al.*, 2010). It allows distinguishing efficiently eolian, fluviatile and deep oceanic transport (Moreno *et al.*, 2002; Stuut *et al.*, 2002; Holz *et al.*, 2004; Hamann *et al.*, 2009; Stuut *et al.*, 2009).

The spatial distribution of the clay-mineral assemblages is examined using **geostatistics** in order to illustrate their spatial variability (*e.g.* Wackernagel, 1988; Haslett *et al.*, 1991; Webster and Olivier, 1990; 2001; Hoover and Wolman, 2005, Jackson *et al.*, 2007; Weindorf and Zhu, 2010; Bout-Roumazeilles *et al.*, submitted). It enables spatial relationships among sample values to be quantified and used for interpolation of values at non-sampled locations in order to produce distribution maps. **Factor analysis** (Albarede, 1995) is used to study the relationship between clay mineralogy and other sedimentological proxies among which grain-size, geochemistry, stable isotope records and pollen associations (Bout-Roumazeilles *et al.*, 1999). The method used is the Principal Component Analysis, which explains the covariance structure of multivariate data through a reduction of the dataset to a smaller number of variables or factors. **Spectral analysis** have been used on some dataseries in order to examine the control of climate on clay terrigenous transfer in the main orbital frequency bands at glacial/interglacial, or to decipher oceanic and atmospheric processes at shorter timescale (Fagel *et al.*, 1992; Bout-Roumazeilles *et al.*, 1997; Debret *et al.*, 2007; 2009).

Clay provenance

Introduction

In the case of the next examples, a standardized approach was used to constrain clay provenance on both continental and marine sites by using (1) previously published data (Biscaye, 1965; Rateev *et al.*, 1969; Potter *et al.*, 1975; Paquet *et al.*, 1984) completed with (2) new samples from loess, tills, lakes, soils, river beds and banks, aerosols, sediment traps, marine top cores and subsurface samples. A geostatiscal approach served to determine the representativeness of data, their consistency and significance and to draw maps of the major clay mineral distribution on both continental (*i.e.* the **Mississippi River** watershed area – Figure 3) and oceanic environment (**Cariaco Basin**, Figure 9). In mixed sedimentary systems, with highly seasonnal eolian and river inputs, as in the **Mediterranean** (Figures 6 and 37), it could be much difficult to obtain a representative database. This study, initiated in 2007, would be achieved in the Mediterranean in the next few years, through an international effort to collect aerosols and marine subsurface samples.



Figure 2: Distribution of smectite (in blue, upper panel) and illite (in orange, lower panel) over the North American continent based on 85 continental and 67 marine sites (Sionneau et al., 2008).

The Gulf of Mexico

The Mississippi River system (*s.l.*) collects runoff from almost half the USA and delivers detrital particles reflecting the nature of drained areas toward the northern Gulf of Mexico (GOM) (Figure 2). Both regional geology of the North American continent and sedimentology of the GOM have been extensively studied (Griffin, 1962; Doyle and Sparks, 1980; Balsam and Beeson, 2003; Ellwood *et al.*, 2006), but a direct comparison between continental mineralogical provinces and marine environments was not available. In that frame, the clay mineral distribution over the continental areas drained by the Mississippi River systems and the factor controlling their distribution on the northern Gulf of Mexico needed to be well constrained. A compilation of 85 new samples and 67 core tops samples from the northern Gulf of Mexico allows us to map clay mineral distributions over both the North American continent and the northern part of the GOM (Figure 2). The study of these terrigenous inputs, mostly composed of clay minerals (Brown and Kennett, 1988), may provide information on past continent (dynamic of the Laurentide Ice Sheet – LIS- during glacial periods, meltwater discharge during deglaciation and precipitations during interglacials) and the hydrological properties of the GOM (Broecker *et al.*, 1989, Clark et al 2001; Clarke *et al.*, 2003; Montero *et al.*, 2009; Montero *et al.*, 2010; Sionneau *et al.*, 2010; Montero *et al.*, 2011).



Figure 3: Main clay mineralogical provinces encompassing the Mississippi River watershed area (Sionneau et al., 2008; Bout-Roumazeilles et al., 2011)

Continental clay distribution

The clay distribution maps allow dividing the Mississippi River watershed into four main distinct mineralogical provinces, reflecting both the petrographic nature of the bedrock and its tectonic and weathering history (Figures 2 and 3).

The widely extended northwestern part of the Mississippi River watershed (from 110°W to 90°W) encompassing the Missouri River (Figure 3) is typically dominated by smectite, deriving from the mineralogy of the Great Plains soils content and the composition of Cretaceous, Tertiary and Pleistocene bedrocks (Allen *et al.*, 1972; Smith, 2003). A specific enrichment in kaolinite characterized the northeastern part of this province, in the Upper Mississippi River basin, deriving from a saprolite formed during Mesozoic on the Precambrian bedrock (Cummings and Scrivner, 1980). The northeastern province extends from 50°N to 35°N from the Great Lake areas to the eastern Mississippi River system including the Tennessee and Ohio Rivers (Figure 3). This province is largely dominated by illite and chlorite, resulting from intense physical weathering of the Appalachian Mountains Paleozoic rocks (Weaver, 1967; Griffin *et al.*, 1968; Potter *et al.*, 1975). The southwestern Mississippi River and Brazos-Trinity River -draining the Colorado Plateau and the late Tertiary uplifted Llano Estacado (Figure 3)- are characterized by the association of illite and kaolinite (Parry and Reeves, 1968; Glass *et*

al., 1973). The southeastern province (Figure 3) is characterized by its content in kaolinite, resulting from the erosion of polygenetic paleosoils soils characterizing the area (Pirkle, 1960; Balsam and Beeson, 2003).

Marine clay distribution

The comparison of marine clay distribution maps with the main oceanic and physiographic features (Figure 3) provides information on the main factors controlling the present-day distribution of terrigenous clay particles within the GOM (Sionneau *et al.*, 2008). The abundance of smectite in surface sediments over the whole GOM (Figure 4) confirms that the main contributor to deep-sea clay sedimentation is the Mississippi River (Griffin, 1962; Chamley and Kennett, 1976) while the other rivers are of local influence. The Apalachicola and Mobile rivers are responsible for local enrichment in kaolinite and chlorite onto the Alabama-Florida shelf, which partly propagates toward deep portions on the GOM (Griffin, 1962; Balsam and Beeson, 2003). Local illite-enrichment onto the Louisiana shelf (Figure 2, lower panel) reflects the Atchafalaya River supply wheras illite and kaolinite are carried through the Rio Grande system toward the Texas continental shelf and slope (Balsam and Beeson, 2003). Sedimentary processes as differential settling during transportation of clay largely modify the initial signal, as evidenced by the offshore gradient of most clay ratios and by the relative enrichment in smectite *versus* other clays at basin scale (Figure 2).



<u>Figure 4:</u> Surface circulation in the GOM (bold black arrows), including the Loop Current Rings and the Cyclonic Rings (modified from Vukovich and Crissman, 1986; Balsam and Beeson, 2003; Schmitz, 2003; Fan et al., 2004; Ohlmann and Niiler, 2005; Smith and Jacobs, 2005). Westward propagation of smectite from the Mississipi River blue arrow), supply of kaolinite (+ illite) on the western shelf of Florida (red and brown arrows), regional supply of kaolinite and smectite on the westernmost part of the GOM (purple arrows), modified from Sionneau, 2008.

On the eastern side of the Mississippi Delta, the distribution of the clay particles is controlled by the anticyclonic Loop Current, smectite being transported eastward onto the western Alabama shelf and kaolinite being transported southward over the Florida shelf (Figure 4). By contrast, on the western side of the Mississippi Delta, westward transport is dominant onto the Louisiana continental shelf whereas eastward transport prevails on the Texas continental slope.

Summary: The rationale for drawing clay minerals distribution maps over the Misississippi River watershed was to follow a source-to-sink approach, in which the very first step would be to constrain the mineralogy of distinct potential provinces using exactly the same chemical and analytical procedures for present-day mapping -soils, surface and subsurface samples- and for past reconstructions based on sediment archives. These maps were indeed used for sedimentological studies of cores from the GOM, pointing out the respective continental areas successively submitted to erosion that further fed the GOM sedimentation over the two last climatic cycles and the Holocene, and giving informations on either advance-retreat phases of the Laurentide Ice Sheet (LIS) and/or changing precipitation distribution over the Mississippi River watershed area (Sionneau *et al.*, 2010; Montero *et al.*, 2009; 2010; 2011; Sionneau *et al.*, submitted).

The Mediterranean Sea

The Mediterranean is a climatic transitional area between the western European continent - under the influence of the Westerlies and the North African continent - controlled by the seasonal migration of the Inter Tropical Convergence Zone ITCZ (Figure 5). Studying the respective detrital contribution of European river supplies *versus* North African eolian inputs may help to understand the relationships between high and low-latitudes climate. The clay mineralogy of surface sediments, soils, and aerosols were compiled in order to characterize the main present-day sources area and to identify the respective contribution of eolian *versus* fluviatile supply to deep-sea sedimentation (Bout-Roumazeilles *et al.*, 2007; Combourieu-Nebout *et al.*, 2008).



Figure 5: Main low-altitude (red arrows) and high-altitude (thick black arrows) wind trajectories, rivers supply (green arrows, thickness proportional to present-day annual detrital discharge), and main oceanic water masses (LIV: Levantine Intermediate Water, AW Atlantic Modified Water, WMDM: Western and eastern Mediterranean Deep Water) in the Mediterranean. SAL: Saharan Air layer, NSAL: northern branch of the SAL (Saliot, 2005; Bout-Roumazeilles et al., 2007).

Clay mineral sources

The Rhône, Pô and Ebro Rivers (Figure 5), carrying erosion products, supply mostly illite toward the western Mediterranean (Chamley, 1989; Alonso and Maldonado, 1990; Tomadin, 2000). The Aegean rivers dominantly transport smectite toward Eastern Mediterranean, reflecting the specific weathering regime that prevailed on the continent (Erhmann *et al.*, 2007). The Nile River, draining basaltic domains, is responsible for a major input in smectite in the eastern Mediterranean (Revel *et al.*, 2010).

Palygorskite is characteristic of the sub-arid belt (Singer and Galan, 1984; Chamley *et al.*, 1989) where it is formed under chemically restricted conditions. Its main present-day source areas are located in the Saharan belt, in western Morocco (El Mouden *et al.*, 2005) and Tunisian (Grousset *et al.*, 1992). Its peculiar fibrous morphology favours eolian transport but prevents it from any fluviatile transport. Palygorskte is common in Saharan wind blown particles and may be transported over long-range distance, crossing the Mediterranean through meridian transfers (Robert *et al.*, 1984; Coudé-Gaussen *et al.*, 1982; Molinaroli, 1996).



Figure 6: Clay mineralogy of (a) peri-Mediterreanean river particles and sediments and (b) dust and aerosols (e.g. Bout-Roumazeilles et al., 2007; Bout-Roumazeilles et al., submitted).

Illite, kaolinite and smectite can also be transported through eolian processes (Figure 6). Illite displays a North-South gradient on the North African continent, being more abundant in the western Saharan belt (Paquet *et al.*, 1984). By contrast kaolinite abundance is maximum in the southeastern Sahara (Guerzoni *et al.*, 1999), in the Sahelian belt (Pastouret *et al.*, 1978; Caquineau *et al.*, 1998), and in the well-drained lateritic soils characterizing equatorial regions further South (Chamley, 1989) while smectite displays a southeastward increase (Sarnthein *et al.*, 1982; Paquet *et al.*, 1984; Chamley, 1989).

Specific transportation patterns

The occurrence of palygorskite in lake deposits from Corsica, Sardinia, Spain and in the French Alps results from specific atmospheric configuration allowing its transportation across the Mediterranean. The reconstruction of the back trajectories associated with major dust outbreaks reaching Europe (Avila *et al.*, 1997; Rodriguez *et*



al., 2001) allows proposing synoptic patterns that likely promote the northward transportation of palygorskite. These events are seasonally driven by a decreased intensity and/or a northward migration of the Westerlies.

Figure 7: Main potential sources of palygorskite, (a) air back-trajectories for different dust events and (b) main average dust-event trajectories reaching Europe (Bout-Roumazeilles et al., 2007)

Summer outbreaks occur as a depression trench is created between the remote Azores High and the Algerian High (Coudé-Gaussen, 1982; Bergametti *et al.*, 1989a; Moulin *et al.*, 1997; Rodriguez *et al.*, 2001; Torres-Padron *et al.*, 2002). Palygorskite-rich dust originated from western and central part of the Sahara is transported toward the western Mediterranean (Figure 7, route 3). Dust outbreaks reach the northwestern and central Mediterranean (route 1) during winter as a North-South depression corridor initiates between the Azores high and the central Mediterranean high (Rodriguez *et al.*, 2001; Torres-Padron *et al.*, 2002; Magri and Parra, 2002), being constrained by the respective position of the high-pressure cells and the Atlas Mountains. Spring and early summer dust events favor the air masses to cross the central and eastern Mediterranean (Moulin *et al.*, 1997), initiating in palygorskite-rich area of Tunisia (route 1a) while late summer events are shifted westward and reach Corsica and Italy (Bergametti *et al.*, 1989c). The anecdotic transport of palygorskite-rich dust (route 2) originating from western Morocco occurs during fall as a low cell pressure develops off the southwest Spain simultaneously with the Algerian high cell pressure (Rodriguez *et al.*, 2001).

Summary: Compiling various mineralogical data from the peri-Mediterranean continents – mainly from literature-, from dust and aerosols – from sampling and collector, and from recent marine deposit – top core and sediment traps-, and comparying the obtained databse with present-day river and wind deliveries and with air back-trajectories allow to identify the most adequate mineralogical tracers for river *versus* eolian supply over the Mediterranean, providing a well-constrained frame for reconstructing their past variations, in relation with the climatic evolution of the area.

The Cariaco Basin

The mineralogical composition of 95 surface samples from the Cariaco Basin and Orinoco delta was investigated in order to constrain the clay-mineral main provenance and distribution over the basin. The spatial variability of the clay mineral distribution in the Cariaco Basin and in the Orinoco delta (Figure 8) was specifically studied using geo-statistical tools. These approaches generated distribution maps for each clay-mineral species and characterized specific clay association for each geographical area. This study gives new insights on some debating ideas about sedimentary transfers in the Cariaco Basin.



Figure 8: Bathymetry of the Cariaco Basin. Location of the samples studied, main geographical areas as referred in the text. Respective position of the ODP site1002, core PL07-71BC, and mooring of the sediment traps referred in the text.

Distribution of clay minerals

The contribution of the Amazon/Orinoco plume to the Cariaco sedimentation has been extensively investigated in the past few decades (Muller-Karger and Varela, 1990; Muller-Karger and Castro, 1994; Clayton *et al.*, 1999; Peterson *et al.*, 2000; Lorenzoni, 2005; Peterson and Haug, 2006; Martinez *et al.*, 2010). Our dataset indicates that the clay-mineral fraction carried along with the Amazon-Orinoco plume would likely be enriched in smectite when entering the Cariaco Basin. The lack of any significant enrichment in smectite on the northeastern entrance demonstrates that the Amazon-Orinoco plume does not contribute to the Cariaco basin deep sedimentation, in agreement with other evidences including satellite imagery of the plume, salinity profiles and surface sediment geochemistry (Müller-Karger and Castro, 1994; Lorenzoni, 2005; Martinez *et al.*, 2010).

The metamorphic rocks constituting the coastal range appear to be the main source of illite, *via* the Tuy River, for the northwestern side, whereas the Interior range is likely the main source of illite for the northeastern with some minor contribution from the Gulf of Cariaco *via* the Manzanares River (Figure 9). The estimated contribution of the Tuy area to clay sedimentation is twice that of the Manzanares area (Figure 9).

The kaolinite in the Cariaco Basin is widely distributed along the coast between the Tuy-Tac area and the Unare and Neveri Rivers. The Mesozoic and Cenozoic sedimentary formations outcropping in the Unare drainage basin are a major source of kaolinite (Hackley *et al.*, 2006; Guerrero-Alves *et al.*, 2007). Our data indicates that the contribution to clay sedimentation by the Unare, Neveri and Tuy rivers is of similar importance (Figure 9). This is in agreement with previous estimation suggesting that the major sediment sources to the Cariaco basin are the Tuy, Unare and Neveri rivers (Elmore *et al.*, 2009; Lorenzoni *et al.*, 2009; Martinez *et al.*, 2010). But it contrasts with the idea that the Unare River, despite its much larger drainage basin, represents only 10% of the Tuy River discharge (Milliman and Syvitski, 1992; Lorenzoni *et al.*, 2009).



<u>Figure 9:</u> Distribution of the main clay mineral species in the Cariaco Basin using ordinary kriging: a. clay-size fraction ($\mu g/g$ sediment), b. illite, c. chlorite, d. smectite, e. kaolinite, f. regular illite-smectite mixed-layers.

The distribution of the regular illite-smectite mixed-layer minerals (Figure 9) characterized the eastern part of the Cariaco Basin with maximum abundances in the Manzanares and in the Araya areas. The occurrence and relative abundance of illite-smectite mixed-layers (IS) in the easternmost part of the basin is likely related to the nearby-outcropping Mesozoic and Cenozoic sedimentary rocks from the interior range that did not undergo severe metamorphism and thus promoted the preservation of these mixed-layer within the clay-mineral fraction (Figure 9). This very well constrained source is useful for deciphering the time-evolution of the clay mineral content from the Cariaco Basin sediment cores with respect to sea-level changes and/or modifications of the rainfall pattern over northern Venezuela.

New insights

Our new insights on clay-mineral provenance and on the respective contributions of local rivers are used to further examine the results from previous studies in the Cariaco Basin and to propose alternative explanation for the observed variations in the clay-mineral records.

Elmore *et al.* (2009) analyzed the clay content in sediment traps from the CARIACO Time-series Station (Figure 8) in the eastern sub- basin and in core tops from the Unare shelf. Their results evidenced the dominance of kaolinite in sediment traps driven by seasonal variability of the terrigenous flux in the Cariaco Basin, with enhanced river discharge during summer and fall (*i.e.* the rainy season) when the ITCZ lays in its northern position. The proportion of illite within sediment traps was interpreted by the authors as reflecting the eolian

supply to the basin corresponding to a mean annual eolian contribution to Cariaco Basin deep sedimentation of 10%. Our data demonstrates that the Neveri, Manzanares or Tuy rivers are all major sources of illite within the Cariaco Basin (Figure 10). Due to the location of the mooring, any major supply from the Tuy River is unlikely. The distribution maps suggest that the presence of illite in the sediment traps may correspond to a contribution from Neveri River or Manzanares River rather than reflecting eolian supply.



<u>Figure 10:</u> Position of the main geographical areas in a binary diagram: I/S=illite/smectite ratio, I/(C+K)= illite/(chlorite+kaolinite) ratio. ODP 1002 glacial and interglacial average values from Clayton et al., 1999; PL07-71BC from Black et al., 1999; sediment traps from Elmore et al., 2009.

Clayton *et al.* (1999) examined the clay mineral content of site ODP1002 (Figure 10) and found modifications of the illite to smectite ratios (I/S) at orbital timescale, which they attributed to potential contributions from the Amazon-Orinoco system, considering the higher I/S ratio of the samples. However, the position of the ODP samples in the I/S *versus* I/(C+K) – illite to (chlorite plus kaolinite) diagram (Figure 10) allows us to rule out any major contribution from the Orinoco plume during interglacials. Our surface data suggests that the clay mineral compositions of both glacial and interglacial samples from the ODP 1002 site may be reproduced by linearly mixing the supplies of the Tuy and Unare rivers (Figure 10): mixing 5% Tuy River and 95% Unare River reproduces the composition during glacial while mixing 40% Tuy River and 60% Unare River successfully reproduces the average Holocene values.

Summary: This study was the very first attempt to obtain a complete mineralogical set of surface samples from the Cariaco southern continental shelf. The results provided new and original maps of present-day clay minerals distribution from the main rivers, which deliver terrigenous material toward the Caciaco basin. Our clay mineral analyses were performed on the same samples as the ones studied by Martinez *et al.* (2010) and give the opportunity to compare mineral and geochemical detrital proxies. Martinez *et al.* (2010). Our clay mineral data were consistent with the zones identified by Martinez *et al.* (2010) and allowed a clearer differentiation of the Neveri-Unare region from Margarita-Araya region. Any difference between the chemical and mineralogical approaches results from the fact that chemical elements are not distributed as individual species but belong to different mineral structures among which clay minerals. In this sense, the clay mineral distribution maps are smoother relative to chemical maps (each clay species may have its own chemical variability) and are thus believed to provide more straightforward information.

Related publications

- Bout-Roumazeilles, V., Riboulleau, A., Armynot du Châtelet, E., Lorenzoni, L., Tribovillard, N., Murray, R.W., Müller-Kager, F., Astor, Y.M. Clay minerals of surface sediments as a tool for deciphering the respective contributions by several particle-load suppliers to the Cariaco Basin. *JGR-Ocean submitted*.
- Bout-Roumazeilles, V., Nebout, N.C., Peyron, O., Cortijo, E., Landais, A. and Masson-Delmotte, V. 2007. Connection between South Mediterranean climate and North African atmospheric circulation during the last 50,000 yr BP North Atlantic cold events. *Quaternary Science Reviews*, 26: 3197-3215.
- Bout-Roumazeilles V. and Trentesaux, A. 2007. Sedimentologic analysis of cores recovered from the RV Marion Dufesne cruise in the Gulf of Mexico, 2-18 July, 2002, in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., Initial Report of the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002: U.S. Geological Survey Open-File Report 2004-1358, 29 pp.
- Combourieu Nebout N., <u>Bout-Roumazeilles, V</u>., Dormoy, I., Peyron, O., 2009. Sécheresses récurrentes en Méditerranée au cours des derniers 50 000 ans. Science et changements planétaires/Sécheresse, 20 (2): 210-6.
- Riboulleau, A., Tribovillard, N., Baudin, F., <u>Bout-Roumazeilles, V</u>., Lyons, T., 2011. Unexpectedly low organic matter content in Cariaco Basin sediments during the Younger Dryas. Origin and implications. *CR Geosciences*, 343: 351-359.
- Sionneau, T., <u>Bout-Roumazeilles, V.</u>, Biscaye, P.E., Van Vliet-Lanoe, B. and Bory, A. 2008. Clay mineral distributions in and around the Mississippi River watershed and Northern Gulf of Mexico: sources and transport patterns. *Quaternary Science Reviews*, 27: 1740-1751.

Fluviatile transfers – the Gulf of Mexico

Introduction

The Gulf of Mexico is a key area for the global climatic system (Figure 11) because its warm and salty water mass take part in the global thermohaline circulation (THC) (Broecker, 1991). Any change of the hydrology of the GOM may thus affect the THC and global climatic conditions (Broecker *et al.*, 1989; Bond, 1995; Rahmstorf, 1995; Manabe and Stouffer, 1995; 1997, Fanning and Weaver, 1997). The GOM hydrological properties are likely influenced by freshwater –meltwater supplies from the Mississippi River. Terrigenous inputs associated with these events were poorly investigated up to now, although it may provide additional informations on the link between continental and marine records (Bout-Roumazeilles, 1997; 1999; 2007), on the LIS glacial dynamic (Dyke, 2004) and on drainage conditions over North America (Clark *et al.*, 2001; Tarasov and Peltier, 2006; Carlson *et al.*, 2007).



Figure 11: Physiography of the northern GOM with bathymetry of the intraslope domain. Location of the main sediment cores cited.

The Images Cruise PAGE in the GOM in 2002 on board of the RV Marion Dufresne collected a series of sediment cores recording the last climatic cycles which offered a very unique opportunity to decipher the terrigenous signal associated with these freshwater supplies: either freshwater discharge resulting from the melting of the Laurentide Ice Sheet during glacial periods (Montero *et al.*, 2009; Sionneau *et al.*, 2010; Bout-Roumazeilles *et al.*, in prep.) or even from megaflood episodes associated with migration of the precipitation belt during interglacial periods (Montero *et al.*, 2011).

Provenance of freshwater pulses during the last deglaciation

Episodic meltwater discharge entered the GOM *via* the Mississippi River during the last deglaciation. The climatic impact of these meltwater discharges has been debating for years. These freshwater discharges were extensively described in the Gulf of Mexico (Kennett and Shackleton, 1975; Williams, 1984; Kennett *et al.*, 1985; Flower *et al.*, 2004, Hill *et al.*, 2006; Meckler *et al.*, 2008). As these melt water events were responsible for the huge supply of freshwater into the GOM, there were thought to have a potential impact on the hydrology of the GOM (Fairbanks, 1989; Broecker and Denton, 1990; Rahmstorf, 1995; Manabe and Stouffer, 1997). However, some authors argue that these meltwater discharges had little effect on the THC because the freshwater

signal was not propagating toward the Atlantic Ocean, according to the lack of any clear evidence on the northeastern part of the GOM (Roche *et al.*, 2007; Carlson, 2009).



<u>Figure 12:</u> Comparison between meltwater records from the Louisiana slope – LOUIS cores (Aharon, 2003), from the Orca Basin- EN32-PC6 (Flower et al., 2004), and clay mineral ratio S/(I+C) for Orca Basin (MD02-2552- Sionneau et al., 2010) and Pigmy Basin (MD02-2553- Montero et al., 2009). The smectite-rich events are delimited by blue shading.

The meltwater discharges originating from the Laurentide Ice Sheet likely delivered fine-grained detrital particles to the GOM *via* the Mississippi River (Knox, 1996; Brown and Kennett, 1998). During deglaciation the southern margin of the LIS encompassed the smectite-rich northwestern Mississippi provinces and the northeastern province where illite and chlorite predominate (Sionneau *et al.*, 2008). According to this specific characteristic, the clay mineral ratio between smectite and illite plus chlorite (S/ (I+C) is used to document the origin of these deglacial megafloods in sediment cores from the GOM (Montero *et al.*, 2009; Sionneau *et al.*, 2010). These results allow better constraining the connection between glacial history modelling (Clark *et al.*, 2001; Dyke, 2004; Tarasov and Peltier, 2006; Carlson *et al.*, 2007) and the evolution of the GOM hydrological properties (Kennett and Shackleton, 1975; Kennett *et al.*, 1985; Brown and Kennett, 1998; Aharon, 2003; Flower *et al.*, 2004).



<u>Figure 13:</u> Records of meltwater discharges in GOM cores between 15 and 10 ka cal. BP: MWP-1A (Fairbanks, 1989); MWF: Meltwater floods on the Louisiana Shelf (Aharon, 2003), δ^{18} O foraminifer record from core EN32-PC6, Orca Basin (Flower et al., 2004); reworked nannosossils from core EN32-PC4, Orca Basin (Marchitto and Wei, 1995); clay mineral ratio S/(I+C) from core MD02-2552, Orca Basin (Sionneau et al., 2010), accumulation rate of terrigenous carbon from DSDP site 619, Pigmy Basin (Jasper and Gagosian, 1990); clay mineral ration S/(I+C), C/N ratio and grain-size mode from core MD02-2553, Pigmy Basin (Montero et al., 2009). Units 1 to 4 are bsed on their sedimentological and geochemical characteristics. Shaded interval indicates meltwater pulses from the southwest margin of the LIS.

In the Orca Basin (Figure 12), the typical glacial illite and chlorite-rich sedimentation is interrupted during deglaciation (between 20 and 12.9 ka cal. BP) by recurrent episodes of enhanced smectite supply that are synchronous with freshwater pulses originating from the southern margin of the melting LIS (Figure 12) evidenced by δ^{18} O records from the Orca basin (Leventer *et al.*, 1982; Flower *et al.*, 2004) and the Louisiana slope (Aharon, 2003) and by continental studies (Fisher, 2003; Dyke, 2004; Teller *et al.*, 2005).

The clay composition indicates that the early freshwater pulses (MeltWater Floods: MWF-1 to MWF-2 between 18.8 and 16.1 ka cal. BP) occurred in a series of separate floods originating from the northwestern Mississippi River and Missouri River watersheds (Sionneau *et al.*, 2010). Their timing and chronology are consistent with previous evidences of the LIS retreat (Mickleson and Colgan, 2003) and with discharge modelling (Tarasov and Peltier, 2006). However the freshwater discharge occurring at 16.5 ka cal BP evidenced on the Louisiana shelf (Aharon, 2003) is not associated with any change in the mineralogical association (Figure 12). This peculiar event is contemporaneous with the fragmentation of the LIS on its Atlantic margin during Heinrich event 1 (Bond and Lotti, 1995; Vidal *et al.*, 1997). By contrast with the other MWF events, the destabilization of southeastern margin of the LIS likely promoted the erosion of the illite and chlorite-rich Great Lake area (Figure 12), and did not modify the glacial clay association (Sionneau *et al.*, 2010).



Figure 14: Positions of the ITCZ and Jet Stream, main moisture inflow patterns toward the Mississippi River watershed area and surface oceanic conditions in the GOM during summer and winter (Ziegler et al., 2008; Wang and Enfield, 2001; Knox, 2000, 2003; Forman et al., 1995; Liu and Fearn, 2000). Main mineralogical provinces after Sionneau et al., 2008.

The most recent MFW events evidenced in the clay records (15.8 to 12.9 ka cal BP) are associated with the so-called Meltwater Spike (MWS) defined by a major $\delta^{18}O_{SW}$ excursion in the Orca Basin (>2.5‰) (Kennett and Shackleton, 1975; Leventer *et al.*, 1982; Broecker *et al.*, 1989; Flower and Kennett, 1990; Brown and Kennett, 1998; Flower *et al.*, 2004) and are synchronous with the MeltWater Pulse MWP-1A (Tarasov and Peltier, 2005). The Meltwater Spike was investigated in the nearby Pigmy basin (Figure 13) where high accumulation rates (up to 300 cm/kyr) allow a high-resolution study of this peculiar event (Montero *et al.*, 2009). The stair-step patterns displaying by clay mineralogy, geochemistry and grain-size records reveals the poly-phased nature of the MWS.

According to its specific sedimentological characteristics (Figure 13), the early phase of the MWS is attributed to the initial erosive flood of the main northeastern Mississippi River channel that likely corresponds to the proglacial Lake Wisconsin outburst (Knox, 1996). Geochemical and mineralogical data indicate that the most intense meltwater pulse remobilized clay-rich terrace deposits from the northwest part of the Mississippi and Missouri Rivers watershed. According to the precise chronostratigraphy of the core, this major terrigenous event occurred simultaneously with the most intense period of freshwater discharge previously described or modelled (Licciardi *et al.*, 1999; Tarasov and Peltier, 2005). The sedimentological record of the late phase of the MWS (Figure 13) indicates a return to quasi-normal conditions, with a progressive decrease of the erosional processes and a northeastward migration of the main clay provenance (Montero *et al.*, 2009).

Summary: The mineralogical study of meltwater floods characterizing the last deglaciation reveals that the early freshwater pulses originated from the northwestern Mississippi and Missouri provinces, suggesting instability of the southwestern margin of the LIS, consistently with reconstructions of the LIS retreat and discharge modelling. The detailed study of the main meltwater discharge (MWS) reveals its polyphased signature with an initial erosive phase, a main flooding phase, and a progressive return to normal conditions.

Holocene changes in precipitation regimes over North America

The reduced influence of glacial processes during interglacial periods allows investigating the impact of varying atmospheric configuration both on the evaporation-precipitation budget in the GOM, on the associated moisture transfer toward the North American continent and on the hydrological regime of the Mississippi River system (Figure 14). The Atlantic Warm Pool (AWP) is the main source of moisture (Wang and Enfield, 2001) and moisture transfer toward the North American continent is primarily controlled by atmospheric configuration, itself seasonally driven by the respective position of the Jet Stream; the Bermuda High and the ITCZ (Forman *et al.*, 1995; Liu and Fearn, 2000; Harrison *et al.*, 2003; Knox; 2003).



Figure 15: Comparison of the mineralogical (S/I+C) and geochemical (K) signatures of the sediments from Pigmy basin throughout the Holocene (Montero et al., 2010) with paleoclimate records from the GOM and Caribbean area (Hodell et al., 1991; Haug et al., 2001; Poore et al., 2004; Kennedy et al., 2006; Richey et al., 2007; Nurnberg et al., 2008; Mueller et al., 2009).

The core MD02-2553 from Pigmy basin provides a high-resolution record of the Holocene variability. Its chronology is based on sixteen AMS 14C radiocarbon dates (Poore *et al.*, in press), with a mean sedimentation rate of 35.9 cm/ka (Montero *et al.*, 2010). Mineralogical (S/I+C) and geochemical (K and Ti) data from Pigmy Basin (Figure 15) indicates fluctuations of the Mississippi River discharge during the Holocene (Montero *et al.*, 2010). The sedimentary record evidences repetitive variations of the main terrigenous supply, which oscillated between the northwestern smectite-rich Mississippi and Missouri Rivers provinces and the northeastern illite and chlorite-rich Great Lakes area (Figure 15).



<u>Figure 16:</u> Schematic summer reconstructions of regional atmospheric circulation patterns during the early (right panels) and late Holocene (right panels) and paleoclimatic implications. High S/(I+C) ratio (upper panels) corresponds to predominant wet periods in central North America while low S/(I+C) ratios (lower panels) corresponds to predominant dry periods. Position of the Jet Stream modified from Knox, 2000; 2003. Mean summer position of the Bermuda High modified from Forman et al., 1995 and Liu and Fearn, 2000. Orange/yellow shadings refer to large/small AWP extension respectively. Position of the ITCZ and meridional extension of the AWP through the Holocene are monitored using paleoclimate records from the circum-Caribbean region and the northern GOM (Montero et al., 2010).

During the early Holocene, the remaining LIS still played some role on the climate system and its progressive melting may have impacted the Mississippi River terrigenous supply (Figure 15). By contrast, during the midand late Holocene, the disappearance of the LIS ruled out any glacially-driven sedimentary changes. The observed variations in the sedimentary record may thus reflect modifications of the continental drainage area, resulting from the repetitive meridian migration of the precipitations belt over the North American continent (Knox, 2000; 2003). The comparison of our data with previously published records (Hodell *et al.*, 1991; Haug *et al.*, 2001; Willard *et al.*, 2005; Kennedy *et al.*, 2006; Denniston *et al.*, 2007; Nordt *et al.*, 2008; Mueller *et al.*, 2009) allows constraining the geographical areas submitted to dry/wet conditions in relation both with the respective position of the Jet-Stream, the High and Low pressure cells and the ITCZ, and with the extension of the Atlantic Warm Pool (AWP) (Figure 16). It provides additional information (Figure 16) on the variations of the main moisture pathway from the Caribbean-GOM area and on the position of the associated precipitation belt over the North American continent throughout the Holocene (Montero *et al.*, 2010). This whole dataset allows reconstructing two main atmosphere-ocean configurations that successively predominated during the Holocene (Figure 16).

The northern position of the Jet Stream and southwest migration of the Bermuda High result in concentrating the precipitation over the northwestern Mississippi River while the northeastern province experienced dry conditions. By contrast, when the Jet Stream is located southward and the Bermuda High displaced northeastward, precipitations mostly fall over the northeastern province and along the Atlantic margin (Figure 16). These two configurations are modulated throughout the Holocene by the position of the ITCZ and the northward extension of the AWP (Poore *et al.*, 2003; Richey *et al.*, 2007; 2009, Wang *et al.*, 2008), which both experienced modification as the LIS progressively disappeared (Lovvorn *et al.*, 2001; Shuman *et al.*, 2002; Mayewski *et al.*, 2004; Nordt *et al.*, 2008) (Figure 17).

Clay mineral variations exhibit variations very similar with maximum sea-salt sodium concentrations (ssNa) in Greenland. Smectite is inversely correlated to high ssNa (Montero *et al.*, 2010), which is believed to be an indicator of storminess and sea-spray in the atmosphere of high-latitude regions. The variability of Mississippi River runoff is thus likely related to changes in high-latitude atmospheric circulation. Indeed the sedimentary record is characterized by a 2.5 ka cyclicity, consistent with the ssNa concentration signal (Figure 17), which supports a dominant atmospheric control (O'Brian *et al.*, 1995; Stuiver *et al.*, 1995; Alley *et al.*, 1997; Mayewski *et al.*, 2004; Debret *et al.*, 2007; 2009) on North American hydrological and erosional changes (Montero *et al.*, 2010).



<u>Figure 17</u>: Multitaper spectral analysis of Greenland GISP2 sea-salt sodium concentrations (ssNa) (O'Brien et al., 1995) and clay mineral S/(I+C) ratio from core MD02-2553, Pigmy Basin, Gulf of Mexico (Montero et al., 2010).

<u>Summary:</u> Our results highlight modifications of moisture transfer throughout the Holocene, and were interpreted as resulting from two dominant atmospheric configurations that successively controlled the precipitation distribution over the North American continent, with an apparent cyclicity of 2.5 ka. The consistency between the GOM terrigenous clay record and Greenland atmospheric parameters suggests a rapid transfer of the initial external forcing through atmospheric processes.

Contrasting rainfall patterns over North America during the Holocene and the Eemian

The Eemian is characterized by higher boreal summer insolation compared with the Holocene (Berger and Loutre, 1991; CAPE project Members, 2001; 2006) and by the early disappearance of the LIS (Carlson, 2008). Contrastingly with the Holocene, the LIS deglaciated before the insolation reached its maximum during the Eemian allowing the radiation to be fully effective (Figure 18).

The long and precise sedimentary record from the core MD02-2549 collected in La Salle basin was investigated in order to check the impact of these slight differences both in insolation and ice-sheet extent on the precipitations patterns over the North American continent (Montero *et al.*, 2011). The chronostratigraphy of the core (Montero *et al.*, 2011) is based on tuning carbonate content to the LR04 (Lisiecki and Raymo, 2005).



<u>Figure 18:</u> Sedimentological records over the Holocene and Last Interglacial periods : clay mineral ratio S/(I+C) (blue), kaolinite % (red), K_{XRF} abundance (orange) in cores MD02-2553, Pigmy Basin and MD02-2549, La Salle Basin (Montero et al., 2011); Sea-surface temperatures (green) derived from Mg/Ca ratio of G. ruber in core MD02-2575, De Soto Canyon

(Ziegler et al., 2008); June insolation at 30°N (Berger and Loutre, 1991). The area of the Laurentide Ice Sheet (LIS) is represented as a fraction of the Last Glacial maximum LIS area (Shuman et al., 2005).

The Eemian is characterized by lower smectite and larger kaolinite concentrations (Figure 18), reflecting different terrigenous supply during the two timeslices (Montero *et al.*, 2011). It reveals larger contribution from the illite-rich northeastern Great Lakes province and from the kaolinite-rich Upper Mississippi province (Sionneau *et al.*, 2008) during the Eemian compared with the Holocene.

According to their present-day distribution over the North American continent (Gustavsson *et al.*, 2001; Kujau *et al.*, 2010), geochemical elements (Figure 18) support a reduced contribution of the northwest and southeast provinces during the Eemian relative to the Holocene (Montero *et al.*, 2011). It indicates that the main moisture flux, controlling partly the precipitation distribution, reached a rather large area encompassing both the northwest and northeastern provinces. These findings are supported by the unusual development of paleosols in the North Mississippi River during the Eemian (Ruhe, 1974; Forman *et al.*, 1995; Muhs *et al.*, 1999; Hall and Anderson, 2000; Forman and Pierson, 2002).



Figure 19: Reconstructed atmospheric configurations for the late Holocene (left panel) and for the Eemian (right panel) periods and their impact on climate conditions and moisture transfer (Montero et al., 2011).

The observed difference in detrital provenances during the Eemian and the Holocene is assumed to result from the distinct LIS extent and boreal summer insolation intensity that characterize the two interglacials (Montero *et al.*, 2011). Indeed, higher boreal insolation resulted in warmer summer temperature (Berger and Loutre, 1991; CAPE project Members, 2001; 2006) and increased the latitudinal temperature gradient (Kaspar and Cubasch, 2007), which modified the moisture transfer patterns. It also likely favoured enhanced enpansion of the AWP and a northward migration of the ITCZ during summer (Figure 19) compared to the Holocene (Ziegler *et al.*, 2008). Moreover, the early retreat of the LIS during the Eemian modified the respective position of the Jet Stream (Figure 19) and of the Bermuda High (Forman *et al.*, 1995; Bartlein *et al.*, 1998, Webb *et al.*, 1998; Shuman *et al.*, 2002). These combined effects modified the mean atmospheric configuration during the Eemian (Figure 19), promoting the intense pumping of moisture from the GOM and Caribbean areas and distributing precipitation over widely extended continental areas encompassing the Upper Mississippi River and the northeast Great Lakes province (Montero *et al.*, 2011).

Summary: The comparison of geochemical and mineralogical signature of sediment deposited during the Holocene and the Eemian points out the impact of slight modification of insolation and ice-sheet extension both on moisture transfer and precipitation distribution. The reconstructed atmospheric circulation suggests wetter conditions over the Mississippi River watershed area during the Eemian, and highlights the sensitivity of atmospheric circulation and moisture transfer patterns to small changes in radiative forcing.

Related publications

- Bout-Roumazeilles V. and Trentesaux, A. 2007. Sedimentologic analysis of cores recovered from the RV Marion Dufesne cruise in the Gulf of Mexico, 2-18 July, 2002, in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., Initial Report of the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002: U.S. Geological Survey Open-File Report 2004-1358, 29 pp.
- Montero-Serrano, J.C., <u>Bout-Roumazeilles, V.</u>, Tribovillard, N., Sionneau, T., Riboulleau, A., Bory, A. and Flower, B. 2009. Sedimentary evidence of deglacial megafloods in the northern Gulf of Mexico (Pigmy Basin). *Quaternary Science Reviews*, 28 (27/28): 3333-3347.
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- Tribovillard, N., <u>Bout-Roumazeilles, V.</u>, Algeo, T., Lyons, T.W., Sionneau, T., Montero-Serrano, J.C., Riboulleau, A. and Baudin, F. 2008. Paleodepositional conditions in the Orca Basin as inferred from organic matter and trace metal contents. *Marine Geology*, 254: 62-72.
- Tribovillard, N., <u>Bout-Roumazeilles, V.</u>, Sionneau, T., Serrano, J.C.M., Riboulleau, A. and Baudin, F. 2009. Does a strong pycnocline impact organic-matter preservation and accumulation in an anoxic setting? The case of the Orca Basin, Gulf of Mexico. *Comptes Rendus Geoscience*, 341: 1-9.

Oceanic Transfers – the North Atlantic Ocean

Introduction

The knowledge of carbon cycle budget is one of the biggest chalenge in paleoclimatology, and relationships between CO_2 concentrations and modification of deep oceanic circulation during glacial periods are still a matter of debate. The high northern latitude oceans influence the global environment through the formation of permanent and seasonal ice cover, transfer of sensible and latent heat to the atmosphere, and by deep-water formation and deep ocean ventilation which control or influence the oceanic and atmospheric carbon content. The North Atlantic Ocean is a key area where much of the world's deep waters are formed with associated regional ocean-atmosphere heat flux. In that frame, modification of the North Atlantic deep water might have played an active role in changing CO_2 distribution through complex atmosphere-ocean exchanges.

Modifications in terrigenous supply toward the northwestern Atlantic during termination 2

Formation of North Atlantic Deep Water (NADW) is one of the fundamental processes controlling the thermohaline circulation (Duplessy *et al.*, 1988; Broecker and Peng, 1989). There is compelling evidence for modification of circulation in the North Atlantic during glacial periods but debate as to the magnitude and nature of the re-configuration (Boyle, 1988; Duplessy *et al.*, 1988; Broecker and Peng, 1989; Oppo and Fairbanks, 1990; Hillaire-Marcel *et al.*, 2001).



<u>Figure 20:</u> Sketch map showing the main geological units according to their ages and/or petrography, locations of studied cores and ODP sites, bathymetry and actual deep-water mass circulation in the North Atlantic Ocean.

In the North Atlantic Ocean the clay fraction of Pleistocene sediments typically are mostly of terrigenous origin (Biscaye, 1965; Chamley, 1989; Fagel et al., 1996; Bout-Roumazeilles et al., 1997; 1999; Vandaraveroet

et al., 2000) due to the large surrounding continental masses (Figure 20). Our methodology is to use changes in clay mineralogy and combined large magnitude variations in Sr-Nd-Pb isotope ratios of clays as proof of changing source provenance (Fagel *et al.*, 1996; 1997; 1999; 2001, 2002; 2004; Innocent *et al.*, 1997, 2000), focusing on termination II - Marine isotope stage 6/Marine isotope stage 5 (MIS6-MIS5) - in the northwestern Atlantic Basin displaying the most proeminent changes in the detrital records (Bout-Roumazeilles *et al.*, 1999; Fagel *et al.*, 2006).

Two cores from the northwestern Atlantic basin were studied, SU90-11 (44°N, 40°W) and SU90-12 (51°N, 39°W), respectively located at 3615 m and 2950 meter-depth (Figure 20). For each site an age model is based on benthic and/or planktonic δ^{18} O records.



<u>Figure 21:</u> Mineralogical and isotopic compositions of clay particles for cores SU90-11 (plain) and SU90-12 (dotted) between 70 and 170 in ka cal. BP (see Figure 1 for location of cores). Left panel: % of illite-vermiculite mixed-layer (pink), % of illite (green) and % of smectite (blue). Right panel : 87 Sr/ 86 Sr isotope ratios (pink); 207 Pb/ 204 Pb isotope ratios (green); $\varepsilon_{Nd} = ({}^{143}$ Nd/ 144 Nd/0.512636-1)*10⁻³. The diamond represents the isotopic signatures of the clay fraction associated with ice-rafted deposit (IRD).



<u>Figure 22:</u> Upper panel: ε_{Nd} vs ⁸⁷Sr/⁸⁶Sr isotope compositions (crosses) of potential source areas (see Figure 20 for color legend), Shaded areas represent average isotope composition of potential provenances (modified from Thierens et al., 2012), Colored rectangles refer to the corresponding terranes on Figure 20, with respect to bedrock ages (e.g. Thierens et al., 2012; Farmer et al., 2003; Grousset et al., 2001; Revel et al., 1996b). ε_{Nd} vs. ⁸⁷Sr/⁸⁶Sr isotope composition of samples from cores SU90-11 (circles) and SU90-12 (squares) (Figure 21). Mixing lines between the potential source areas are represented. Lower panel: enlargement of the upper panel; sample ages are indicated within the symbols. Blue, red and green symbols correspond to glacial, interglacial and glacial-interglacial (G-IG) transition deposits.

MIS 6 is dominated by illite and smectite whereas the presence of illite-vermiculite mixed-layer characterized MIS5. A peak in smectite marks termination II at both sites while illite decreases (Figure 21). In the northwestern Atlantic Basin (Figure 20), chlorite and illite derive mainly from the Precambrian craton of the North American Continent, Baffin Island, and Greenland (Nielsen *et al.*, 1989; Fagel *et al.*, 1997; Bout-Roumazeilles *et al.*, 1999) while the illite-vermiculite mixed-layer originates from the Appalachain Paleozoic rocks (Bout-Roumazeilles *et al.*, 1999; Vanderaveroet *et al.*, 2000). The smectite is mainly advected from from the northeastern basin *via* deep circulation (Fagel *et al.*, 1996; 2001; Bout-Roumazeilles *et al.*, 1997; Kissel *et al.*, 1997).

Typically glacial sediments are characterized by an ε_{Nd} of around -16, relatively low ⁸⁷Sr/⁸⁶Sr ratios (0.729) and have high ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb (Figure 22). In contrast MIS5 sediments have much lower ε_{Nd} values (-22) and higher ⁸⁷Sr/⁸⁶Sr ratios up to 0.736, lower ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb. In addition glacial-interglacial (G-IG) samples define significantly different domains on Nd-Sr and Pb-Pb diagrams (Figures 22 and 23).

Glacial sediments plot around the mixing line between the SE Canadian Paleozoic Provinces and the Gulf of St. Lawrence River area. The isotopic compositions of samples from early MIS6 point out that the northeastern Canadian Proterozoic and Archean provinces constitute a third end-member (Grousset *et al.*, 1988; Gwiazda *et al.*, 1996; Revel *et al.*, 1996b; Innocent *et al.*, 1997; Winter *et al.*, 1997; Hemming *et al.*, 1998; Fagel *et al.*, 1999) (Figure 22). In contrast during the interglacial stage 5 (Marine Isotopic Stage - MIS5), sediments plot near a mixing line between the southeastern Canadian Paleozoic Provinces and the Archean Labrador and West Greenland Provinces. The combined Sr-Nd isotope data establish that the main sedimentary supply changed at the Glacial-Interglacial transition with Archaean-Early Proterozoic sources becoming more important.



<u>Figure 23:</u> Conventional ²⁰⁸Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb diagram for cores SU90-11 (squares) and SU90-12 (circles) (see Figure 20 for location and Figure 21 for sample ages), and isotope composition of potential sources (Gwiazda et al., 1996; Innocent et al., 1997; Winter et al., 1997; Hemming et al., 1998; Fagel et al., 2002; 2004). Mean data for Proterozoic and Phanerozoic Terranes are also shown. Sample ages are indicated within the symbols. Blue and red symbols correspond to glacial and interglacial deposits. The blue and red shaded areas refer to MIS6 and MIS5 respectively.

Combined Sr-Nd-Pb isotope variations and the petrographic character of the continental areas surrounding the Labrador sea, demonstrate unequivocally that the Archaean and Early Proterozoic areas of Hudson Bay and Baffin Island constituted the main terrigenous sources for clay particles during interglacial stage 5 (Figure 22). The inferred clay provenance during interglacial stage 5 is similar to present-day
distribution. In contrast, during glacial stage 6 the major source of detrital material was characterized by much younger Nd model ages. Nd-Sr-

Lower ²⁰⁶Pb/²⁰⁴Pb ratios during MIS 5 (Figure 23), suggest clay particles being derived from old crust which have undergone high grade metamorphism that resulted in U and Th depletion (e.g., Archaean-Early Proterozoic of Labrador and W. Greenland). By contrast, the more radiogenic Pb data from the MIS6 must be derived from younger Phanerozoic terranes that have not undergone U and Th depletion (*e.g.*, Panafrican terranes and Paleozoic of southern Canada) (Gwiazda *et al.*, 1996; Innocent *et al.*, 1997; Winter *et al.*, 1997; Hemming *et al.*, 1998; Fagel *et al.*, 2002; 2004).

Pb isotope compositions suggest that the Paleozoic terranes of southern Canada are the most probable sources (Figures 22 and 23). Although ice-sheet development would obviously have changed the regions of continental crust undergoing the most extensive weathering, this process alone could not explain the observed variation in clay provenance. If ocean circulation during glacial times had continued exactly as in interglacial times, a Baffin Bay isotopic signature would be recorded in material derived from the continental shelf where sediments had accumulated during the previous interglacial periods (Wand and Hess, 1996; Bout-Roumazeilles *et al.*, 1999; Hesse *et al.*, 1999). Furthermore the progressive retreat of the continental ice-sheet at the MIS6-MIS5 transition cannot explain the rapid change in the dominant terrigenous supplies within ± 2 kyr. The rapid change in the Nd isotope signature at the stage 6-stage 5 boundary establishes a rapid change in provenance and hence deep-water circulation. This interpretation is reinforced by the rapid increase of smectite at the MIS6-MIS5 transition (Figure 21), which evidences the temporarily supply of deep-water originating from the northeastern Atlantic basin, suggesting early NADW penetration toward the northwestern Atlantic basin.

Summary: We document changes in the provenance of terrigenous supply in the northwestern Atlantic basin at the transition between glacial marine stage 6 and interglacial stage 5 through isotopic geochemical and mineralogical studies of terrigenous clay-sized particles. The isotopic signatures of the clay fraction clearly show a greater proportion of northern sources during interglacial stage 5 compared with stage 6. Changes in terrigenous mineralogy and geochemistry during Termination II indicate rapid changes both in provenance and in deep circulation, suggesting an early NADW penetration toward the northwestern Atlantic basin.

Contrasting G/IG terrigenous provenances in the northeastern Atlantic

In the northeastern Atlantic basin, smectite is the main component of the terrigenous fraction deposited during interglacials (Figure 24). According to its mineralogical and geochemical signature, smectite is a secondary volcanic product, originating mostly from Iceland and the Faeroe Islands. Smectite is redistributed into the basin by deep-water masses (Fagel *et al.*, 1996) flowing along the mid-atlantic ridge and building smectite-rich contourites (Figure 20). By contrast, the clay mineralogy of sediments deposited during glacial periods (Figure 24) in the northeastern Atlantic basin is mostly composed of illite, chlorite and kaolinite, originating from the western and northwestern parts of Europe whereas smectite is strongly reduced (Bout-Roumazeilles *et al.*, 1997).



Figure 24: Variations of the smectite percentage in cores MD99-2247, MD95-2014, SU90-33 and ODP site 984 from the northeastern Atlantic basin (Kissel et al., 1997; Bout-Roumazeilles et al., 1997; Bout-Roumazeilles et al., 1999). See Figure 20 for cores location.

The increase supply of inherited clays (*i.e.* illite and chlorite) resulting from the intensification of physical weathering, on the continent (Chamley, 1989; Bout-Roumazeilles *et al.*, 1997; Bout-Roumazeilles *et al.*, 1999) could not explain totally the amplitude of the observed mineralogical changes. Alternatively, the decrease of smectite supply during glacials could either result from the presence of an ice-sheet over Iceland preventing from smectite export toward the ocean or from modifications of the deep circulation (Bout-Roumazeilles *et al.*, 1997). Both physical and mineralogical proxies support the hypothesis of decrease of the Iceland Scotland Overflow Water (ISOW) strength during glacial (Kissel *et al.*, 1997).



<u>Figure 25:</u> Upper panal: ε_{Nd} vs. ${}^{87}Sr/{}^{86}Sr$ isotope compositions (crosses) of potential source areas (see Figure 20 for color legend), Shaded areas represent average isotope composition of potential provenances (modified from Thierens et al., 2012), Colored rectangles refer to the corresponding terranes on Figure 20, with respect to bedrock ages (e.g. Thierens et al., 2012; Farmer et al., 2003; Grousset et al., 2001; Revel et al., 1996b). ε_{Nd} vs. ${}^{87}Sr/{}^{86}Sr$ isotope composition of samples from cores ODP984 (squares)) and SU90-08 (circles and diamonds). Mixing lines between the potential source areas are represented. Lower panel: enlargement of the upper panel; sample ages are indicated within the symbols. Blue, red and green symbols correspond to glacial, interglacial and G/IG transition deposits.

Clay sedimentation was studied at the ODP site 984 (Figure 24) during the last million years. Changing G/IG terrigenous provenance at Termination II (MIS6-MIS5 transition) and its implications on the deep-circulation were specifically investigated using radiogenic isotopes (Sr-Nd-Pb). Distinct Sr-Nd-Pb isotope signatures depending on age and thermo-tectonic evolution characterize different domains surrounding the northeastern Atlantic basin. The "young" volcanogenic system encompassing Iceland, the Greenland thulean province, the Faeroe islands and the Azores, characterized by low ⁸⁷Sr/⁸⁶Sr, and positive values of the ε_{Nd} (Figure 25). The "old" crustal system, characterized by high ⁸⁷Sr/⁸⁶Sr and negative values of ε_{Nd} corresponds to Scandinavia and Europe. The Pb isotopic composition allows distinguishing the Sveconorwegian belt, the Scandinavia panafrican, European variscan and panafrican crusts (Figure 26).

The clay particles deposited at OSP site 984 during Stage 6 have high values of 87 Sr/ 86 Sr ratio and negative value of ϵ_{Nd} , indicating a dominant crustal supply the northwestern part of Europe – Scandinavia or British Isles (Figure 25). However, both 206 Pb/ 204 Pb and 208 Pb/ 204 Pb ratios show very radiogenic values indicating that the main terrigenous illite supply during stage 6 resulted from a mixing between European panafrican and paleozoic norwegian provenances (figure 26).

At the MIS6-MIS5 transition, the ⁸⁷Sr/⁸⁶Sr ratio decreases rapidly down to 0.709 (Figure 25), while the ε_{Nd} increases rapidly reaching positive values. The large range in ⁸⁷Sr/⁸⁶Sr is coupled with a large decrease in illite (Figure 24). Over the same period the ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb isotope ratio decrease down and remains less radiogenic during stage 5 than during stage 6, reflecting an increase volcanogenic contribution (Figure 26). The unradiogenic character of the Sr isotopes and the positive value of the ε_{Nd} during MIS5, associated with the increase of the smectite within the clay fraction, confirm that the main detrital supply to deep-sea clay sedimentation during the interglacial is transported from Iceland toward the basin *via* the ISOW.



<u>Figure 26:</u>²⁰⁸Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb for cores SU90-08 and ODP site 984. Mean data for potential terranes are shown.

Summary: Mineralogical and geochemical data indicate distinct terrigenous provenances in the northeastern Atlantic basin during MIS6 and MIS5. It points out a dominant West European source, implying weak deep-water transportation *via* the ISOW during MIS6. By contrast, the ISOW appears to be the main sedimentary supplier during MIS5. These results suggest a severe oceanic re-organization during termination II in the northeastern Atlantic basin.

Related publications

- Bout-Roumazeilles, V., Cortijo, E., Labeyrie, L. and Debrabant, P. 1999. Clay mineral evidence of nepheloid layer contributions to the Heinrich layers in the northwest Atlantic. *Palaeogeography Palaeoclimatology Palaeoecology*, 146: 211-228.
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Habilitation à diriger des Recherches

Atmospheric transfers – the Mediterranean

Introduction

The Mediterranean is a transitional area where northern and southern climatic influences tightly interact (*e.g.* Magny *et al.*, 2009). Previous studies provided evidences of contrasting seasonality across the Mediterranean during the Holocene (Cheddadi *et al.*, 1991; Ariztegui *et al.*, 2000; Magny *et al.*, 2002; Magny *et al.*, 2007, Tzedakis, 2007; Zanchetta *et al.*, 2007; Sadori *et al.*, 2008; Roberts *et al.*, 2008; Frigola *et al.*, 2009; Roberts et al., 2011; Jalut *et al.*, 2009; Peyron *et al.*, 2011; Vannière *et al.*, 2011), but estimating the respective atmospheric and oceanic control on Mediterranean climatic evolution through their impact on eolian and fluviatil systems is still complex. In this frame, combining clay mineralogy with grain-size analyses and geochemical tracers would allow retracing significant variations of detrital supply in the Mediterranean and inferring any major past modifications of both atmospheric and oceanic terrigenous transfers patterns.

North African eolian supply toward the western Mediterranean and the tropical Atlantic during the last glacial period

Complex interactions between the European westerly wind system and atmospheric configurations over the Mediterranean have been shown in several sedimentary records (Cacho *et al.*, 2000; Combourieu-Nebout *et al.*, 2002; Moreno *et al.*, 2002; 2005; Sanchez-Goni *et al.*, 2002). The eolian contribution to deep-sea sediments is of major importance in the Mediterranean (Prospero, 1981a; 1981b; Loye-Pilot *et al.*, 1986; Pye, 1987; Bergametti *et al.*, 1989, Tomadin and Lenaz, 1989; Matthewson *et al.*, 1995; Guerzoni and Chester, 1996). Indeed, massive plumes of desert dust export clay-mineral particles to the Atlantic Ocean and to the Mediterranean (Rea *et al.*, 1985; Guerzoni and Chester, 1996).



Figure 27: Main low- and high- wind trajectories, and rivers supply.Location of the sediment cores mentionned in the text. Major, secondary and minor dust sources modified from D'Almeida, 1986; Brooks and Legrand, 2000; Caquineau et al., 2002; Israelevich et al., 2002; Prospero et al., 2002; Goudie, 2003; Formenti et al., 2011.

Saharan dust originating from southern Sahara and Sahelian regions (Figure 27) are seasonally transported toward the tropical Atlantic Ocean either by northeast trade winds or through the Saharan Air Layer (Schütz, 1980; Coudé-Gaussen *et al.*, 1987; Bergametti *et al.*, 1989b; Grousset *et al.*, 1992; 1998; Matthewson *et al.*, 1995; Chiapello *et al.*, 1995; 1997; Moulin *et al.*, 1997; Cole *et al.*, 2009). Saharan dust reaches the Mediterranean (Figure 27) either transported at high altitude by the northern branch of the Saharan Air Layer (SAL) or *via* regional meridian wind systems (Propero *et al.*, 1981; Coudé-Gaussen *et al.*, 1982; Bergametti *et al.*, 1989b; Bergametti *et al.*, 1989c; Guerzoni *et al.*, 1997; Moulin *et al.*, 1997; Rodriguez *et al.*, 2001; Torres-Padron *et al.*, 2002; Ginoux *et al.*, 2004).

Combined clay mineralogy and pollen association were studied on the ODP site 976 from Alboran Sea thoughout the last glacial, with specific emphasis on the North Atlantic cold climatic events (Mcmanus *et al.*, 1994). Our approach focused on the relationship between the occurrence of steppic pollen and wind-blown clay particles (palygorskite) in order to provide additional informations on the connection between climate and atmospheric systems during these cold climatic events. An increase of palygorskite and the abundance of semi-arid vegetation specifically characterize the Heinrich- like events (Figure 28). The peculiar mineralogical signature (illite to kaolinite ratio = I/K ratio) of these events and the presence of endemic *Argania* pollen, pinpoint the southern Morocco as a main source for the dust input during the cold North Atlantic climatic events (Bout-Roumazeilles *et al.*, 2007; Combourieu-Nebout *et al.*, 2008).



<u>Figure 28:</u> Palygorskite content (%), semi-desert vegetation abundance (%) at ODP site 976, Alboran Sea. Heinrich events are shaded. Black dots highlight the presence of Argania pollen (Bout-Roumazeilles et al., 2007).

The presence of palygorskite suggests that the continental aridity evidenced by the semi-desert pollen variations was associated with specific atmospheric configurations favouring dust transport from northern Africa to the western Mediterranean (Figure 29). Decennial observations of the main trajectories of Saharan dust outbreaks reaching Europe demonstrate the influence of the westerly winds regime on meridian dust transport (*e.g.* Avila *et al.*, 1997; Rodriguez *et al.*, 2001). Seasonal atmospheric back-trajectories, mineralogical and pollen records allow reconstructing the main transportation pattern of wind-blown particles during the Heinrich-like events (Coudé-Gaussen *et al.*, 1982; Bergametti *et al.*, 1989a; Moulin *et al.*, 1997; Rodriguez *et al.*, 2001; Torres-Padron *et al.*, 2002; Combourieu-Nebout *et al.*, 2002; Bout-Roumazeilles *et al.*, 2007). We conclude that summer-like atmospheric configuration would have favored the incursion of a depression trench between the Azores high and the Algerian anticyclone, promoting the transport of particles from the western part of Morocco toward the western and central part of the Mediterranean (Bout-Roumazeilles *et al.*, 2007).

Similar intensification of dust-winds from North Africa is also evidenced in glacial lacustrine and terrestrial records from southern Europe (Narcisi, 2000; Magri and Parra, 2002; Giraudi, 2004). Our results suggests persistent summer-like atmospheric configuration over the Mediterranean during the North Atlantic cold events. This dominant meridian transfer implies that the westerly regime was weak (Figure 29), disrupted of shifted northward during the Heinrich events (HE), supporting the hypothesized link between north Atlantic cold events and the westerly regime over Europe (Rohling *et al.*, 1998; Cacho *et al.*, 2000; Combourieu-Nebout *et al.*, 2002; Moreno *et al.*, 2002; Sanchez-Goni *et al.*, 2002). Indeed, the reconstructed synoptic situation (Figure 29, left) is very similar with the atmospheric configuration characterizing positive phase of the North Atlantic Oscillation (Figure 29, right), suggesting a direct connection between the extension of the Iceland-Azores pressure gradient, the jet stream and stormback latitudinal patterns, and the Saharan dust outbreaks occurrence and intensity (Bout-Roumazeilles *et al.*, 2007).



Figure 29: Synoptic atmosphere configurations over the Mediterranean and the North Atlantic Ocean cold events (left) compared with positive phase of the North Atlantic Oscillation (right) (Hurrell, 1995).

In the tropical Atlantic Ocean (core MD03-2705, Figure 26) Heinrich like events are also characterized by enhanced supply of fibrous clay minerals -sepiolite and palygorskite (Figure 30) - associated to a high content in smectite (Jullien *et al.*, 2007). Sediments deposited during these events are characterized by high dust content and peculiar geochemical and grain-size signature (Jullien *et al.*, 2007). The isotopic signatures of these deposits indicate a provenance from inner African regions (Grousset *et al.*, 1998; Jullien *et al.*, 2007). The abundance of fibrous clay minerals, which formed through desiccation processes in Mg-rich environments (Singer and Galan, 1984; Chamley, 1989), as well as the presence of freshwater diatoms (Jullien *et al.*, 2007) both suggest that eastern African Lakes may be the source of these dust outbreaks.



<u>Figure 30</u>: Temporal distribution of dust abundance, fibrous clay minerals and grain-size in core MD03-2705 (Jullien et al., 2007) and palygorskite from ODP site 976, Alboran Sea (Bout-Roumazeilles et al., 2007).

These findings indicate rather arid conditions over the North African continent during the Heinrich-like events, as evidenced in the Mediterranean (Combourieu-Nebout *et al.*, 2002; Bout-Roumazeilles *et al.*, 2007). According to the regional atmospheric patterns, both low- and high-altitude winds were likely enhanced, suggesting dominant winter atmospheric configurations over the northern intertropical area (Jullien *et al.*, 2007) contrasting with the evidenced summer-like atmospheric configurations over the western Mediterranean (Bout-Roumazeilles *et al.*, 2007).

Summary: Combined pollen and clay minerals analyses provide new insights on the atmospheric configuration in the Albotran Sea during cold climatic events of the last climatic cycle. The reconstructed synoptic situation is very similar to the one described for positive phases of the North Atlantic Oscillation. An increased proportion of dust characterizes these events in the tropical North Atlantic Ocean, likely associated with intensified southward shift of the ITCZ. These results highlight that the Saharan dust export toward the Mediterranean and the tropical Atlantic are controlled by distinct seasonally-driven transportation processes (Bout-Roumazeilles *et al.*, 2007; Jullien *et al.*, 2007; Skonieczny *et al.*, 2011; Malaizé *et al.*, 2012). It suggests a seasonal balance between the two atmospheric domains during the North Atlantic cold climatic events.

Related publications

- Bout-Roumazeilles, V., Nebout, N.C., Peyron, O., Cortijo, E., Landais, A. and Masson-Delmotte, V. 2007. Connection between South Mediterranean climate and North African atmospheric circulation during the last 50,000 yr BP North Atlantic cold events. *Quaternary Science Reviews*, 26: 3197-3215.
- Combourieu Nebout N., <u>Bout-Roumazeilles, V.</u>, Dormoy, I., Peyron, O., 2009. Sécheresses récurrentes en Méditerranée au cours des derniers 50 000 ans. Science et changements planétaires/Sécheresse, 20 (2): 210-6.
- Debret, M., <u>Bout-Roumazeilles, V.</u>, Grousset, F., Desmet, M., McManus, J.F., Massei, N., Sebag, D., Petit, J.R., Copard, Y. and Trentesaux, A. 2007. The origin of the 1500-year climate cycles in Holocene North-Atlantic records. *Climate of the Past*, 3: 569-575.
- Debret, M., Sebag, D., Crosta, X., Massei, N., Petit, J.-R., Chapron, E. and <u>Bout-Roumazeilles, V.</u> 2009. Evidence from wavelet analysis for a mid-Holocene transition in global climate forcing. *Quaternary Science Reviews*, 28: 2675-2688.
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- Malaize B., Jullien E., Tisserand A., Skonieczny C., Grousset F.E., Eynaud F., Kissel C., Bonnin J., Karstens S., Martinez P., Bory A., <u>Bout-Roumazeilles V.</u>, Caley T., Crosta X., Charlier K., Rossignol L., Flores J. A., Schneider R. 2012 The impact of African aridity on the isotopic signature of Atlantic deep waters across the Middle Pleistocene Transition. *Quaternary Research*, 77, 182-191.
- Skonieczny, C., Bory, A., <u>Bout-Roumazeilles, V.</u>, Abouchami, W., Galer, S. J. G., Crosta, X., Stuut, J.-B., Meyer, I., Chiapello, I., Podvin, T., Chatenet, B., Diallo, A., Ndiaye, T. 2011. The 7-13 March 2006 major Saharan outbreak: Multi-proxy characterization of mineral dust deposited on the West African margin. *Journal of Geophysical Research*, doi:10/1029/2011JD016173.

Habilitation à diriger des Recherches

Outlooks

Conclusions and outlooks

Clay mineralogy and geochemistry of terrigenous clay-size particles provide clues about provenance and transportation processes and pathways. Because they are conservative, these proxies are powerful tools to retrace past variations of fluviatile, oceanic and atmospheric transfers, complementary with other paleoceanographic/paleoclimatic proxies and modeling reconstructions. The synthesis of results acquired over more than a decade- thanks to three very talentuous PhD students and to a collective team effort- clearly stresses the need for performing integrated and standardized approaches, primarly based on a precise knowledge of the petrographic characteristics of the main source areas.

Using these procedurse on a brand new fieldwork -the Gulf of Mexico - was, to my point of view, a total success, and allowed us to obtain original and <u>new insights on fluviatil transfers.</u> The mineralogical study of meltwater floods pointed out the provenance of the associated detrital load, evidencing instability of the southwestern margin of the LIS, consistent with modeling, and revealed polyphased sequences within the terrigenous discharges. Two dominant atmospheric configurations successively controlled the precipitation distribution over the North American continent during the Holocene. The coherence between the GOM mineralogical and Greenland atmospheric cyclicities suggests a rapid transfer of the initial external forcing through atmospheric processes. Finally, even slight modifications of insolation and ice-sheet extension significantly impacted moisture transfer and precipitation distribution during the Eemian, promoting wetter conditions over the Mississippi River watershed than during the Holocene.

<u>Deep-oceanic circulation was investigated</u> in the northwestern and northeastern Atlantic basins at the transition between glacial marine stage 6 and interglacial stage 5 using a similar approch. The evidenced changes in terrigenous mineralogy and geochemistry during Termination II indicate rapid changes both in provenance and in deep circulation, suggesting an early NADW penetration toward the northwestern Atlantic basin. By contrast, weaker deep-water transportation *via* the ISOW was evidenced in the northeastern basin during MIS 6 compared with MIS5. These results highlight a severe oceanic re-organization during termination II.

<u>Atmospheric transfers</u> were investigated in the Mediterranean and in the North East Tropical Atlantic Ocean, where Saharan dust outbreaks may contribute significantly to deep-sea sedimentation. Our results provided new insights on the atmospheric configuration over these two regions. In the western Mediterranean, a northward penetration of Saharan dust - due to a northward shift of the westerlies - occurred during the North Atlantic cold climatic events, similar to positive phases of the North Atlantic Oscillation, while an intensified southward shift of the ITCZ characterized the cold climatic events in the tropical North Atlantic Ocean. These results highlight that the Saharan dust export toward the Mediterranean and the tropical Atlantic are controlled by distinct seasonally-driven transportation processes, and suggests a seasonal balance between the two atmospheric domains during the North Atlantic cold climatic events.

All these results allow to identify and to pinpoint some questions of major interest for paleoclimatic studies, which will guide future projects that will be further detailed in the chapter. According to the state-of-the-art and to national/international scientific prospectives, focusing our analytical approach on some key-areas will/would improve the understanding of the relationship between paleoclimate and transfer processes within the ocean and the atmosphere:

- To what extent the **high-latitude climate affect the subtropical hydrology in the Gulf of Mexico**? Reversely, what is the impact of subtropical oceanic and atmospheric conditions on moisture flux and precipitation distribution over the North American continent? Two related topics are in progress concerning: 1) the origin and propagation of the "Meltwater Spike" in the Gulf of Mexico and 2) the low-latitude insolation forcings on atmospheric reconfiguration during MIS3 over the North American continent.
- Could **past changes of deep-circulation off Antarctica** be monitored precisely using terrigenous tracers? This would be tentatively achieved by reconstructing particles provenance and transfers in sediment cores along the main water-masses pathways;
- Is it possible to **monitor past changes in Saharan dust export toward the Mediterranean** using clay mineralogy? This project combines proxy calibration, time-series acquisition and analyses of archives.

Origin and propagation of the "meltwater spike" in the Gulf of Mexico during the deglaciation

We have seen in the previous paragraphs that rapid changes of the Laurentide ice-sheet triggered major meltwater pulses in the Gulf of Mexico during the last deglaciation (Figure 31). These events were evidenced by their imprints on hydrological proxies (Aharon, 2003; 2006; Flower *et al.*, 2004), through modelling approaches (Licciardi *et al.*, 1999; Tarasov and Peltier, 2006), or by sedimentary records (Meckler *et al.*, 2008; Montero *et al.*, 2009, Sionneau *et al.*, 2010). However the relationship between the most prominent "Meltwater Spike" (15.8 – 12.9 ka cal BP) and the 20-meters sea level rise associated with the Meltwater Pulse 1A (14.6 –14.1 ka cal BP) is still debating (Peltier, 2005; Carlson, 2009). The contribution of the LIS to the MWP-1A through its southern outlet (GOM *via* the Mississippi River) is questioning, especially because the Atlantic Meridional Overturning Circulation (AMOC) does not show any evidence of freshwater discharge out flowing from the GOM (McManus *et al.*, 2004). Some alternative hypotheses proposed that the freshwater discharge may be "sneaked" into the deep-ocean (Roche *et al.*, 2007), being transported as hyperpycnal flows (Aharon, 2006).



<u>Figure 31:</u> The "meltwater spike" in the Gulf of Mexico: Calculated discharge in dSv (Tarasov and Peltier, 2005); Mississippi River discharge in Sv (Licciardi et al., 1999); δO^{18} % measured on planktonic foraminifera G. ruber on cores from the Louisiana shelf (Aharon, 2003) and δO^{18} % measured on planktonic foraminifera G. ruber in the Orca Basin (Flower et al., 2004). The blue shaded area indicates the MWS. The MWP1A chronology and associated sea-level rise is shown for comparison (Bard et al., 1990).

Mineralogical and geochemical characteristics of terrigenous sediments deposited in the northwestern GOM during the major deglacial meltwater spike give some new insights on these questions (Montero et al., 2009;

Sionneau *et al.*, 2010). The compilation of data from a series of cores along a West-East transect across the northern GOM allows constraining the origin and propagation of the detrital supply associated with the most prominent freshwater discharge (Figure 32).

The Meltwater Spike (MWS) is marked by a light isotopic δ^{18} O planktonic signal (Figure 32), recording the addition of freshwater in the Humphrey basin (Sionneau, 2008), in the La Salle basin (Montero, 2009), in the Pigmy basin (Meckler *et al.*, 2008) and in the Orca basin (Flower *et al.*, 2004). By contrast, the easternmost cores (MD02-2575/2576 De Soto Canyon) do not display any significant isotopic signal associated to this event (Nürnberg *et al.*, 2008). The MWS is marked by a major increase in smectite *versus* illite and chlorite in the Pigmy, Orca and La Salle basins, associated with increased sedimentation rates (up to 100-300 cm/kyr). The clay mineral record from De Soto Canyon does not evidence any significant smectite supply nor freshwater signal in the δ^{18} O planktonic record. By contrast, the clay mineral record from the westernmost site (MD03-2641 Humphrey Basin) does not show any evidence of any specific detrital supply associated with the evidenced freshwater supply (Figure 32).



<u>Figure 32:</u> Sedimentary records of the Meltwater Spike in the northern GOM. From West to East : MD03-2641 from Humphrey Basin (Mallarino et al., 2006; Sionneau, 2008), MD02-2549 from La Salle Basin (Montero et al., 2009), MD02-2553 from Pigmy Basin (Montero et al., 2010), MD02-2552 (Sionneau et al., 2010) and EN32-PC6 (Flower et al., 2004) from Orca basin, and cores MD02-2575/76 (Nurnberg et al., 2008; Meunier, 2009) from De Soto Canyon.

These results allow constraining the western and eastern propagation of the detrital signal associated to the main meltwater spike (Figure 32). The mineralogical signature of the MWS combined with the absence of any isotopic freshwater signal in the planktonic record from De Soto Canyon suggests that the meltwater spike may have propagated eastward as hyperpycnal flow(s). By contrast, a prominent freshwater signal recorded in the Humphrey Basin (Figure 32) whereas the detrital fraction remains unchanged suggests that the hyperpycnal flow did not extend further westward whereas the isotopic signal reached the western part of the basin *via* buoyancy processes or hypopycnal flows (Figure 33) (Bout-Roumazeilles *et al.*, in prep.).



Figure 33: Reconstructed terrigenous and freshwater discharges propagation in the GOM during the MWS, based on sedimentary evidences.

Comparison of these sedimentary evidences with modelled freshwater flows in the GOM allows evaluating the consistency between modelling and observations (Clark *et al.*, 2001; Peltier, 2005; Stanford *et al.*, 2006; Meckler *et al.*, 2008; Montero *et al.*, 2009; Roche, 2009; Sionneau *et al.*, 2010).

The reconstructed freshwater flux associated with the MWS flowing through the southern outlet (*i.e.* the Mississippi River) is assumed to range between 0.042 Sv and 0.102Sv ¹(Licciardi *et al.*, 1999; Tarasov and Peltier, 2000). For comparison, the present-day averaged annual flow of the Mississippi River is 0.018Sv, *i.e.* one order of magnitude lower than this estimation. But the Mississippi River flow shows strong interannual variability due to precipitations seasonality (up to 0.07 Sv) and/or abrupt climatic events, and even reached 0.3Sv during the historical megaflood of 1927 (Michel, 2005). Both high- and low-flux are thus considered for calculations.

Some authors proposed that the meltwater pulse occurred as a series of hyperpycnal flows (Aharon, 2003; Carlson, 2009). Hyperpycnal flows would indeed have less impact on surface hydrological proxies as the freshwater signal propagated slowly upward as buoyant plumes while sediment loads settled down (Aharon, 2003; 2006). Hyperpycnal are characterized by suspended loads ranging from 36kg/m^3 -due to buoyancy considerations- to 5 kg/m³ if considering convective instability (Mulder *et al.*, 2003). The density of the sediment varies from 1.2kg/m³ to 2.5kg/m³ according to its grain-size and nature (Winters *et al.*, 2007). The present-day averaged turbidity of the Mississippi River is around 0.38 to 0.45 kg/m³ - with rather large geographical variations (2.7 kg/m³ in the Missouri River)- corresponding to a total solid supply of 222 .10⁶ t/yr (Martin and Meybeck, 1979). Two densities (5 to 36 kg/m³) corresponding to dense –weak hyperpycnal flows are used for calculations.

Finally, the geographical extension of the meltwater propagation is also an important parameter, because the regional/local accumulation rates would be different if the plumes propagated over either widely extended area²

 $^{^{1}}$ 13% to 30% of the total 0.36 to 0.4 Sv sea-level rise.

² with the GOM superficy = $1.55*10^6$ km²

(1/2 GOM surface) or restricted area (1/8 GOM surface). Our reconstructed propagation of the terrigenous pulse suggests a distribution over 180 000 km² (Figure 33), corresponding to the one eighth of the GOM total area. Our calculations thus take in account various extension of the detrital supply associated with the MWS ranging from half to 1/8 of the GOM superficies (table 1).

The confrontation of modelled and measured data indicates that the hypothesis of dense hyperpychal flows (36kg/m³) is not consistent with the observations, even considering error propagation. Calculation gives 1589 cm of terrigenous sediment associated with the MWS at the lowest, assuming the largest extension of the deposit (GOM/2) and minimum meltwater flux (0.042Sv) while observations indicate that the most prominent meltwater discharge of the MWS occurring between 14.6 to 14.1 ka cal BP is physically characterized by the accumulation of 40 to 200 cm of terrigenous fine-grained sediments depending on core location (Meckler *et al.*, 2008; Montero-Serrano *et al.*, 2009; Sionneau *et al.*, 2010; Bout-Roumazeilles *et al.*, submitted).

The hypothesis of a "weak" hyperpycnal flow (5kg/m³) is thus more consistent with the observations, resulting in the accumulation of a 220 to 325cm-thick layer, assuming a largest extension of the deposits (GOM/2) and intermediate meltwater flux (up to 0.062Sv). These results highlight the weak consistency between models and observations, considering that the spreading of the meltwater discharge is in any case (GOM/2) overestimated compared with our reconstructed maximum propagation (GOM/8).

Low-latitude insolation forcings on atmospheric reconfiguration during MIS3 over the North American continent

The ${}^{18}O_{SW}$ from the Orca Basin reveals six major meltwater events between 44 and 42.8 ka, between 39.6 and 37.2 ka, around 35ka, between 34 and 31.3 ka and between 30 and 28.5 ka (Hill *et al.*, 2006; Flower *et al.*, 2011). Only three major meltwater events have been evidenced in the northwest GOM sediments (Bryant Canyon) based on both oxygen isotopic record and sedimentological signatures at 45ka, 37 ka and as a series of events centered at 31ka (Tripsanas et al., 2007). Only the longest and largest meltwater events seem to be contemporanous in the two records, taken in account varying precision on the age control (Figure 34). Surprisingly, the main meltwater events recorded in the Gulf of Mexico are not systematically or similarly associated with modifications of the terrigenous signal. The sedimentological and mineralogical records of some of the meltwater discharges (F1 and F6) are similar to the signatures of the main meltwater event (Melt Water Spike, ca 14.6-14.1 ka) characterizing the last deglaciation suggesting destabilization of glacial lobes along the SW margin of the LIS (Montero *et al.*, 2009; Sionneau *et al.*, 2010). By contrast, the two main meltwater events (F2 and F4) occurred during distinct sedimentological context without being characterized by any specific mineralogical association whereas they are contemporaneous with two important phases of Lower Mississippi Valley terraces (Rittenour *et al.*, 2005) suggesting enhanced detrial supply but constant provenance.

Deciphering the apparent dismatching between the meltwater discharges as recorded in the GOM (Hill *et al.*, 2006; Tripsanas *et al.*, 2007; Flower *et al.*, 2011) and the main changes in detrital clay provenance may give additional information on the debating relationship between the LIS melting episodes, Greenland D/O oscillations, Antarctic Warming and the AMOC variations (Clark *et al.*, 2001; Hill *et al.*, 2006; Clark *et al.*, 2007; Flower *et al.*, 2011). Recent studies (Hill *et al.*, 2006; Flower *et al.*, 2011) showed that the major melting events recorded in the GOM do not match the D/O oscillations but rather match the Antarctic warm events as recorded in the oxygen isotopic record of EDML (EPICA Dronning Maud Land) ice core (EPICA members, 2006). The longest and largest meltwater spikes from Orca Basin (F2 and F4) started during HE and coincides with a major reduction of the AMOC (Curry and Oppo, 1997; Skinner and Elderfield, 2007; Zahn *et al.*, 1997), but persisted during the following interstadial as the AMOC had already resumed.

Surface oceanic conditions, which control evaporation in the GOM and thus moisture availability, are mainly controlled by low-latitude summer insolation, while being insensitive to winter conditions (Ziegler *et al.*, 2008). Even if the relationship between the meridional overturning circulation and the GOM hydrological properties is still debating, most records agree in evidencing enhanced seasonality during the Heinrich Events (Ziegler *et al.*, 2008; Flower *et al.*, 2011). Comparison of our results with climate simulations indicates that the precipitation distribution and hence atmospheric re-organization are indeed controlled by summer insolation. Although the variations of summer insolation during MIS3 appears to slow to directly trigger melting events (Flower *et al.*, 2011), they are consistent with the timing of the main modifications of atmospheric configurations: the westward migration of the precipitation belt occurred as the insolation change rates at 45° and 30°N is maximum –or minimum difference in inter-hemispheric insolation - (around 37ka), whereas the shift back to its eastern position coincide with lower rate of summer insolation change (around 42 and 31ka) – maximum differences

between northern and southern insolation (Figure 34). These mineralogical transitions associated with major shifts in precipitation distribution occurred after the meltwater episodes, suggesting that the meltwater discharges may take part in triggering the atmospheric re-organization evidenced in our sedimentological records.



<u>Figure 34</u>: Comparison between clay mineral record from core MD02-2552 and other paleoclimatic records of the last glacial period (46 to 26 ka BP). a: summer insolation at 30°N and 30°S; b: chlorite to kaolinite ratio (C/K); c: magnetic susceptibility; d: kaolinite %; e: a* reflectance parameter; f: $\delta^{18}O$ record from northGRIP (Rasmussen et al., 2006); g: $\delta^{18}O$ from EDML (EPICA Members, 2006); h: $\delta^{18}O_{sw}$ record (MD02-2551) F1 to F5 = meltwater floods (Flower et al., 2011); i: Meltwater events in the Bryant Canyon (Tripsanas et al., 2007).

The main atmospheric re-organizations, occurring after the largest and longest meltwater events and not matching the Dansgaard/Oeschger (D/O) oscillations, are consistent with insolation variations, being synchronous with extreme summer insolation differences between the North and South hemispheres. Meltwater discharge, which may contribute to modify the LIS configuration and the GOM hydrological properties and

would ultimately affect large-scale circulation, likely take part in the trigger of the evidenced atmospheric reorganization by crossing a threshold, although the insolation variation rate appear to be the main driver of the system.

Our studies in the GOM stressed the need for better constraining the links between high-latitude phenomena (*i.e.* retreat/advance phase of the LIS) and the low-latitude GOM hydrological properties, and for identifying cause(s), consequence(s) and feedbacks. We plan to study (1) one major meltwater event directly linked with ice-sheet evolution during the deglaciation on a series of core over a West-East and a North-South transect in order to draw the maximum extension of the associated terrigenous flow and to test the hypothesis of a "weak" hyperpycnal westward flow and (2) a series of freshwater discharges during MIS3 likely linked to varying precipitation regime over the North American continent, in order to test the role of low latitude insolation on moisture inflow toward the North American continent.

Quaternary changes in the terrigenous provenance off Antarctica

The knowledge of carbon cycle budget is one of the biggest chalenge in paleoclimatology, and relationships between CO_2 concentrations and modification of deep oceanic circulation during glacial periods are still a matter of debate. In that frame, modification of the Antarctic Circum Current (ACC) pattern might have played an active role in changing CO_2 distribution through complex atmosphere-ocean exchanges (Figure 35).



Figure 35: Antarctic simplified geological map and oceanic circulation, modified from Hemming et al., 2007.

Multiproxy analyses (clay mineralogy, grain-size distribution, elemental geochemistry) of a core collected off Wilkes Land (Antarctica) revealed major modifications of terrigenous sedimentation during glacial intervals (Marine Isotopic Stage 2, MIS6, MIS8, MIS10) suggesting deep-currents reorganization (Figure 35). The detrital particles deposited during glacial stages are mainly cohesive particles (diameter <10 μ m) representing 60% of terrigenous particles whereas the proportion of sortable silt (± 30 μ m) increased up to 70% during interglacials. The abundance of sortable silts during interglacials suggests the supply of detrital material through deep-circulation (Figure 36). The proportion of smectite increases during interglacials whereas it decreases during glacial periods. MIS 2 and 6 are characterized by enhanced contribution of chlorite whereas MIS 10 and 12 are marked by an increased supply of kaolinite (Figure 36).

The supplies in chlorite and kaolinite fine-grained particles reflect some contributions from a proximal source (Archean/Proterozoic and Mesozoic terranes respectively (Figure 35), whereas the smectite contribution, associated with enhanced sortable-silt supply, likely records long-range transportation. Antarctica is the best candidate for proximal supply of chlorite and illite according to its local geological settings. The volcanic East Antarctic Peninsula *via* the Polar current or the Kerguelen Plateau *via* the Antarctic Circupolar Current may be considered as distal sources for smectite. Sedimentological and geochemical data thus indicate that detrital sedimentation results from both proximal continental inputs (*i.e.* Wilkes Land Antarctica) and distal volcanic supplies during interglacial intervals (Holocene, MIS5, MIS7, MIS9 and 11). The volcanic contribution seems to vanish during glacial periods as the result of major alteration of deep circulation (Figure 36).

In order to further investigate this interpretation, the provenance of the fine detrital fraction needs to be constrained using radiogenic isotopes (Figure 35). The old continental crust from Wilkes Land is characterized by low epsilon Nd, and high Sr and Pb isotopic ratios (Hemming *et al.*, 2007; Roy *et al.*, 2007; van de Flierdt *et al.*, 2007). By contrast, distal oceanic volcanic sources, either Kerguelen Plateau (KP) or the Antarctic Peninsula (AP), would provide rather different isotopic composition (low ⁸⁷Sr/⁸⁶Sr, positive epsilon Nd values).



<u>Figure 36:</u> Clay mineral composition (% smectite); grain-size mode (μ m) from core MD03-2603 (Wilkes Land) during the last climatic cycles.

⁸⁷Sr/⁸⁶Sr ranges (Figure 36) stress major changing provenance of the clay-size particles over the last climatic cycle with low Sr isotope ratios occurring during the Holocene contrasting with high ratio during the last deglaciation (termination I). The lowest Sr compositions clearly reflect distal oceanic supply from volcanic areas during the deglaciation while the highest Sr ratios is directly related with prominent proximal inputs from the adjacent Wilkes Land old continental crust during glacial. Moreover, maximum ⁸⁷Sr/⁸⁶Sr amplitude is observed during the oldest part of the record whereas minimum range characterizes the last termination.

According to regional geology (Figure 35) and previously published Sr isotopic ratios distribution around Antarctica, the less radiogenic Sr characterizing the Holocene may result from volcanic supply from either the Kerguelen Plateau; *via* the Antarctic Circumpolar Current (ACC) or the Antarctic Peninsula, *via* the westward flowing currents South of the ACC. The ε_{Nd} displays higher values (Figure 37) during the interglacials and lower values during glacials. The last climatic cycle displays a striking feature with lower ε_{Nd} during MIS1 than during MIS2-4. This result confirms the major modification/reorganization of deep circulation during the last climatic cycles evidenced by the ⁸⁷Sr/⁸⁶Sr record. The whole set of data samples plot on a mixing line between a "young" volcanic end-member and an "old" crustal end-member in the ε_{Nd} wersus ⁸⁷Sr/⁸⁶Sr diagram, but define rather distinct domains. The IG samples plot near the "volcanic" end-member whereas the G samples are located near the "crustal" end-member (Figure 37).



<u>Figure 37:</u> \mathcal{E}_{Nd} versus ⁸⁷Sr/⁸⁶Sr isotopic ratios of interglacial (red) and glacial (blue) clay-size fraction from core MD03-2603 (Wilkes Land). Green diamonds correspond to Holocene samples.

Previous studies around Kerguelen Plateau evidenced modifications of the ACC during the last glacial period compared with the Holocene (Dezileau *et al.*, 2000; Mazaud *et al.*, 2007), taking part of the interhemispheric see-saw phenomenon between the North Atlantic and southern ocean (Barker *et al.*, 2009). In that frame, Pb is used to discriminate between the different volcanic sources. Kerguelen Archipelago and Antarctic Peninsula are characterized by close ⁸⁷Sr/⁸⁶Sr and ε_{Nd} ratios but display distinct Pb isotopic ratios (Hole *et al.*, 1993; Xu *et al.*, 2007). The ²⁰⁸Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb lead isotopic ratios display similar variations, exhibiting a larger range of variability over the older part of the record (MIS13 to MIS5) compared to the last climatic cycle. Interglacial periods are characterized by higher lead isotopic ratios relative to glacial stages (Figure 37). Surprisingly, the lead isotopic data suggests that the Kerguelen Archipelago was potentially a source for detrital particles during previous IG periods, but could not explain the last climatic cycle specific trend (Kempton *et al.*, 2002).

These results evidence that the deep circulation displayed much stronger variations during former climatic cycles compared to the last one. The dataset indicates that the relative contribution of advected material through deep-water masses *versus* proximal inputs was enhanced during interglacial stages 5, 11 and 13, while deep advection was drastically reduced during glacial stages 10 and 12. The isotopic results suggest varying intensity of deep water-masses reorganization at glacial-interglacial timescale over the last climatic cycles. Mineralogical and geochemical investigations are planned on a serie of cores collected in 2011 and 2012 on the Kerguelen Plateau during the INDIEN-Sud cruise (PI Alain Mazaud from LSCE, Gif-sur-Yvette, France), in order to test our hypothesis by investigating both clay mineralogy and geochemistry near the Kerguelen, and to provide informations on the relationship between the ACC spatial variability and the sedimentary supplies off Wilkes Land.

Respective contribution of eolian and fluviatile inputs to central Mediterranean deep sedimentation during the Holocene

The respective atmospheric and oceanic control on Mediterranean climatic evolution through their impact on eolian and fluviatil systems is still complex. A multiproxy study of the terrigenous supply would help retracing the variability of both eolian and fluviatil systems and would improve the knowledge of the interactions between the biosphere and the geosphere in the Mediterranean area -one of the main objectives of the Charmex and Paleomex programs -.

Indeed, the nature and provenance of fine-grained terrigenous particles in the Mediterranean are mainly controlled by the balance between fluviatile supplies - driven by precipitation regime on the surrounding continents - and eolian supplies from the Sahara (Bergametti *et al.*, 1989a; 1989c; Matthewson *et al.* 1995; Guerzoni et Chester, 1996; Foucault et Mélières, 2000; Goudie et Middleton, 2001). But these detrital supplies display a strong seasonal variability with extreme events linked to global or regional climatic conditions. Consequently, studying the past variability in eolian/fluviatile contributions is a challenge which requires (1) characterizing present-day eolian supply to the Mediterranean; (2) mapping present terrigenous sediment distribution and (3) investigating the past variability of terrigenous supply in selected sediment cores.

(1) In that frame, the mineralogical and geochemical signatures of terrigenous particles transported from the Sahara and Sahel toward the Mediterranean and the Tropical Atlantic allow characterizing present-day dust outbreaks. This approach was successfully tested at the M'Bour ground station (Figure 38) in Senegal where dust input has been monitored for 5 years (Skonieczny *et al.*, 2011). We intend to develop a similar approach - monitoring mineralogical and geochemical signatures of atmospheric deposit - at master stations within the Charmex program (Figure 38). Combining the provenance tracing with atmospheric back trajectories would allow better constraining present-day Sahara dust transport-patterns across the Mediterranean.

(2) The present-day mineralogical composition of sediments will be investigating by using previously published database (Biscaye, 1965; Chamley, 1989; Bout-Roumazeilles *et al.*, 2007) with additional top-core analyses. Data will be treated using geostatistics in order to draw distribution maps and to highlight geographical areas that need complementary analyses. Additional sampling using multitubes or box-cores would then be requested in the frame of the Paleomex program (proxy calibration). This database will be used to determine the contribution and propagation of the main rivers supply and the redistribution of sediments by water-masses, and to identify areas of dominant dust deposition.

(3) The results already obtained on the site ODP 976 from the Alboran Sea (Bout-Roumazeilles *et al.*, 2007) and on core MD03-2705 from the tropical Atlantic (Skonieczny *et al.*, in prep) will be combined with a series of cores located in the Mediterranean (MD04-2797 and MD90-917) and in the Gulf of Cadiz (IODP339) in order to investigate the past variability of terrigenous supply *via* eolian processes (Saharan dust), river discharges and oceanic water-masses (Figure 38). The core MD04-2797 is ideally located in the Sicilian-Tunisian strait to record past variations of the terrigenous eolian transfer from North Africa, because of the weak local fluviatile supply (Figure 38). Moreover, deep sedimentation may be influenced by the saline Levantine Waters which flow westward at intermediate and deep water depths (Saliot, 2005) below the shallow Modified Atlantic Water flowing eastward (Astraldi *et al.*, 1999; 2002; Béranger *et al.*, 2004; Gasparini *et al.*, 2005). The clay mineral, grain-size and geochemical studies of sediment deposited on the Sicilian-Tunisian Strait help retracing atmospheric *versus* river terrigenous supplies variability since the last glacial in central Mediterranean. Although the eolian supply is dominant at the studied site (Figure 39) - excepted during the sapropel S1- both flux and the main provenance of particles display strong variations, related to aridity/moisture balance and vegetation cover, driven by large-scale atmospheric reorganization.

The Bølling-Allerød is marked by increased terrigenous flux while both illite and palygorskite became main components of the clay mineral fraction (Figure 39). The concomitant dominance of silt-size particles suggests an eolian origin for this enhanced detrital supply. The geochemical and mineralogical data indicate a dominant Saharan contribution, pinpointing central and northern Algeria as a main provenance (Caquineau *et al.*, 1998; Kandler *et al.*, 2009; Formenti *et al.*, 2008; 2011). This increased eolian contribution from Sahara highlights contrasting regional climatic evolution, with the development of moist conditions over the north and eastern Mediterranean during the Bølling-Allerød (Ramrath *et al.*, 2000; Allen *et al.*, 2002; Zielfofer *et al.*, 2008; Incarbona *et al.*, 2010), while glacial aridity persisted on the southern Mediterranean.

The onset of the Holocene is marked by a major change of clay mineralogy and cristallinity corresponding to a southward migration of the main clay provenance toward the Sahelian belt. This change is associated with a progressive development of the Mediterranean vegetation and the southward shift of the ITCZ. Similar signals are recorded in the northeastern Tropical Atlantic Ocean and off Portugal, suggesting a large-scale atmospheric reorganization. The occurrence of such a coarse-grained proximal supply during the Younger Dryas (YD), consistent with the presence of loess deposits and coastal dunes in Tunisia (Coudé-Gaussen *et al.*, 1987; Grousset *et al.*, 1992; Crouvi *et al.*, 2010) and further supported by model suggesting that Libyan desert and coastal areas are major coarse-grained dust sources for central and eastern Mediterranean (Callot *et al.*, 2000), may thus reflect local eolian activity forced by ocean-atmosphere linkage at global scale.

Surprisingly, peculiar mineralogical and grain-size data characterize early Holocene sedimentation (Figure 40). Enhanced supply of smectite is associated with the dominance of very fine grain-size particles. According to geological settings, abundant smectite may originate from the Nile River (Revel *et al.*, 2010) or from the Aegean Sea (Erhmann *et al.*, 2007). Moreover, major present-day dust events recorded in tropical Africa (Skonieczny *et al.*, 2011) are enriched in smectite, likely originating from southeastern Sahel. The very fine grain-size characterizing the interval may either result from remote eolian supply or from oceanic transfer through the nepheloid layer. Eolian processes, however, are not supported by geochemical data (Ti/Al). Similar supply of smectite is observed in core SL123 (Erhmann *et al.*, 2007), suggesting that the Aegean Sea may be a potential source of smectite, *via* the deep Mediterranean westward flow. However, a Levantine provenance is supported by the high particulate organic carbon observed in core MD04-2797 (Figure 40), which indicate presapropelic conditions in the bottom water (Rouis *et al.*, 2010) contemporaneous with the deposition of the S1 sapropel in the eastern Mediterranean (Rossignal-Strick, 1985; Kallel *et al.*, 1997; Rossignol-Strick and Paterne, 1999; Ariztegui *et al.*, 2000; Rohling *et al.*, 2002).



Figure 38: Location of the studied sediment cores: MD04-2797 from the Sicilian-Tunisian strait, MD90-917 in the Adriatic Sea, MD03-2705 from the tropical Atlantic, ODP976 from the Alboran Sea IODP339 sites in the Gulf of Cadiz. Ground base stations: M'Bour (AMMA program), Majorca, Ersa and Lampedusa (CHARMEX project. Main low level (red arrow) and altitude winds (black arrow), rivers supply (green arrow, thickness proportional to annual suspended supply) in the Mediterranean Sea. SAL : Saharan Air Layer, NSAL : northern branch of the Saharan Air Layer. The limit between Sahara and Sahel is reported. Main surface (AW), intermediate (Levantine Intermediate Water, LIW) and deep water masses (Saliot, 2005). Position of the sediment cores mentionned in this study. Major, secondary and minor dust sources modified from Formenti et al., 2011 ; D'Almeida, 1998 ; Brooks and Legrand, 2000 ; Caquineau et al., 2002 ; Prospero et al., 2002 ; Israelevich et al., 2003. Clay mineralogy of peri-Mediterranean river particles (green circles), sediments/soils (black circles) and dust particles (red circle). Modified from Bout-Roumazeilles et al., 2007, additionel ata from Cyprus, Levantine Sea : e.g. Hamann et al., 2009 ; data from northwest Aegean province and West Turkey province : e.g. Ehrmann et al., 2006 ; data from Marmara Sea : Armynot du Châtelet et al., submitted ; North and South Libya dust from O'Hara et al., 2006).



Figure 39: Comparison of multiproxies data, a : I/K, Ca/Fe and their interpretation on particles provenance for the Bølling-Allerød, b : grain-size compared with Zr/Al during the Younger Dryas, c : quartz content (counts/s), Ti/Al ratio and kaolinite % over the last 3000 yr, d : Smectite (%), characterizing the sapropel S1, % of clay, content in Pd (counts/s) and terrigenous mass accumulation rates (MART).



<u>Figure 40:</u> MART, Pd _{XRF} (counts), % of clay-size particles, and smectite % from core MD04-277 - Sicilian_Tunisian strait- % of cohesive particles from core SL112 – Levantine Sea (Hamann et al., 2009), smectite/illite ratio from ODP site 976 - Alboran Sea (Bout-Roumazeilles et al., 2007), smectite/illite ratio from sites SL123 and SL148- Aegean sea (Erhmann et al., 2007)

Outlooks



Figure 41: Clay mineral composition from core MD90-917, Adriatic Sea (LAMA project).

In the Adriatic Sea (core MD90-917, Figure 38), the clay mineralogy is mostly influenced by terrigenous supply from the Pô River, delivering illite and chlorite from the Alps. The period of enhanced fluviatile supply, related to intense precipitation or glaciers melting, is marked by simultaneous increases in both illite and chlorite abundance (Figure 41; blue lines). By contrast, the increase in illite while chlorite remained stable (Figure 41; green line) highlight a specific eolian supply from North Africa. Finally, the smectite variations are likely related to intermediate/deep transportation.

In order to increase our understanding of the past variability of eolian/fluviatile contributions around the Mediterranean, an integrated approach including the characterization of present-day eolian supply to the Mediterranean – based on our experiment at M'Bour, Senegalese coast, and following recommandations of the Charmex program -, the mapping of present-day terrigenous sediment distribution –using sediment archives and bibliography, completed by additional analyses on surface sediments in the frame of the Paleomex program - and the investigation of specific time-slices in targeted sediment cores will be developed- using well-dated and well-constrained cores of reference. Studying the clay mineralogy of sediments off Portugal and from the Gulf of Cadiz³ (Figure 38) would nicely complete the investigations on the Mediterranean and Tropical Atlantic areas. Indeed the Gulf of Cadiz contouritic sediments would allow inferring the oceanic contribution to sedimentation, and to check the potential influence of intermediate/deep water masses on the supply of smectite. In that frame, the mineralogical study of sediments that have been collected during IODP339 expedition in the Gulf of Cadiz is also planned.

³ see IODP full proposal at http://iodp.tamu.edu/scienceops/expeditions/mediterranean_outflow.html

Acknowledgments

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Associate Scientist CNRS Earth Sciences department University Lille 1 59655 Villeneuve d'Ascq email : <u>viviane.bout@univ-lille1.fr</u> Date of birth : 1st May 1968 French citizen Married – five children

Primary Research Interests

Clay mineralogy, elemental and isotopic geochemsitry – Paleoceanography Terrigenous oceanic and atmospheric transfers – High-resolution climatic variability Atmosphere-ocean linkages

Education

1995 :	PhD thesis in Sedimentary Geology and Geochemistry, University Lille-France
1992 :	Master thesis in Geophysics, Geochemistry and Geology, University Paris XI- France

Professional Experience

- Since 2003 : Associate Scientist CNRS (CR1) Earth Sciences dept. University Lille 1 (France)
- 1998-2003 : Associate Scientist CNRS (CR2) Earth Sciences dept. University Lille 1 (France)
- 1997-1999 : Post-doctoral fellowship Earth Sciences faculty- VU Amsterdam (Netherlands)
- 1996-1997 : Assistant Scientist, Earth Sciences dept. University Lille 1 (France)
- 1995-1996 : Assistant Scientist, Earth Sciences dept. –University Caen (France)

Other Scientific and Academic Activities

- 2011-2014 : President of the CNFH (Comission Nationale de la Flotte Hauturière) French National Committee evaluating shipboard cruise applications
- 2011-2014 : Invited member of the COSS (Comité d'Orientation Stratégique et Scientifique) de la Flotte française
- 2011-2014 : Invited member of the Unité Mixte de Service Flotte Océanographique Française
- 2011-2014 : Invited member of the CSOA (Ocean Atmospheric Scientific Council)
- 2010 : Vice-director of IMAGES-France committee
- 2008-2010 : Member of the CNFE- Evaluation of shipboard cruise applications
- 1998 : Member of the IMAGES-France committee
- 1995 : Affiliated to the American Geophysical Union

Shipboard Experiences

- 2007 : Co-chief scientist on the CAMOA cruise, R/V Marion Dufresne Atmospheric sampling across the South Atlantic Ocean Capetown (RSA) to Punta Arenas (Chile)
- 2005 : Shipboard sedimentologist on the MARCO POLO 1 cruise, R/V Marion Dufresne Coring in the South China Sea (IMAGES)
- 2002 : Chief scientist on the PAGE cruise, R/V Marion Dufresne Coring in the Gulf of Mexico and Caribbean sea (IMAGES)
- 1999 : Shipboard scientist on the GINNA cruise, R/V Marion Dufresne Coring in the North Atlantic Ocean (IMAGES)
- 1995 : Shipboard sedimentologist on the ODP162 cruise, Joides Resolution Drilling the North Atlantic Gateways

Education activities

PhD. Advisor / co-advisor

- 2011 : Charlotte Skonieczny Contribution du matériel terrigène éolien déposé en Méditerranée et en Atlantique Tropical Nord-Est à l'étude des changements climatiques récents (Advisors : Nicolas Tribovillard & Aloys Bory)
- 2009 : Jean Carlos Montero Serrano Sedimentary and paleoclimate dynamics of the Gulf of Mexico during the last climatic cycle (Advisor : Nicolas Tribovillard)
- 2008 : Thomas Sionneau -Transferts continent-océan : enregistrement du dernier cycle climatique par les sédiments terrigènes du Golfe du Mexique. (Advisor: Brigitte van Vliet-Lanoe)

Second year Master students

- 2010 : Guillaume Meunier Comparaison des apports terrigènes argileux dans le Golfe du Mexique à l'Holocène et au stade isotopique 5: implications sur la variabilité du régime des précipitations
- 2008: Arnaud Beucherie Analyse minéralogique de la carotte MD03-2603 marge continentale Antarctique- interaction entre évolution du climat et processus sédimentaires dans l'océan Austral depuis 400 000 ans
- 2008: Camille Butruille Variabilité climatique de la Mousson Est-asiatique au cours de l'Holocène et du dernier maximum glaciaire : étude de l'upwelling du Vietnam
- 2007: Sutieng Ho Evolution de l'upwelling du Vietnam en Mer de Chine depuis 85ka : étude sédimentologique en relation avec la mousson du Sud-Est asiatique
- 2006: Amar Saidj Caractérisation minéralogique et granulométrique des sédiments terrigènes lors de la dernière transition glaciaire/interglaciaire en Atlantique Nord (bassin d'Islande)
- 2005: Thomas Vigreux Variabilité haute-résolution de la nature et du flux des apports détritiques dans le Golfe du Lion pendant la dernière période glaciaire
- 2005: Charles Verpoorter Traçage à très haute-résolution des oscillations climatiques rapides lors du dernier cycle climatique par la minéralogie et la géochimie de la fraction argileuse terrigène de l'Atlantique Nord (MD99-2247)
- 2005 : Elise Quentel Etude des propriétés géoacoustiques des sédiments du Golfe de Cadix corrélations entre la célérité, la granularité et les processus sédimentaires
- 2004 : Thomas Sionneau Relation entre les variations de la calotte glaciaire Laurentide et l'enregistrement sédimentaire dans le bassin d'Orca (Golfe du Mexique)
- 2004 : Aurélien Van Welden Variations haute résolution des apports terrigènes dans le Golfe du Lion pendant la dernière période glaciaire : caractérisation des événements climatiques rapides
- 2002: Mélanie Turpin Enregistrements minéralogiques et géochimiques de la variabilité climatique rapide du dernier cycle climatique dans l'océan Atlantique nord: implications paléocéanographiques
- 2001: Deloffre Julien Signal climatique à haute résolution et conséquences paléocéanographiques dans l'hémisphère Sud

First year Master students

- 2009: Guillaume Meunier Relations entre la variabilité climatique sur le continent nord-américain et les modifications des apports terrigènes dans le golfe du Mexique au cours du stade isotopique 3
- 2008: Erwan Gensac Calibration et mise à jour des facteurs de corrections (facteurs de Biscaye) modulant le calcul des proportions des différents minéraux au sein de la fraction argileuse
- 2007: Hélène Delattre Caractérisation de la circulation océanique en Mer de Norvège et en Atlantique Nord durant le stade isotopique marin 5
- 2006: Sutieng Ho Etude d'une carotte de Mer de Chine du Sud: foraminifères, granulométrie et minéralogie des argiles
- 2006: Guillaume Gosselin Utilisation du spectrocolorimètre comme outil de corrélation de 2 carottes marines sédimentaires prélevées en mer de Chine du Sud
- 2004: Aurélien van Welden Variations haute résolution des apports terrigènes dans le Golfe du Lion pendant la dernière période glaciaire : caractérisation des événements climatiques rapides
- 2000 : Frédéric Rozan Enregistrement de l'évolution du climat et de la calotte glaciaire au large du Groenland par l'étude de la fraction argileuse des sédiments du site ODP 987
- 2000 : Gilles Dumont Etude sédimentologique et caractérisation des niveaux de cendres volcaniques de la carotte SU90-31 (Atlantique Nord)

Fundings

- 2012: PNRCC 2012 (Programme National de Recherche sur la Connaissance et la Conservation du patromoine culturel matériel) projet ARTEMIE : ARgiles et TEos ou la consolidation des tablettes en terres crues mésopotaMIEnnes (PI: Anne Bouquillon, Louvre)
- 2011: MISTRAL-TERMEX: projet CYCLAMEN (PI: Nathalie Combourieu-Nebout, LSCE Gif-sur-Yvette)
- 2010: Europlanet ATOS 2 Antartic Terrigenous Oceanic Supply (PI: Viviane Bout-Roumazeilles)
- 2009: Europlanet ATOS- Antartic Terrigenous Oceanic Supply (PI: Viviane Bout-Roumazeilles)
- 2008: ANR- LAMA Holocene climatic variability in the Mediterranean (PIs: Michel Magny, Chronoenvironnement Besançon & Nathalie Combourieu-Nebout, LSCE Gif-sur-Yvette)
- 2007: University Lille 1 Bonus Qualité Recherche Clean Lab (PI: Bory Aloys)
- 2006: CNRS Clean Lab installation (PIs: Aloys Bory and Viviane Bout-Roumazeilles)
- 2003: INSU AdHoc Ocean High latitude forcings on the GOM hydrology (PIs: Viviane Bout-Roumazeilles and Laurent Labeyrie, LSCE Gif-sur-Yvette)
- 2002: EXXON and USGS financial support for the PAGE cruise in the GOM (R/V Marion Dufresne) (PIs: Laurent Labeyrie, LSCE Gif-sur-Yvette and Viviane Bout-Roumazeilles)
- 2001: IFREMER Sedimentological study of cores from the PRISMA cruise (PI: Viviane Bout-Roumazeilles)
- 2000: University Lille 1- Improvement of XRD facilities (PI: Viviane Bout-Roumazeilles)
- 1999: National Research Grant- Mineralogical and Geochemical tracing of paleoceanographic variations (PI: Viviane Bout-Roumazeilles)

Habilitation à diriger des Recherches

Publications list

Peer-reviewed publications

Submitted

- 39. Sionneau, T., <u>Bout-Roumazeilles, V.</u>, Meunier, G., Kissel, C., Flower, B., Bory, A., Tribovillard, N. Sedimentological and mineralogical evidences of atmospheric re-organization during MIS 3 over the North American continent. Submitted to *Quaternary Science Reviews*.
- Lafon, O., Thankamony, A.S.L., Rosay, M., Aussenac, F., Lu, X., Trébosc, J., Vezin, H., Amoureux, J.P., <u>Bout-Roumazeilles, V.</u> Indirect and direct ²⁹Si dynamic nuclear polarization of nanoparticules. Submitted to *Langmuir*.
- 37. Daniau, A.L., Sanchez-Goni, M.F., Martinez, P., Urrego, D.H., <u>Bout-Roumazeilles, V.</u>, Desprat, S. Precession frocing of fire activity in subtropical southern Africa over the past 170,000 years. Submitted to *Nature Geosciences*.
- 36. <u>Bout-Roumazeilles, V</u>., Combourieu-Nebout, N., Desprat, S., Siani, G., Turon, J.-L.Tracking atmospheric and riverine terrigenous supplies variability during the Holocene and last glacial in central Mediterranean. Submitted to *Climate of the Past*.
- 35. Armynot du Châtelet, E., <u>Bout-Roumazeilles, V.</u>, Coccioni, R., Frontalini, F., Guillot, F., Kaminski, M.A., Récourt, P., Riboulleau, A., Trentesaux, A., Tribovillard, N., Ventalon, S. Environmental control on shell structure of agglutinated foraminifera in the Marmara Sea. Submitted to *Marine Geology*.
- 34. <u>Bout-Roumazeilles, V.</u>, Riboulleau, A., Armynot du Châtelet, E., Tribovillard, N., Murray, R.W., Lorenzoni, L., Müller-Karger, F. Clay minerals of surface sediments as a tool for deciphering the respective contributions by several particleload suppliers to the Cariaco Basin. Submitted to *Journal of Geophysical Research-Oceans*.
- 33. Skonieczny, C., Bory, A., <u>Bout-Roumazeilles, V.</u>, Abouchami, W., Galer, S., Crosta, X., Diallo, A., Ndiaye, T. A threeyear time series of mineral dust deposits on the West African margin : sedimentological and geochemical signatures and implications for marine paleo-dust records interpretation. Submitted to *Earth and Planetary Science Letters*.

2012

32. Malaize, B., Jullien, E., Tisserand, A., Skonieczny, C., Grousset, F. E., Eynaud, F., Kissel, C., Bonnin, J., Karstens, S., Martinez, P., Bory, A., <u>Bout-Roumazeilles, V.</u>, Caley, T., Crosta, X., Charlier, K., Rossignol, L., Flores, J. A., Schneider, R., 2012. The impact of African aridity on the isotopic signature of Atlantic deep waters across the Middle Pleistocene Transition. *Quaternary Research*, 77: 182-191.

2011

- Montero-Serrano, J.C., <u>Bout-Roumazeilles, V.</u>, Carlson, A.E., Tribovillard, N., Bory, A., Meunier, G., Sionneau, T., Flower, B.P., Martinez, P., Billy, I., Riboulleau, A. 2011. Contrasting rainfall patterns over North America as recorded by sediments of the northern Gulf of Mexico. *Geophysical Research Letters*, 38, L14709, doi:10.1029/2011GL048194.
- Tribovillard, N., <u>Bout-Roumazeilles, V.</u>, Riboulleau, A., Baudin, F., Danelian, T., Riquier, L. 2011. Transfer of germanium to marine sediments: insights from its accumulation in radiolarites and authigenic capture under reducing conditions. Some examples through geological ages. *Chemical Geology*, **282** (3-4): 120-130.
- Riboulleau, A., Tribovillard, N., Baudin, F., <u>Bout-Roumazeilles, V.</u>, Lyons, T. 2011. Unexpectedly low organic matter content in Cariaco Basin sediments during the Younger Dryas. Origin and implications. *CR Geosciences*, 343: 351-359.
- 27. Skonieczny, C., Bory, A., <u>Bout-Roumazeilles, V.</u>, Abouchami, W., Galer, SJG, Crosta, X., Stuut, J.B., Meyer, I., Chiapello, I., Podvin, T., Chatenet, B., Diallo, A., Ndiaye, T., The 7-13 March 2006 major Saharan outbreak: Multiproxy characterization of mineral dust deposited on the West African margin. *Journal of Geophysical Research*, **116** : D18210, doi : 10.1029/2011JD016173.

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- Montero-Serrano, J.C., <u>Bout-Roumazeilles</u>, V., Sionneau, T., Tribovillard, N., Bory, A., Flower, B.P., Riboulleau, A., Martinez, P., Billy, I. 2010. Changes in precipitation regimes over North America during the Holocene as recorded by mineralogy and geochemistry of Gulf of Mexico sediments. *Global and Planetary Change*, 74 (3-4):132-143.
- Debret, M., Chapron, E., Desmet, M., Rolland-Revel, M., Magand, O., Trentesaux, A., <u>Bout-Roumazeille, V.</u>, Nomade, J., Arnaud, F. 2010. North western Alps Holocene paleohydrology recorded by flooding activity in Lake Le Bourget, France. *Quaternary Science Reviews*, **29** (17-18) : 2185-2200.
- Sionneau, T, <u>Bout-Roumazeilles, V.</u>, Flower, B.P., Bory, A., Tribovillard, N., Kissel, C., Van Vliet-Lanoë, B., Montero Serrano, J.C. 2010. Provenance of freshwater pulses in the Gulf of Mexico during the last deglaciation. *Quaternary Research*, 74 (2): 235-245.

- Montero-Serrano, J.C., <u>Bout-Roumazeilles, V.</u>, Tribovillard, N., Sionneau, T., Riboulleau, A., Bory, A. and Flower, B. 2009. Sedimentary evidence of deglacial megafloods in the northern Gulf of Mexico (Pigmy Basin). *Quaternary Science Reviews*, 28 (27/28): 3333-3347.
- 22. Armynot du Chatelet, E., <u>Bout-Roumazeilles, V.</u>, Riboulleau, A. and Trentesaux, A., 2009. Sediment (grain size and clay mineralogy) and organic matter quality control on living benthic foraminifera. *Revue de Micropaléontologie*, **52**: 75-84.
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