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## Teleconnexions atmosfera-oceà a la regió intertropical durant el Plistocè inferior

Patricia Povea de Castro



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# TELECONNEXIONS ATMOSFERA-OCEÀ A LA REGIÓ INTERTROPICAL DURANT EL PLISTOCÈ INFERIOR

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# Teleconnexions atmosfera-oceà a la regió intertropical durant el Plistocè inferior

Programa de Doctorat de Ciències del Mar

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“Necesito del mar porque me enseña  
no sé si aprendo música o conciencia  
no sé si es ola sola o ser profundo  
o sólo ronca voz o deslumbrante  
suposición de peces y navíos.”

*EL MAR*

*Pablo Neruda*



*Als meus pares*





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“Las cosas son así: a veces tienes ante ti una calle larguísima. Te parece tan terriblemente larga, que nunca crees que podrás acabarla. Y entonces te empiezas a dar prisa, cada vez más prisa. Cada vez que levantas la vista, ves que la calle no se hace más corta. Y te esfuerzas más todavía, empiezas a tener miedo, al final estás sin aliento. Y la calle sigue estando por delante. Así no se debe hacer. Nunca se ha de pensar en toda la calle de una vez, ¿Entiendes? Sólo hay que pensar en el paso siguiente, en la inspiración siguiente, en la siguiente barrida. Nunca nada más que en el siguiente.”

*MOMO, Michael Ende*

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## RESUM

Els sediments marins profunds són claus per a la comprensió de la variabilitat del clima al llarg de la història de la Terra. Aquests sediments contenen una gran varietat d'indicadors per reconstruir canvis tan de l'oceà com de l'atmosfera, elements claus dins del sistema climàtic. Els sediments marins, formats per components lítics i biogènics, ofereixen una àmplia varietat d'informació paleoambiental. Per una banda, la fracció lítica prové principalment dels continents adjacents i el seu estudi ofereix l'oportunitat d'entendre els processos de transport que han estat responsables de la seva deposició. Per tant, poden proporcionar informació sobre les aportacions eòliques i fluvials, de les característiques i les condicions climàtiques de la zona d'origen de les partícules i, en certs contextos, poden també donar informació sobre els corrents oceànics profunds. Així, la fracció lítica té un pes important per reconstruir les condicions atmosfèriques passades, com ara la direcció del vent, la ubicació i la intensitat dels cinturons de pluja. Per altra banda, l'anàlisi dels components biogènics marins proporciona informació de les condicions oceanogràfiques. En aquesta fracció queden reflectides les propietats de la massa d'aigua en què es van formar. Entre la gran varietat de components biogènics que romanen en els sediments marins, l'estudi de foraminífers bentònics, que habiten a sobre o dins dels sediments marins, reflecteixen les condicions de les aigües profundes de l'oceà, com ara la temperatura, la densitat, patrons de productivitat, nutrients i oxigen.

Durant el període estudiat (2,3-1,6 Ma) que correspon al Plistocè inferior, el clima de la terra oscil·lava cíclicament entre períodes glacials i interglacials. El començament de la glaciació de l'hemisferi nord es va produir abans, a 2,75 Ma, quan els cicles climàtics seguien la periodicitat de la obliquïtat (41 ka). Aquesta va canviar fa aproximadament 1 Ma, quan la periodicitat de l'excentricitat (100 ka) va esdevenir la dominant, al mateix temps que el gel de l'hemisferi nord va assolir la seva extensió màxima. Així, el període estudiat engloba el "món de 41 Ka" amb una evolució progressiva cap a un clima més fred i, aparentment, sense grans transicions climàtiques a escala global, d'acord amb el registre global de  $\delta^{18}\text{O}$  marí. No obstant això, registres tropicals indiquen una reorganització atmosfèrica significativa durant el període de 1,5 a 2 Ma que ha estat associada a una intensificació de la circulació de Walker [Ravelo et al., 2004]. S'ha proposat que els canvis tropicals durant aquest període van actuar com un acoblament atmosfera-océà retro alimentats i amplificats per petits canvis d'insolació seguits per moviments de l'òrbita terrestre [Ravelo et al., 2004]. Però, les característiques i l'evolució temporal d'aquests canvis tropicals no han estat ben descrits.

Aquesta Tesi es centra en la zona del Pacífic Equatorial Oriental, una àrea clau per obtenir registres paleoceanogràfics d'alta resolució a baixes latituds. Concretament, aquest

estudi està centrat en l'anàlisi de dos testimonis del Ocean Drilling Program (ODP), Site 1240 i 1238. Treballs preliminars indiquen l'ocurrència d'intensos canvis en els patrons de sedimentació que estan probablement relacionats amb els canvis en els patrons regionals atmosfera-oceà [Mix et al., 2003]. A més, el període estudiat al ODP 1240 mostra la característica de la presència de noves laminacions de diatomees de l'espècie *Thalassiothrix spp.* que tendeixen a formar xarxes, particularment freqüents en el període previ a 1,85 Ma. La metodologia emprada per a l'anàlisi de la fracció lítica consisteix en l'anàlisi de la mida de gra i anàlisi clúster, el contingut en lítics complementat amb l'estudi de la seva procedència a través de l'anàlisi d'isòtops radiogènics ( $^{87}\text{Sr}/^{86}\text{Sr}$  i  $^{143}\text{Nd}/^{144}\text{Nd}$ ), així com amb l'estudi mineralògic d'aquesta fracció i l'anàlisi del contingut en ferro (Fe) i titani (Ti). Per altra banda, l'anàlisi de la fracció biogènica s'ha focalitzat en l'estudi d'abundància de la fauna bentònica i en l'anàlisi geoquímic del carboni orgànic (TOC, de l'anglès Total Organic Carbon) i l'òpal. A més, el registre de  $\delta^{18}\text{O}$  mesurat en foraminífers bentònics ha permès establir una cronologia sòlida per al període estudiat, des de 1,6 fins a 2,3 Ma.

Durant aquest període, els registres de contingut en Fe, Ti i lítics mostren una extraordinària semblança amb una tendència creixent cap al sostre de la seqüència estudiada. Aquesta tendència presenta una important intensificació a partir de 1,85 Ma, particularment durant els períodes glacials. A més, els elevats continguts en ferro concorden amb alts continguts en TOC i percentatges del foraminífer bentònic *Uvigerina spp.*, el que indica una important fertilització de les aigües superficials per subministrament de pols atmosfèric. Aquesta fertilització hauria incrementat el transport de matèria orgànica cap al fons oceànic el que hauria alimentat els ecosistemes bentònics. Sorprenentment, alts continguts en TOC i òpal també es produeixen durant alguns intervals glacials anteriors a 1,85 Ma, que presenten continguts baixos en ferro i lítics, però en aquest cas, *Uvigerina spp.* no es beneficia d'aquests nutrients. Especialment remarcable és la presència de les laminacions de diatomees (LDO) coincidint amb aquest períodes glacials pre-1,85 Ma. Quan aquestes LDO es formen es produeix un transport molt eficient de matèria orgànica cap al fons, que hauria provocat un canvi dràstic en l'ecosistema bentònic. Sincrònicament a aquests esdeveniments de baix contingut en ferro i material lític, la senyal de  $^{87}\text{Sr}/^{86}\text{Sr}$  i  $^{143}\text{Nd}/^{144}\text{Nd}$  del material litogènic es caracteritza per valors menys radiogènics i per una distribució granulomètrica molt distintiva, amb material més groller i poc seleccionat. Per tant, s'ha interpretat que l'augment de la productivitat de diatomees en el període previ a 1,85 Ma no sembla el resultat de la fertilització per pols atmosfèric, sinó que s'hauria produït a través de l'advecció d'aigües riques en nutrients procedents probablement de l'oceà Austral. Això seria el resultat d'un debilitament dels vents alisis i una dominància de la deposició humida de pols, situació que és consistent amb una migració de la Zona de Convergència Intertropical (ITCZ)

cap al sud, situant-se segurament propera a ODP 1240. Fet que afavoriria l'entrada de pols procedent de Centre Amèrica, amb una senyal menys radiogènica de  $^{87}\text{Sr}/^{86}\text{Sr}$  i  $^{143}\text{Nd}/^{144}\text{Nd}$  i que previsiblement tindria també un gran impacte climàtic en els continents adjacents.

A partir de 1,85 Ma, es va produir una intensificació dels vents alisis durant els períodes glacials que hauria induït a una fertilització de les aigües superficials per ferro. Aquesta intensificació vindria donada per un desplaçament de la ITCZ cap al nord estimulando una major surgència equatorial. Cal destacar el període glacial denominat MIS 56 (Marine Isotope Stage), centrat a 1,65 Ma, amb la formació d'una intensa LDO que suggereix un retorn persistent de la ITCZ cap al sud i, aparentment, superant en intensitat als períodes glacials pre-1,85 Ma. El seu efecte s'ha pogut detectar més al sud, al ODP 1238.

Tot i l'alta productivitat registrada durant els períodes glacials pre i post-1,85 Ma, l'ecosistema bentònic del ODP 1240 mostra diferents respostes, el que suggereix que els processos de transport de la matèria orgànica a l'oceà també van canviar. Diferents processos de deposició s'interpreten com el resultat de les dues posicions glacials diferents de la ITCZ. Així doncs, l'estudi relacionat d'aquestes dues fraccions és d'especial rellevància a l'hora de connectar el sistema atmosfèric amb l'oceànic així com la seva influència en els cicles biogeoquímics i sobretot, en la captació de  $\text{CO}_2$  per part de l'oceà i el seu transport cap al fons marí.

Aquest canvi en el sistema atmosfera-oceà a partir de 1,85 Ma va quedar també registrat al llarg de la regió tropical tant en registres marins (equatorial Atlantic Ocean, ODP 659; western Arabian sea, ODP 722), com continentals (Chinese Loess, China), tots ells modulats per les migracions de la ITCZ. Així, aquests mostren una tendència cap a l'aridificació al llarg de la regió tropical particularment intensificada a partir de 1.85 Ma. Aquesta tendència a l'aridificació també ha tingut un impacte directe en els patrons de vegetació al llarg de la regió tropical africana, on s'observa una progressió des d'una vegetació de tipus arbori (C3), fins a una vegetació de tipus sabana (C4) a partir de 1,85 Ma. La disponibilitat de noves i acurades datacions de Urani/Plom realitzades en formacions de colades (FGIs, de l'anglès Flowstones Formation) de coves de Sud-Àfrica han permès una correlació precisa dels nous registres paleoclimàtics tropicals d'alta resolució, l'evolució paleoclimàtica de Sud Àfrica i aparicions/desaparicions claus en l'evolució dels homínids. La comparació d'aquestes dades mostra una sèrie d'esdeveniments extrems humits que van interrompre sobtadament la llarga i progressiva etapa d'aridificació descrita anteriorment. Curiosament, l'esdeveniment més intens s'ha localitzat a 1,8 Ma. Aquests FGIs només es poden formar sota condicions de pluja extrema i continua a Sud-Àfrica, condicions que es donarien amb una posició fixa de la ITCZ al sud. Aquesta situació va estar afavorida per la configuració orbital, amb mínim d'excentricitat, juntament amb unes condicions de "La Niña-like". Aquests esdeveniments

també s'observen en un altre registre de Sud-Àfrica, concretament de la cova Buffalo, a on es confirma que aquest període humit extrem va interrompre una tendència més lenta cap a l'aridificació. Aquests canvis sobtats haurien sotmès als homínids a una pressió ambiental addicional, quan aquests ja estaven adaptant-se a un medi més àrid. Afavorint així un procés d'especiació amb la desaparició d'especies com *Australopithecus africanus*, *Australopithecus sediba* i *Homo habilis*, i l'aparició de noves espècies com *Homo erectus*.

Així, aquesta Tesi demostra l'elevada inestabilitat que va patir el sistema climàtic durant el Plistocè inferior al llarg de la regió tropical i subtropical, que hauria deixat una petjada important en un dels moments claus de l'evolució dels homínids.

## RESUMEN

Los sedimentos marinos profundos son claves para la comprensión de la variabilidad del clima a lo largo de la historia de la Tierra. Estos sedimentos contienen una gran variedad de indicadores para reconstruir cambios tanto del océano como de la atmósfera, elementos claves dentro del sistema climático. Los sedimentos marinos, formados por componentes líticos y biogénicos, ofrecen una amplia variedad de información paleoambiental. Por una parte, la fracción lítica proviene principalmente de los continentes adyacentes y su estudio ofrece la oportunidad de entender los procesos de transporte que han sido responsables de su deposición. Por lo tanto, pueden proporcionar información sobre las aportaciones eólicas y fluviales, de las características y las condiciones climáticas de la zona de origen de las partículas y, en ciertos contextos, pueden también dar información sobre las corrientes oceánicas profundas. Así, la fracción lítica tiene un peso importante para reconstruir las condiciones atmosféricas del pasado, como la dirección del viento, la ubicación y la intensidad de los cinturones de lluvia. Por otra parte, el análisis de los componentes biogénicos marinos proporciona información de las condiciones oceanográficas. En esta fracción se reflejan las propiedades de la masa de agua en que se formaron. Entre la gran variedad de componentes biogénicos que permanecen en los sedimentos marinos, el estudio de foraminíferos bentónicos, que habitan encima o dentro de los sedimentos marinos, reflejan las condiciones de las aguas profundas del océano, como temperatura, densidad, patrones de productividad, nutrientes y oxígeno.

Durante el período estudiado (2,3-1,6 Ma), que corresponde al Pleistoceno inferior, el clima de la tierra oscilaba cíclicamente entre periodos glaciares e interglaciares. El inicio de la glaciación del hemisferio norte se produjo antes, a 2,75 Ma, cuando los ciclos climáticos seguían la periodicidad de la oblicuidad (41 ka), hasta hace aproximadamente 1 Ma, cuando la periodicidad de la excentricidad (100 ka) se convirtió en la dominante, al tiempo que el hielo del hemisferio norte alcanzó su extensión máxima. Así, el período estudiado engloba el “mundo de 41 Ka” con una evolución progresiva hacia un clima más frío y, aparentemente, sin grandes transiciones climáticas a escala global, de acuerdo con el registro global de  $\delta^{18}\text{O}$  marino. Sin embargo, registros tropicales indican una reorganización atmosférica significativa durante el período de 1,5 a 2 Ma que, según Ravelo et al., 2004, estaría asociada a una intensificación de la circulación de Walker. Los mismos autores proponen que los cambios tropicales durante este período actuaron como un acoplamiento atmósfera-océano. Estos cambios estarían retro alimentados y amplificados por pequeños cambios de insolación, seguidos por movimientos de la órbita terrestre. No obstante, la baja resolución de los datos disponibles hasta la fecha para este periodo no han permitido caracterizar estos cambios

tropicales y su evolución temporal.

Así, esta Tesis pretende abordar la caracterización de estos cambios tropicales durante el Pleistoceno Inferior, gracias a la alta resolución disponible en los registros paleoceanográficos de la zona Pacífico ecuatorial oriental. Concretamente, este estudio está centrado en el análisis de dos testigos del Ocean Drilling Program (ODP), Site 1240 y 1238. Además, se aborda su comparación con otros testigos marinos y continentales a lo largo de la región tropical y subtropical. Trabajos preliminares han indicado la ocurrencia de intensos cambios en los patrones de sedimentación en estos testigos, probablemente relacionados con cambios en los patrones regionales atmósfera-océano [Mix et al., 2003]. Además, el periodo estudiado en el ODP 1240 tiene la característica de la presencia de nueve laminaciones de diatomeas de la especie *Thalassiothrix spp.* que tienden a formar redes, y se concentran particularmente en el periodo previo a 1,85 Ma. La metodología utilizada para el análisis de la fracción lítica consiste en el análisis del tamaño de grano y análisis clúster, el contenido en líticos complementado con el estudio de su procedencia a través del análisis de isótopos radiogénicos ( $^{87}\text{Sr}/^{86}\text{Sr}$  y  $^{143}\text{Nd}/^{144}\text{Nd}$ ), así como con el estudio mineralógico de esta fracción y el análisis del contenido en hierro (Fe) y titanio (Ti). Por otra parte, el análisis de la fracción biogénica se ha focalizado en el estudio de abundancia de la fauna bentónica y en el análisis geoquímico del carbono orgánico (TOC, del inglés Total Organic Carbon) y el ópalo. Además, el registro de  $\delta^{18}\text{O}$ , medido en foraminíferos bentónicos, ha permitido establecer una cronología sólida para el período estudiado.

Durante este periodo, los registros de contenido de Fe, Ti y líticos muestran un extraordinario parecido con una tendencia creciente hacia el techo de la secuencia estudiada. Esta tendencia presenta una importante intensificación a partir de 1,85 Ma, particularmente durante los periodos glaciales. Además, los elevados contenidos en hierro concuerdan con altos contenidos en TOC y porcentajes del foraminífero bentónico *Uvigerina spp.*, lo que indica una importante fertilización de las aguas superficiales por suministro de polvo atmosférico. Esta fertilización habría incrementado el transporte de materia orgánica hacia el fondo oceánico lo que a su vez habría alimentado a los ecosistemas bentónicos. Sorprendentemente, altos contenidos en TOC y ópalo también se producen durante algunos intervalos glaciales anteriores a 1,85 Ma, que también presentan contenidos bajos en hierro y líticos, pero en este caso *Uvigerina spp.* no se beneficia de estos nutrientes. Especialmente remarcable es la presencia de las laminaciones de diatomeas (LDO) coincidiendo con estos períodos glaciares pre-1,85 Ma. Cuando estas LDO se forman se produce un transporte muy eficiente de materia orgánica hacia el fondo, que habría provocado un cambio drástico en el ecosistema bentónico. Sincrónicamente a estos eventos de bajo contenido en hierro y material lítico, la señal de  $^{87}\text{Sr}/^{86}\text{Sr}$  y  $^{143}\text{Nd}/^{144}\text{Nd}$  del material litogénico se caracteriza

por valores menos radiogénicos y por una distribución granulométrica muy distintiva, con material más grosero y poco seleccionado. Por lo tanto, el aumento de la productividad de diatomeas en el período previo a 1,85 Ma no parece el resultado de la fertilización por polvo atmosférico, sino que se habría producido a través de la advección de aguas ricas en nutrientes procedentes probablemente del océano Austral. Esta situación sería compatible con un aparente debilitamiento de los vientos alisios y una dominante deposición húmeda de polvo, situación que es consistente con una migración de la Zona de Convergencia Intertropical (ITCZ) hacia el sur, situándose seguramente cercana a ODP 1240. Situación que favorecería la entrada de polvo procedente de Centro América, con una señal más radiogénica de  $^{87}\text{Sr}/^{86}\text{Sr}$  y  $^{143}\text{Nd}/^{144}\text{Nd}$  y que previsiblemente tendría también un gran impacto climático en los continentes adyacentes.

A partir de 1,85 Ma, se produjo una intensificación de los vientos alisios durante los períodos glaciares que habría inducido a una fertilización de las aguas superficiales por hierro. Esta intensificación vendría dada por un desplazamiento de la ITCZ hacia el norte estimulando a su vez un mayor afloramiento ecuatorial. Cabe destacar el período glacial denominado MIS 56 (Marine Isotope Stage), centrado en 1,65 Ma con la formación de una intensa LDO, que sugiere un retorno persistente de la ITCZ hacia el sur y, aparentemente, superando en intensidad a los períodos glaciares pre-1,85 Ma. Su efecto se ha podido detectar más al sur, en la localización del ODP 1238.

A pesar de la alta productividad registrada durante los períodos glaciares pre y post-1,85 Ma, el ecosistema bentónico del ODP 1240 muestra diferentes respuestas, lo que sugiere que los procesos de transporte de la materia orgánica en el océano también cambiaron. Diferentes procesos de deposición se interpretan como el resultado de las dos posiciones glaciares distintas de la ITCZ. Así pues, el estudio relacionado de estas dos fracciones es de especial relevancia a la hora de conectar el sistema atmosférico con el oceánico, así como su influencia en los ciclos biogeoquímicos y sobre todo, en la captación de  $\text{CO}_2$  por parte del océano y su transporte hacia el fondo marino.

Este cambio en el sistema atmósfera-océano a partir de 1,85 Ma quedó también registrado a lo largo de la región tropical, tanto en registros marinos (océano Atlántico ecuatorial, ODP 659; mar Arábigo occidental, ODP 722), como continentales (Chinese Loess, China), todos ellos modulados por las migraciones de la ITCZ. Así, éstos muestran una tendencia hacia la aridificación a lo largo de la región tropical particularmente intensificada a partir de 1,85 Ma. Esta tendencia a la aridificación también habría tenido un impacto directo en los patrones de vegetación a lo largo de la región tropical africana, donde se observa una progresión desde una vegetación de tipo arbóreo (C3), hasta una vegetación de tipo sabana (C4) a partir de 1,85 Ma. La disponibilidad de nuevas y precisas dataciones de Uranio/

Plomo (U/Pb) realizadas en formaciones de coladas (FGIs, del inglés Flowstones Formation) de cuevas de Sudáfrica han permitido una correlación detallada de los nuevos registros paleoclimáticos tropicales de alta resolución, la evolución paleoclimática de Sudáfrica y apariciones/desapariciones claves en la evolución de los homínidos. La comparación de estos datos muestra una serie de eventos extremos húmedos que interrumpieron repentinamente la larga y progresiva etapa de aridificación descrita anteriormente. Curiosamente, el evento más intenso se ha localizado a 1,8 Ma. Estos FGIs sólo se pueden formar bajo condiciones de lluvia extrema y continúa en Sudáfrica, condiciones que se darían con una posición fija de la ITCZ en el sur. Esta situación estaría favorecida por la configuración orbital, con un mínimo de excentricidad, junto con unas condiciones de “La Niña-like”. Estos eventos también se observan en otro registro de Sudáfrica, concretamente de la cueva Buffalo, donde se confirma que este período húmedo extremo interrumpió una tendencia más lenta hacia la aridificación. Estos cambios repentinos habrían sometido a los homínidos a una presión ambiental adicional, cuando éstos ya se estaban adaptando a un medio más árido. Favoreciendo así un proceso de especiación con la desaparición de especies como *Australopithecus africanus*, *Australopithecus sediba* y *Homo habilis*, y la aparición de nuevas especies como *Homo erectus*.

Así, esta Tesis demuestra la elevada inestabilidad que sufrió el sistema climático durante el Pleistoceno inferior a lo largo de la región tropical y subtropical, que habría dejado una huella importante en uno de los momentos claves de la evolución de los homínidos.



## ABSTRACT

Deep marine sediments are key to the comprehension of the climate variability along the Earth's history. These sediments contain a large variety of indicators to reconstruct the past changes in the ocean and the atmosphere, which are indeed the climate conditions monitoring. Marine sediments, composed by lithic and biogenic compounds, offer a wide variety of paleoambiental information. Lithic fraction comes mainly from the surrounding continent and its study gives the chance to understand transport processes which have been responsible of its deposition. Thereby, it can provide information about eolian and fluvial supply, climatic conditions and characteristics about particles source area, and in some contexts, can also give information about deep oceanic currents. Thus, lithic fraction has an important weight to reconstruct past atmospheric conditions, as wind direction, location and intensity of the rainfalls belts. Besides, the biogenic fraction, which is formed in the ocean, gives information of the oceanographic conditions. Through this fraction are reflected the conditions of the water mass where it was formed. Between the huge variety of biogenic elements which are preserved in marine sediments, the study of benthic foraminifera reflects the conditions of the deep water masses of the ocean, like temperature, density, productivity patterns, nutrient and oxygen.

During the studied period that corresponds to the early Pleistocene, the Earth's climate oscillated cyclically between glacial and interglacial periods. The beginning of the Northern Hemisphere Glaciation (NHG) occurred before, at 2.75 Myr, and from that moment the climate cycles have followed the obliquity periodicity (41 kyr). This became progressively amplified along the  $\delta^{18}\text{O}$  record until 1 Myr when the eccentricity became (100 kyr) dominant at the same time that Northern Hemisphere ice reached its maximum extension. Thus, the studied period englobes the "41-kyr Earth's" with a progressive evolution towards a colder climate. Instead of this, several tropical records show a significant atmospheric reorganization during the period between 1.5 and 2 Myr which has been associated to a major development of the Walker circulation [Ravelo et al., 2004]. It has been proposed that these tropical changes during this period acted as a coupled feedback between atmosphere and ocean, and amplified by few insolation changes followed by Earth's orbit movements [Ravelo et al., 2004]. But, characteristics and time evolution of these tropical changes haven't been well described.

The present PhD dissertation is centered on the Eastern Equatorial Pacific, a key region to obtain high-resolution paleoceanographic records at low latitudes. Concretely, this study is focused on the analysis of two sediment core sites from the Ocean Drilling Program (ODP), Site 1240 and 1238. Preliminary works on these sites indicate the occurrence of intense

changes in the sedimentation patterns, that are probably related with changes in the atmosphere-ocean regional patterns [Mix et al., 2003]. Besides, ODP 1240 shows the presence of nine laminated diatom oozes of *Thalassiothrix spp.* which tends to form grids, particularly present during the period before to 1.85 Myr. The methodology used for the lithic fraction analysis consists on grain size and cluster analysis, lithic content complemented with radiogenic isotopes analysis ( $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$ ), mineralogical content, iron (Fe) and titanium (Ti) content. On the other hand, biogenic fraction analysis has been focused in the benthic foraminifera abundance and the geochemical analysis of Total Organic Carbon (TOC) and opal. In addition, this  $\delta^{18}\text{O}$  record has allow us to construct a solid chronology for the studied period, from 2.3 until 1.6 Myr.

During this period, Fe, Ti and lithic contents show an extraordinary resemblance with an increasing upward trend to the top of the sequence. This trend presents an important intensification from 1.85 Myr, particularly during glacial periods. Besides, the higher contents in Fe and TOC, and the abundance in benthic foraminifera *Uvigerina spp.*, that would demonstrate an important fertilization of the surface ocean by atmospheric dust supply. This fertilization would increased the organic matter transport towards the deep sea, feeding the deep benthic ecosystems. Surprisingly, higher TOC and opal contents are also produced during some glacial intervals prior to 1.85 Myr, which show lower iron contents, but in this case, *Uvigerina spp.* didn't benefit these nutrients. Specially remarkable is the presence of the LDO coinciding with those glacial periods previous to 1.85 Myr. When these LDO are formed, is produced a very efficient transport of organic matter to the deep sea, which would incited a drastic change on the benthic ecosystem. Sinchronically, iron, titanium and lithic content are low, and this lithic material is characterized by a low radiogenic signal ( $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$ ), a specific histogram, coarser and less classified. Thereby, the diatom productivity increase previous to 1.85 Ma was not the result from atmospheric dust fertilization, but it would be produced probably through the advection of nutrient rich waters coming from the Southern ocean. This is interpreted as a reflex of a trade winds weakening and a major dust deposition by wet way, situation that is consistent with a southwards migration of the Intertropical Convergence Zone (ITCZ), locating close to ODP 1240. This situation would favor the dust entrance from Central America, with a lower signal of radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$ , and would also has a major climate impact on adjacent continents.

From 1.85 Myr, an intensification of the trade winds was produced during the glacial periods that would induced a surface ocean fertilization by iron. This intensification would be produced by a northwards ITCZ movement, stimulating an intense equatorial upwelling. It is necessary to remark that the glacial period MIS 56, centered at 1.56 Ma, coinciding with the thickest LDO suggests the persistent ITCZ southward migration, exceding in intensity to

the previous glacial periods at 1.85 Ma. Its effect was able to detect southerly, at ODP 1238.

Instead of the higher productivity registered during the glacial periods pre and post-1.85 Ma, the benthic ecosystem shows different responses, which suggests that the transport processes of the organic matter to the ocean also changed. Different depositional processes are interpreted as the result of two different glacial positions of the ITCZ. Therefore, the ensemble study of these two fractions is specially relevant to connect the atmospheric and oceanic system, as well as its influence in the biochemical cycles, specially in the CO<sub>2</sub> cap- tion from the ocean and its transport to the deep ocean.

This change in the atmosphere-ocean system from 1.85 Ma was also recorded throughout the tropical region in both marine (equatorial Atlantic Ocean, ODP 659; western Arabian sea, ODP 722) and continental records (Chinese Loess, China), all of them modulated by ITCZ migrations. Thus, these show a trend towards aridity throughout the tropical region particularly intensified from 1.85 Ma. This aridity trend has also had a direct impact on ve- getation patterns along the tropical region of Africa, where there is a progression from wood- land C3-pathway to C4 arid-adapted grassland vegetation from 1.85 Ma. The availability of new and accurate Uranium-Lead (U-Pb) dates from Flowstones Formation (FGIs,) in South Africa caves have enabled a precise correlation of the high-resolution paleoclimatic records from tropical belt, the climate evolution of South Africa and the key appearances/disappea- rances in hominid evolution. The comparison of these data shows a series of extreme wet events that interrupted suddenly the long and gradual aridification phase described above. Interestingly, the most intense event was located at 1.8 Ma. These FGIs can be only formed under conditions of extreme and continuous rainfalls in South Africa, conditions that would occur with a fixed position of the ITCZ to the south. This situation was favored by the orbital configuration with an eccentricity minimum, along with “La Niña-like” conditions. These wet events are also seen in another record in South Africa, namely the cave Buffalo, where it is confirmed that this extreme wet period interrupted a slower trend towards aridity. These su- dden changes should subject hominids to an additional environmental pressure when they were already adapting to a drier environment. These new conditions promoted a speciation process with the disappearance of species, such as *Australopithecus africanus*, *Australopithe- cus sediba* and *Homo habilis*, and the emergence of new species such as *Homo erectus*.

Thus, this thesis demonstrates the high instability of the climate system throughout the tropical and subtropical region during the early Pleistocene, which would have left an impor- tant imprint on one of the key moments of the hominids evolution.



## Presentació i estructura de la Tesi

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La present Tesi Doctoral, està integrada per un compendi de dos articles publicats en revistes internacionals indexades en la Journal Citation Reports de l'Institute for Scientific Information (ISI) i un tercer article en preparació, i ha estat estructurada en quatre capítols i annexos.

El Capítol 1 consisteix en una introducció general, on es presenta l'àrea d'estudi i es descriu la metodologia emprada per a dur a terme la Tesi Doctoral.

El capítol 2 engloba els dos articles publicats, un tercer article en preparació i un resum dels resultats obtinguts en aquesta Tesi.

Capítol 2.1. Povea, P., Cacho, I., Moreno, A., Menéndez, M., Méndez, F.J. (2015). A new procedure for the lithic fraction characterization in marine sediments from the high productivity areas: optimization of analytical and statistical procedures. *Limnology and Oceanography: methods* (13), 127-137, doi: 10.1002/lom3.10013. En aquest capítol es presenta un nou protocol metodològic per a la caracterització de la fracció lítica en sediments marins procedents d'àrees amb una elevada productivitat i per tant amb un alt contingut de restes biogèniques. En aquest capítol es posa de manifest la necessitat d'un protocol acurat d'eliminació de la fracció biogènica per tal d'obtenir una caracterització precisa i sense artefactes de la fracció lítica.

Capítol 2.2. Povea, P., Cacho, I., Moreno, A., Pena, L.D., Menéndez, M., Calvo, E., Canals, M., Robinson, R.S., Méndez, F.J., Flores, J. A. (2016). Atmosphere-ocean linkages in the Eastern Equatorial Pacific over the early Pleistocene. *Paleoceanography*, 31, doi:10.1002/2015PA002883. En aquesta secció es presenta l'estudi del sistema acoblat atmosfera-oceà a través de la caracterització a alta resolució de la fracció lítica i biogènica del Pacífic equatorial. En aquesta publicació s'observen grans canvis d'aquesta interconnexió com a conseqüència de migracions de la Zona de Convergència Intertropical durant el Plistocè inferior. A més, es presenta una nova cronoestratigrafia basada en el registre d'alta resolució d'isotops d'oxigen extret de foraminífers bentònics.

Capítol 2.3. Povea, P., Pickering, R., van De Flierdt, T., Bladé, I., Cacho, I., (en preparació). Major atmospheric reorganization in the tropical band during key junctures in hominin evolution. En aquest article es realitza una comparació de diferents registres marins i continentals al llarg de la franja tropical i subtropical per tal d'entendre canvis en el sistema atmosfera-oceà durant el Plistocè inferior i la seva influència sobre moments claus de l'evolució humana.

Els capítols 2.4. i 3, corresponen a la síntesi i discussió dels resultats presentats en el capítol 2.

Per últim, en el capítol 4 es detallen les principals conclusions obtingudes en aquesta Tesi.







# **CAPÍTOL I**

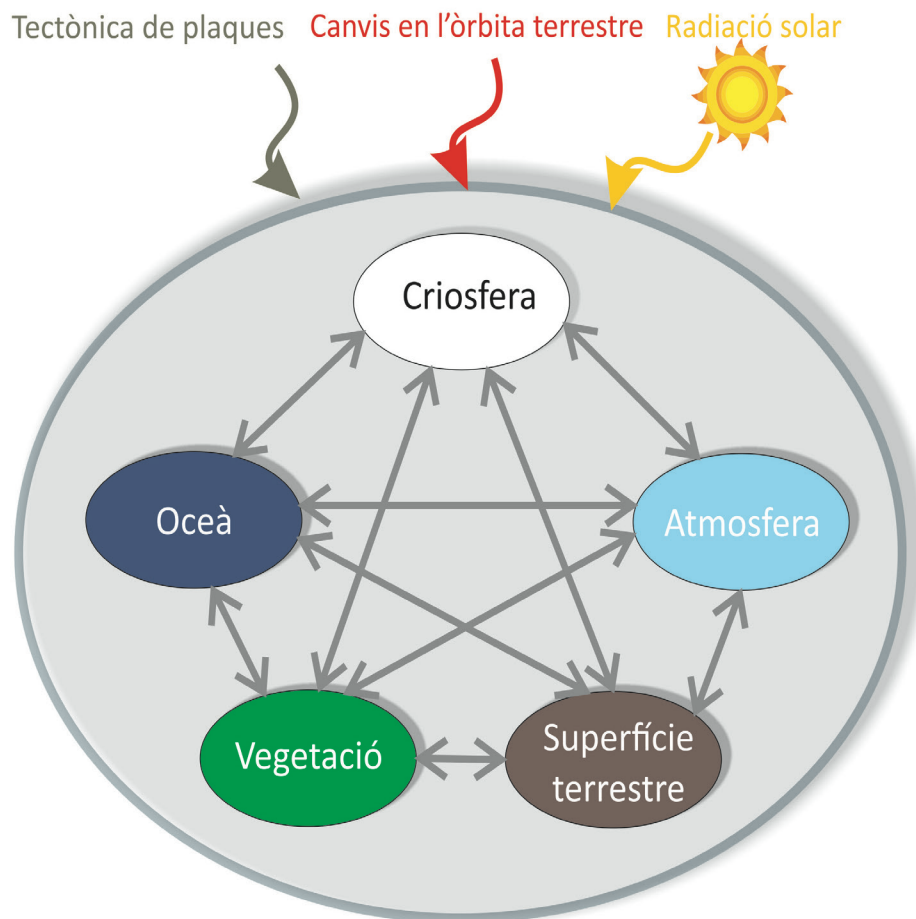
# **INTRODUCCIÓ**





## 1.1. EL SISTEMA CLIMÀTIC TERRESTRE

El sistema climàtic és dinàmic, interactiu, complex i sensible de canviar tant per agents externs com per els mateixos elements interns del sistema, estretament interconnectats entre si (Fig. 1). Els elements propis del sistema climàtic els podem agrupar en grans compartiments com l'atmosfera, l'oceà, la criosfera, la superfície terrestre i la biosfera terrestre. Tots aquests elements són altament sensibles a determinats agents externs, o als denominats forçaments climàtics, responsables d'empènyer el clima del planeta a diferents estats d'equilibri, entre els que destaquen, la tectònica de plaques, els canvis d'insolació pels moviments en l'òrbita terrestre i la radiació solar [Ruddiman, 2001] (Fig. 1).



**Fig. 1.** Diagrama esquemàtic del sistema climàtic, on s'il·lustren tant els elements interns principals, representant la complexitat de les seves interaccions i destacant, a la part superior, els principals forçaments climàtics externs.

Els diferents elements del sistema presenten una resposta molt desigual a aquests forçaments externs. El sistema climàtic pot respondre als canvis interns i externs en un ampli rang d'escala temporal, des d'hores i dies fins a milions d'anys. Així doncs, els diferents components del sistema no es troben mai en equilibri, trobant-se immersos en un procés de reajustament continu i altament complex. Per exemple, el balanç radiatiu del planeta dependrà en gran mesura de la concentració de pols atmosfèric, que d'una banda actuarà reflectint i absorbint la radiació solar, però també incidirà en els patrons de precipitació i en la formació de núvols a escala atmosfèrica [Winckler i Mahowald, 2014].

La presència de l'home a la Terra ha influït d'una manera molt determinant en el sistema climàtic terrestre. Per aquest motiu, l'any 1988 es va crear el Panell Intergovernamental d'Experts sobre el Canvi Climàtic (IPCC, de l'anglès Intergovernmental Panel on Climate Change) amb la missió fonamental d'analitzar, organitzar i avaluar la informació científica disponible sobre el canvi climàtic, i diagnosticar quin era la influència de l'activitat antròpica en els canvis detectats. Aquests informes, que s'han anat publicant regularment cada cinc anys, s'han estructurat en l'avaluació del canvi climàtic, des del vessant físic, l'impacte, adaptació i vulnerabilitat de l'home, fins a la mitigació del canvi climàtic. Segons l'últim informe de valoració del IPCC, de l'any 2014 [IPCC, 2014], l'escalfament global del sistema climàtic és inequívoc i particularment pronunciat en les últimes tres dècades, concretament a partir de l'any 1950. Durant aquest temps l'atmosfera i l'oceà haurien patit canvis sense precedents, amb una major retirada dels casquets de gel als pols i una progressiva pujada del nivell del mar global.

### 1.1.1. Circulació atmosfèrica tropical i la seva interacció amb l'oceà

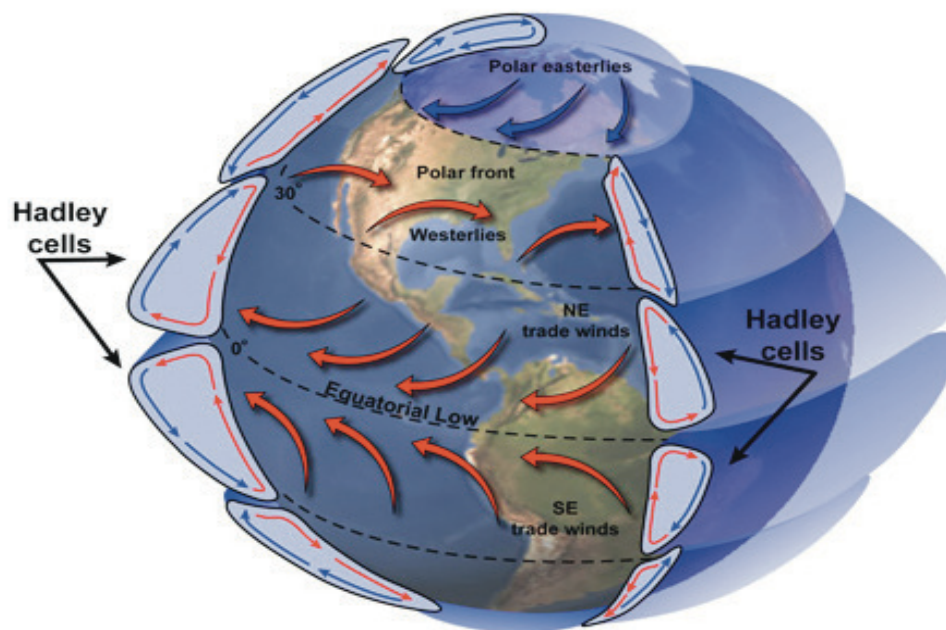
La circulació atmosfèrica global és un fenomen impulsat per l'escalfament desigual entre baixes i altes latituds, on la diferència en radiació solar incident és el motor de l'atmosfera i la rotació terrestre acaba traçant les seves rutes principals. Així doncs, la circulació atmosfèrica és un mecanisme que permet mantenir l'equilibri calorífic del planeta, distribuint l'energia calorífica que es produeix a l'equador, com a conseqüència d'una radiació solar incident més gran, cap a altes latituds. Per altra banda, la configuració definitiva també depèn en gran part de la rotació de la Terra, que provoca una desviació de les masses d'aire respecte a la seva trajectòria inicial. Aquesta desviació ve donada per l'anomenat efecte Coriolis, en honor a Gaspard Gustave de Coriolis, científic francès que va descobrir aquest efecte l'any 1835. Aquest efecte desvia les trajectòries cap a la dreta, o en sentit horari, a l'Hemisferi Nord i cap a l'esquerra, o en sentit antihorari, a l'Hemisferi Sud, mentre que a l'equador l'efecte Coriolis és gairebé inexistent.

Aquests diferents factors produeixen una circulació atmosfèrica latitudinal a través de

tres grans cel·les convectives de circulació per hemisferi, anomenades cel·les de Hadley, Ferrell i Polar, ordenades de menor a major latitud respectivament, i que engloben tota la superfície terrestre. No obstant això, l'atmosfera també pot transportar l'energia amb un component longitudinal, com és el cas de la cel·la de Walker (cf. secció 1.1.1.4), que provoca la transferència d'energia entre el Pacífic oriental i occidental.

#### 1.1.1.1. Cel·la de Hadley

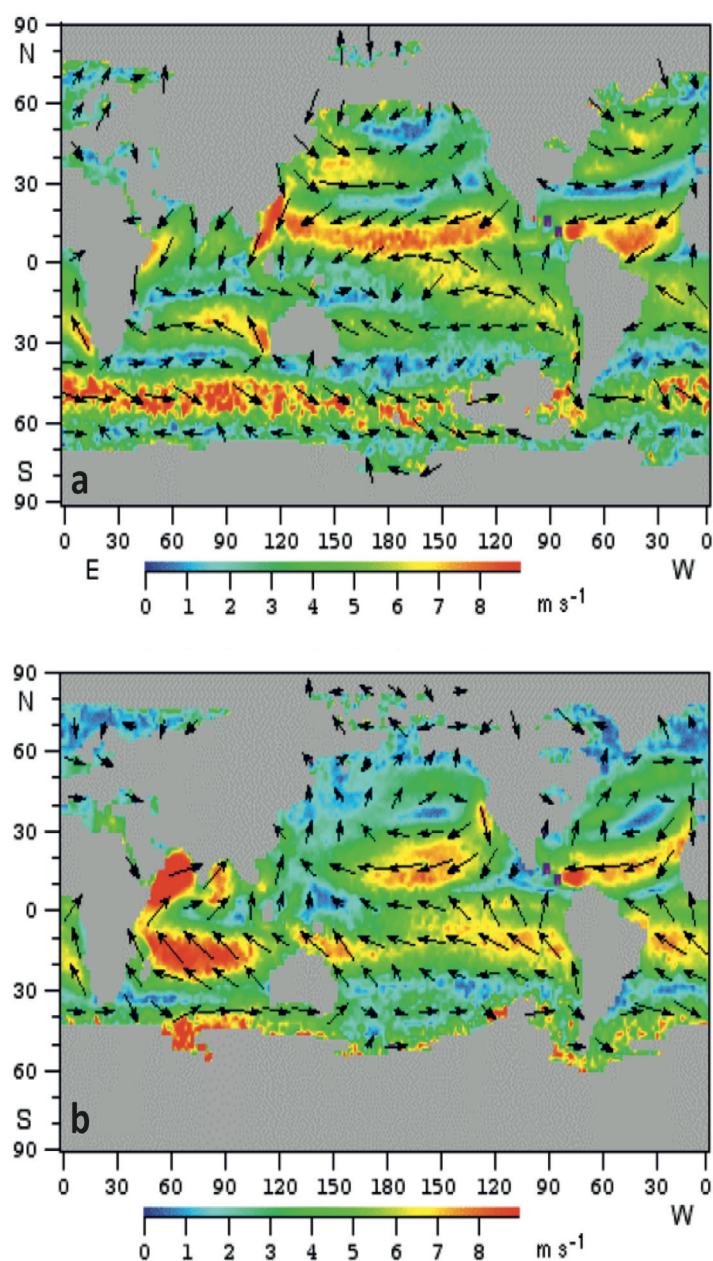
La circulació de Hadley és un component principal en la redistribució global d'energia que se situa entre els tròpics de Càncer i Capricorn ( $30^\circ$  N a  $30^\circ$  S) i que engloba tota la zona tropical terrestre (Fig. 2). Les masses d'aire calent a la regió equatorial ascendeixen fins al límit de la troposfera, com a conseqüència d'una radiació solar rebuda més gran, provocant un cinturó de baixes pressions atmosfèriques. Durant aquest trajecte les masses d'aire es van refredant i guanyant densitat i acaben descendint sobre els tròpics generant un centre d'altres pressions. Aquesta circulació rep el seu nom en honor a George Hadley, advocat anglès del segle XVIII aficionat a la meteorologia, que va ser el pioner en descobrir el funcionament de les cel·les convectives equatorials.



**Fig. 2.** Diagrama il·lustratiu de les cel·les de circulació atmosfèrica global, indicant la localització de la cel·la de Hadley entre els tròpics de Càncer i Capricorn (extret de [http://oceanworld.tamu.edu/resources/oceanography-book/Images/3d\\_hadleySmall.jpg](http://oceanworld.tamu.edu/resources/oceanography-book/Images/3d_hadleySmall.jpg)).

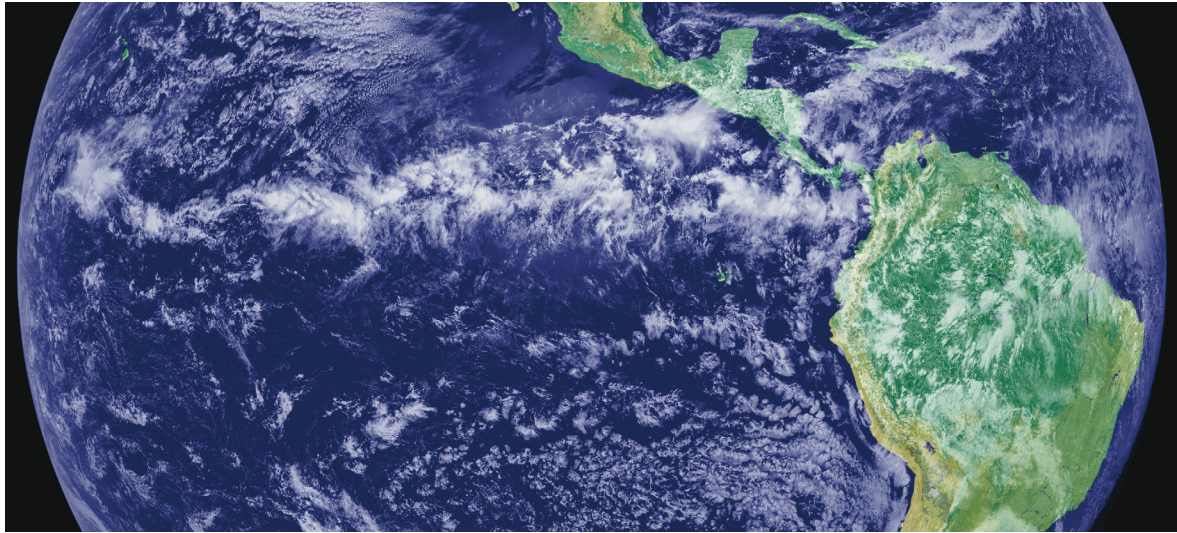
### 1.1.1.2. Zona de Convergència Inter-Tropical (ITCZ)

La Zona de Convergència Inter-tropical (ITCZ, de l'anglès Inter-Tropical Convergence Zone) està definida per la banda de màximes temperatures superficials centrada a la banda equatorial. Aquestes altes temperatures afavoreixen l'ascensió d'aire calent que a la vegada està carregat d'humitat, donant lloc a un extens cinturó atmosfèric de baixes pressions on convergeixen els vents alisis del nord i del sud (Fig. 3). L'aire que ascendeix condensa i produeix elevades precipitacions sota aquesta zona. Per tant, l'ITCZ és també la banda de màximes precipitacions i controla a la vegada el règim hidrològic de les regions tropicals (Fig. 4).

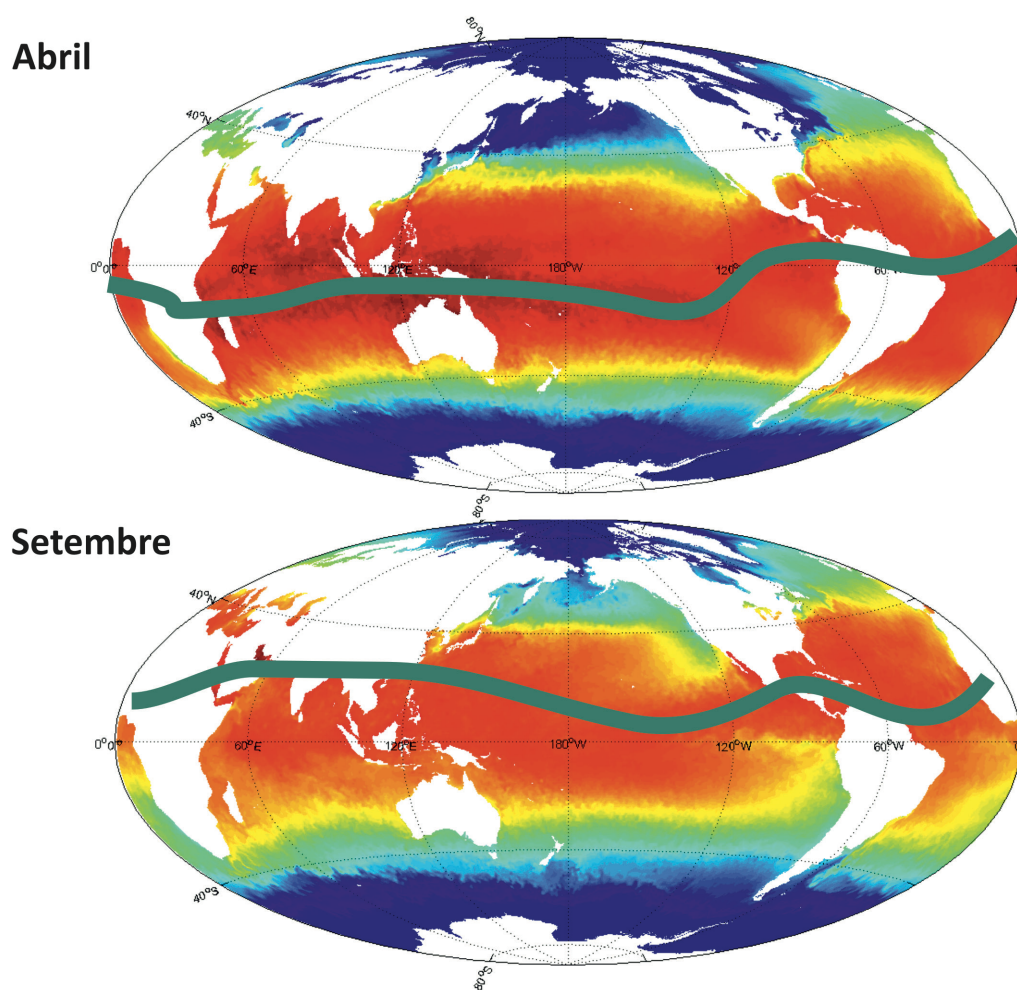


**Fig. 3.** Vents superficials a nivell del mar (a) Gener, (b) Juliol. Cal notar que els colors indiquen la velocitat en  $\text{m}\cdot\text{s}^{-1}$ . Dades extretes de la base de dades de la NOAA, extret de Tomczak i Godfrey, 1994. S'aprecia com els alisis del Pacífic sud són més intensos al mes de juliol.





**Fig. 4.** Combinació de dades de núvols de la NOAA, obtinguts mitjançant el satèl·lit GOES-11 (<http://earth-observatory.nasa.gov>). La zona de convergència intertropical es pot identificar per la franja de nuvolositat que s'observa al centre de la imatge.



**Fig. 5.** Migració estacional de la Zona de Convergència Intertropical (ITCZ) basada en les temperatures superficials oceàniques (SST, de l'anglès Sea Surface Temperatures), on les temperatures més elevades vénen determinades pels colors vermells i les més fredes pels colors blaus. La ITCZ es desplaça cap al sud durant l'hivern i primavera de l'hemisferi nord, mentre que durant l'estiu boreal la ITCZ es desplaça al nord situant-se sobre les SST màximes. Dades obtingudes de la base de dades GIOVANNI de la NOAA.

Tot i aquesta migració estacional (Fig. 5), la ITCZ es troba actualment desviada cap a l'hemisferi nord [Philander et al., 1996; Marshall et al., 2014], com a conseqüència del transport més elevat de calor atmosfèric cap al sud. Particularment, en la regió del Pacífic oriental, la ITCZ es situa sempre al nord de l'equador.

#### 1.1.1.3. Aflorament al Pacífic equatorial oriental

El Pacífic Equatorial es caracteritza per la dominància d'un sistema d'ascens vertical d'aigües (en anglès upwelling) que dona lloc a l'aflorament en superfície d'aigües fredes i riques en nutrients, i que es produeix a causa de l'acció dels vents sobre aquesta regió. Aquest procés és conseqüència del denominat transport d'Ekman, que és una divergència dels corrents oceànics produïts pels vents alisis del sud-est i del nord-est que conflueixen a l'equador. Aquestes aigües generen una llengua freda en les temperatures superficials (Sea Surface Temperatures, SST) i que desplaça la posició de la ITCZ cap al nord, però amb un significat ciclic anual, que dona SST més càlides al gener i més fredes al setembre (Fig. 5) [Mitchell and Wallace, 1992; Kessler et al., 1998]. Fruit d'aquesta estacionalitat es produeix una migració estacional de l'ITCZ, situant-se més al nord durant l'estiu de l'hemisferi Nord i més al sud durant l'hivern de l'hemisferi Nord (Fig. 5). Quan la ITCZ migra a la seva posició més al nord (juliol) es produeix una intensificació dels vents alisis del sud (Fig. 3) i per tant una intensificació de l'aflorament equatorial. L'ascens d'aigües més fredes (Fig. 5) produeix un subministrament excepcional de nutrients en superfície, provocant una fertilització de les aigües superficials i una elevada productivitat biològica. En canvi, quan la ITCZ es situa en la seva localització més al sud (gener), aquests sistemes de vents alisis es debiliten (Fig. 3) i produeixen al seu torn el debilitament de l'aflorament equatorial.

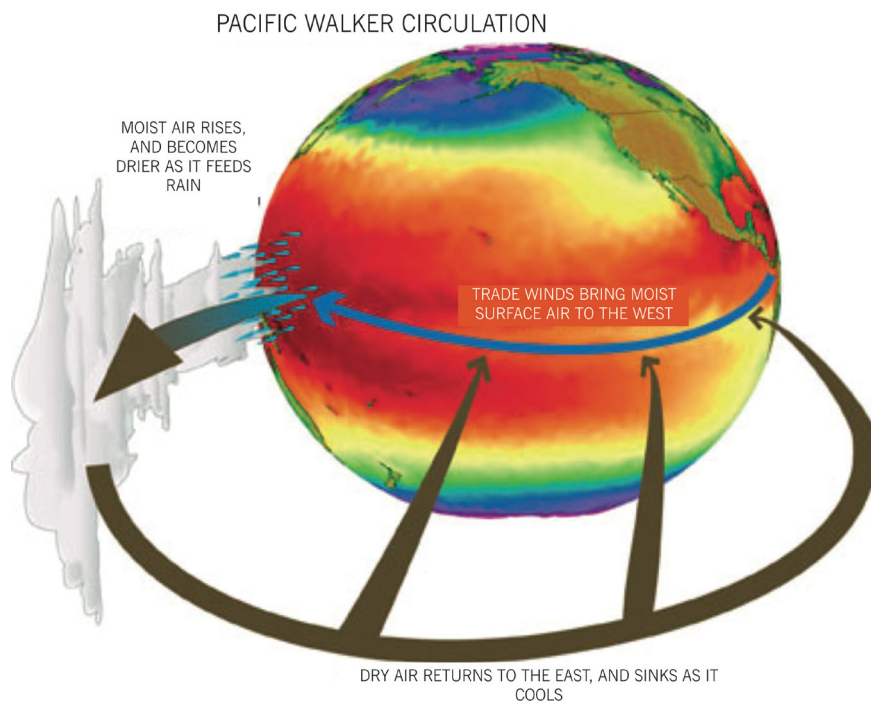
Actualment, aquesta activitat biològica no consumeix tots els macronutrients aportats per l'aflorament donat que aquest és deficitari en ferro, i per tant un subministrament addicional de ferro estimularia la productivitat biològica regional [Martin, 1990]. Els organismes que primer estimularien la seva producció per un augment del contingut en ferro serien les diatomees, i per tant la seva abundància és interpretada com el resultat de l'entrada de ferro al sistema. La font principal de ferro al sistema equatorial del Pacífic oriental és la pols atmosfèrica [Murray et al., 1995; Jickells et al., 2005].

#### 1.1.1.4. Cel·la de Walker

La cel·la de circulació de Walker va ser definida per Gilbert Walker a principis del segle



XX, com un patró circulatori oest – est que es produeix a la regió equatorial del Pacífic. Aquest patró és el resultat de la distribució asimètrica de les temperatures oceàniques superficials entre el Pacífic occidental i l'oriental. La circulació de Walker es produeix quan els intensos vents alisis de l'est arrossegueu l'aire de la part baixa de la troposfera, d'est a oest, on conflueixen en el centre de baixes pressions del Pacífic occidental. En arribar a aquesta regió les masses d'aire carregades d'humitat ascendeixen descarregant a la vegada abundants precipitacions (Fig. 6). Aquestes masses són transportades novament pels vents de l'oest de l'alta troposfera, en sentit oest- est, per finalment descendir a la part oriental del Pacífic, on es genera el centre d'altres pressions. Aquests vents intensos de superfície produeixen també un efecte a escala oceànica desencadenant un apilament de les aigües a la part del Pacífic occidental.

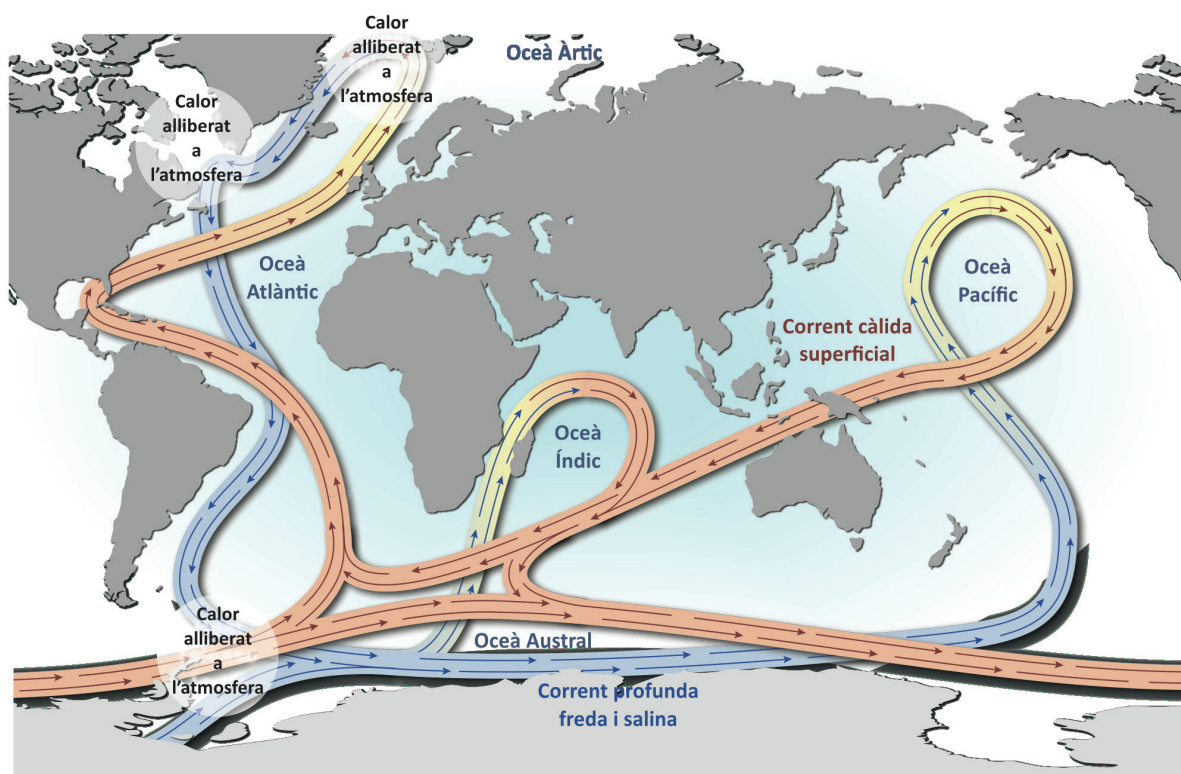


**Fig. 6.** Diagrama il·lustratiu de la circulació de Walker, on els colors vermells indiquen temperatures superficials oceàniques més elevades fins als colors blaus amb temperatures més baixes. La fletxa blava la direcció dels vents en superfície cap al Pacífic occidental, a on l'aire ascendeix carregat d'humitat i provoca intenses precipitacions. La fletxa marró mostra el transport troposfèric en sentit oest-est. Il·lustració de Gabriel Vechi, extret de [http://www.ncar.ucar.edu/research/climate/el\\_nino](http://www.ncar.ucar.edu/research/climate/el_nino).

### 1.1.2. Circulació oceànica i masses d'aigües tropicals

La circulació oceànica global es troba en constant interacció amb l'atmosfera i juga un paper essencial en la distribució latitudinal de calor. El mecanisme responsable d'aquest transport oceànic de calor a escala global és l'anomenada circulació termohalina (de l'anglès conveyor belt) [Broecker and Denton, 1990], que és impulsada per gradients diferents de densitat, fruit de diferències de temperatura i salinitat de l'aigua (Fig. 7). Una de les

àrees claus de l'oceà on es formen aigües profundes és l'Atlàntic Nord, on aigües fredes i salines s'enfonsen i circulen en profunditat cap a l'oceà Austral, Índic i Pacífic, on el progressiu escalfament provoca la somerització d'aquestes aigües, que finalment completen el seu recorregut en superfície cap a l'Atlàntic Nord. Així doncs, aquest sistema de circulació dóna lloc a una transferència global d'energia i sals al llarg del seu recorregut.



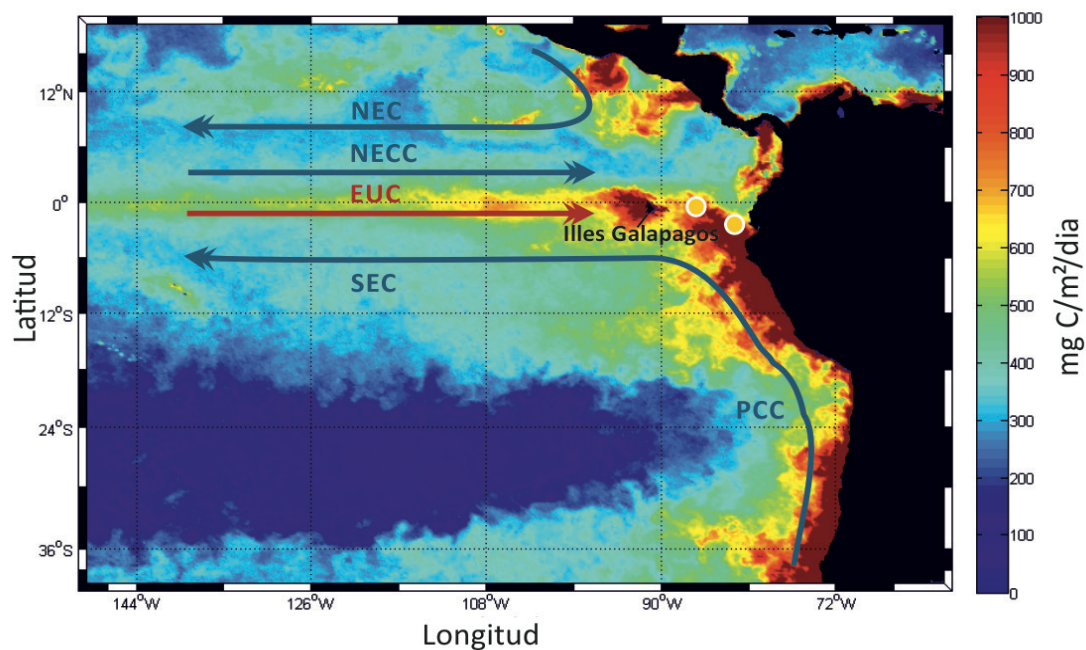
**Fig. 7.** Esquema simplificat de la circulació termohalina global on es situen les principals zones d'alliberació de calor a l'atmosfera [Broecker and Denton, 1990]. Els corrents superficials i càlids estan representats en color taronja, mentre que els corrents profunds freds i salins estan marcats en color blau (modificat de Hugo Ahlenius, UNEP/GRID-Arendal, [http://www.grida.no/graphicslib/detail/world-ocean-thermohaline-circulation\\_79a9](http://www.grida.no/graphicslib/detail/world-ocean-thermohaline-circulation_79a9)).

El motor principal de la circulació oceànica superficial és la intensitat i direcció dels vents superficials, i a més a més existeixen unes forces secundàries, com ara la gravetat, la força de Coriolis i el fregament, entre d'altres. En el context del Pacífic, com ja hem comentat anteriorment, els patrons de circulació oceànica superficial estan estretament lligats a la intensitat i direcció del sistema de vents alisis.

#### 1.1.2.1. Circulació superficial al Pacífic Equatorial

La circulació superficial al Pacífic equatorial oriental, tal com hem vist, és altament sensible a canvis en la posició de la ITCZ i dels vents alisis associats [Wyrtki, 1974]. A la banda nord de l'equador es desenvolupa el corrent superficial nord-equatorial (NEC) a una

latitud d'uns  $10^{\circ}\text{N}$  (Fig. 8), amb un transport actual de 45 Sv (Sverdrups =  $10^6 \text{ m}^3\text{s}^{-1}$ ). Aquest està associat amb els vents alisis del nord-est, i la seva intensitat està molt relacionada amb la intensificació dels vents alisis (Fig. 3) durant l'hivern de l'hemisferi boreal [Kessler, 2006]. El NEC és alimentat pel corrent de Califòrnia (CC), que flueix en sentit sud vorejant la costa nord-americana amb un transport net de 10-12 Sv [Nichols i Williams, 2009] i que es troba format per aigües relativament fredes i salines.



**Fig. 8.** Mapa de concentració de clorofil·la en les aigües superficials del Pacífic equatorial oriental, un indicador de productivitat primària (Model VGPM) [Behrenfeld and Falkowski, 1997]. Les fletxes indiquen els corrents principals superficials i subsuperficials al Pacífic equatorial oriental. Corrent nord-equatorial (NEC, de l'anglès North Equatorial Current), Contracorrent nord-equatorial (NECC, de l'anglès North Equatorial Countercurrent), Corrent equatorial subsuperficial (EUC, de l'anglès Equatorial Undercurrent), Corrent de Peru-Chile (PCC, de l'anglès Peru-Chile Current), Corrent sud-equatorial (SEC, de l'anglès South Equatorial Current). Els punts gros indiquen la posició dels dos testimonis estudiats en la present tesi [Mix et al., 2003].

Al sud de l'equador es situa el corrent sud-equatorial (SEC, de l'anglès South Equatorial Current), entorn dels  $5^{\circ}\text{S}$  (Fig. 8), i presenta un transport de 27 Sv. Aquest està lligat a la força dels vents alisis del sud-est, responent a un patró altament estacional. Així doncs, durant l'hivern de l'hemisferi sud els vents alisis del sud-est són més forts i per tant es produeix una intensificació d'aquest corrent [Kessler, 2006]. A més, aquest corrent és la continuació del corrent del Perú (PCC, de l'anglès Peru-Chile Current) (Fig. 8), que flueix cap al nord, vorejant la costa sud-americana, amb un transport net de 19 Sv [Wooster i Reid, 1963]. Aquest corrent introdueix aigües fredes, salines i riques en nutrients a la regió del Pacífic equatorial.

Entre aquests dos corrents descrits es localitza el contra-corrent Nord-equatorial (NECC, de l'anglès North Equatorial Counter Current) (Fig. 8), que és un corrent amb flux cap a l'est de 10 Sv, i que fluctua sincrònicament amb el corrent nord-equatorial. Així doncs, el NECC varia estacionalment i s'intensifica quan la ITCZ es troba en la seva posició més al nord.

### 1.1.2.2. Circulació subsuperficial al Pacífic Equatorial

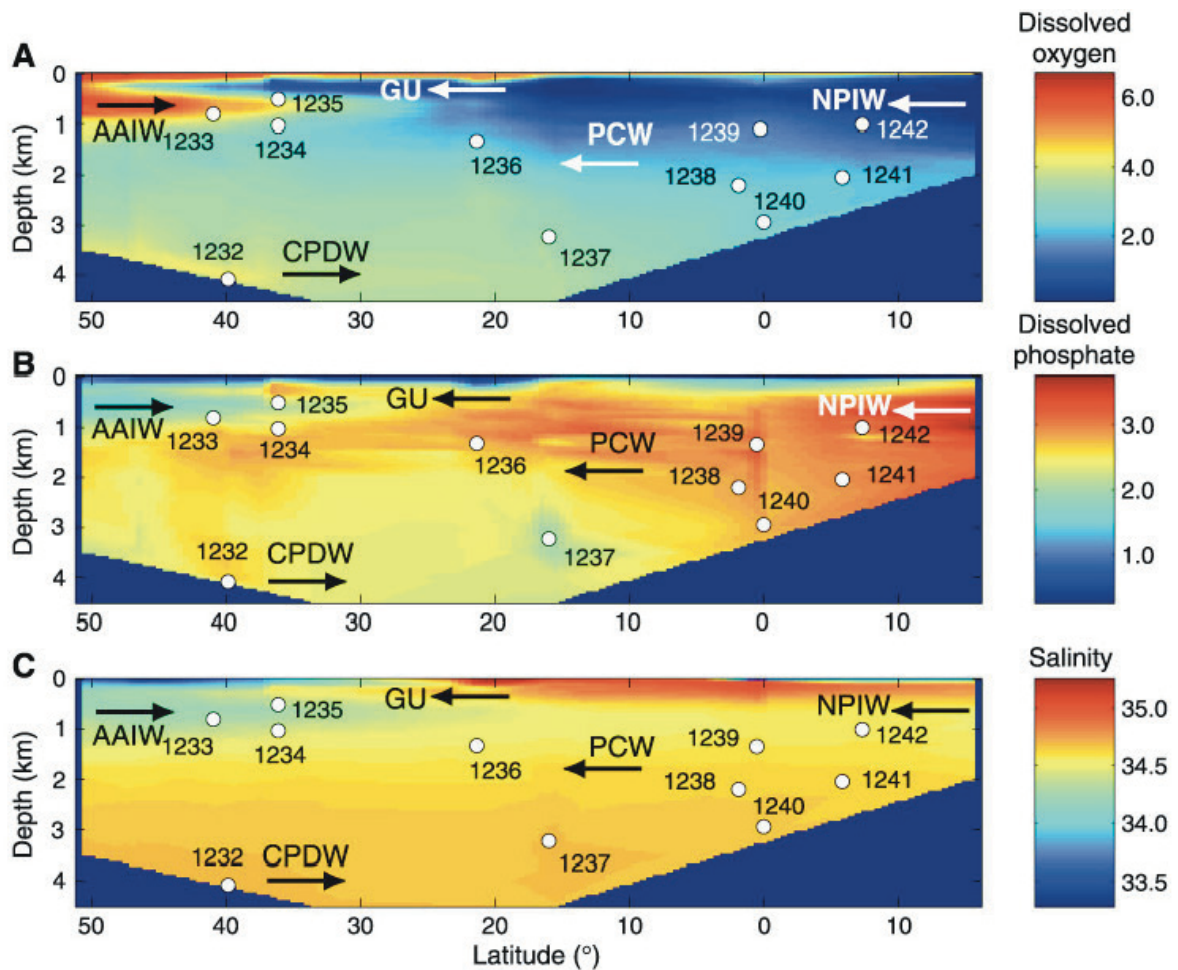
El corrent Subsuperficial Equatorial (EUC, de l'angles Equatorial Undercurrent) és el principal corrent a aquesta latitud que flueix cap a l'est per sota del SEC (Fig. 8), amb un transport que arriba als 35-40 Sv a la part oriental del Pacífic [Lukas, 1986]. El EUC presenta un gruix mitjà de dos-cents metres i una amplada màxima de 400 km [Tomczak and Godfrey, 2001]. Aquest corrent es genera a la part occidental del Pacífic, sent fortament alimentat en origen per aigües de l'hemisferi sud [Calvo et al., 2011; Pena et al., 2013]. El EUC està especialment enriquit en nutrients (Fig. 8), sobretot en nitrats i fosfats, sent la principal font que alimenta l'aflorament equatorial [Kessler, 2006]. A més, és una de les principals aportacions de ferro al Pacífic equatorial oriental juntament amb l'aportació eòlica.

El corrent Intermedi Equatorial (EIC, de l'anglès Equatorial Intermediate Current) s'origina a 150°-160°W com una intensificació del flux cap a l'oest dins del patró general de moviment del SEC amb un transport mitjà de  $7.0 \pm 4.8$  Sv [Tomczak and Godfrey, 2001].

### 1.1.2.3. Masses d'aigua i circulació profunda al Pacífic equatorial oriental

Les aigües intermèdies de l'oceà Pacífic equatorial presenten unes característiques altament asimètriques [Mix et al., 2003], com a resultat de la confluència de dues masses d'aigua de característiques diferents. Per la franja nord arriba l'aigua intermèdia del Pacífic Nord (NPIW, de l'anglès North Pacific Intermediate Water) que es forma al gir subtropical del Pacífic nord-oest amb poca interacció amb l'atmosfera [Talley, 1993]. Aquesta massa d'aigua es caracteritza per temperatures més fredes i menys salines, amb baixos continguts en oxigen i carboni, però amb alts continguts en nutrients (Fig. 9) [Sverdrup et al., 1942; Reid, 1965; Talley, 1993]. Aquesta senyal de salinitat baixa prové de l'àrea subàrtica on la precipitació excedeix l'evaporació [Yasuda, 2004]. Per la franja sud arriba l'Aigua Intermèdia Antàrtica (AAIW, de l'anglès Antarctic Intermediate Water), que en l'actualitat es troba bastant restringida a l'hemisferi sud. Aquesta massa d'aigua conté abundant oxigen, ja que es forma en contacte amb l'atmosfera (Fig. 9). Aquests dos factors donen com a resultat un enriquiment de  $^{13}\text{C}$  d'aquesta massa d'aigua [Kroopnick, 1985].





**Fig. 9.** Perfils verticals al llarg del Pacífic oriental (15°N-50°S) mostrant diferents propietats químiques de les masses d'aigua: (a) oxigen dissolt, (b) fosfat i (c) salinitat. S'indica la localització dels sondeigs extrets durant el ODP-Leg 202 (extret de Mix et al., 2003). Aigua Intermèdia de l'Antàrtida (AAIW, de l'anglès Antarctic Intermediate Water); Aigües profundes del Pacífic Central (CPDW, de l'anglès Central Pacific Deep Water); Corrent Subsuperficial Gunther (GU, de l'anglès Gunther Undercurrent); Aigua Intermèdia del Pacífic Nord (NPIW, de l'anglès North Pacific Intermediate Water); Aigua Central del Pacífic (PCW, de l'anglès Pacific Central Water).

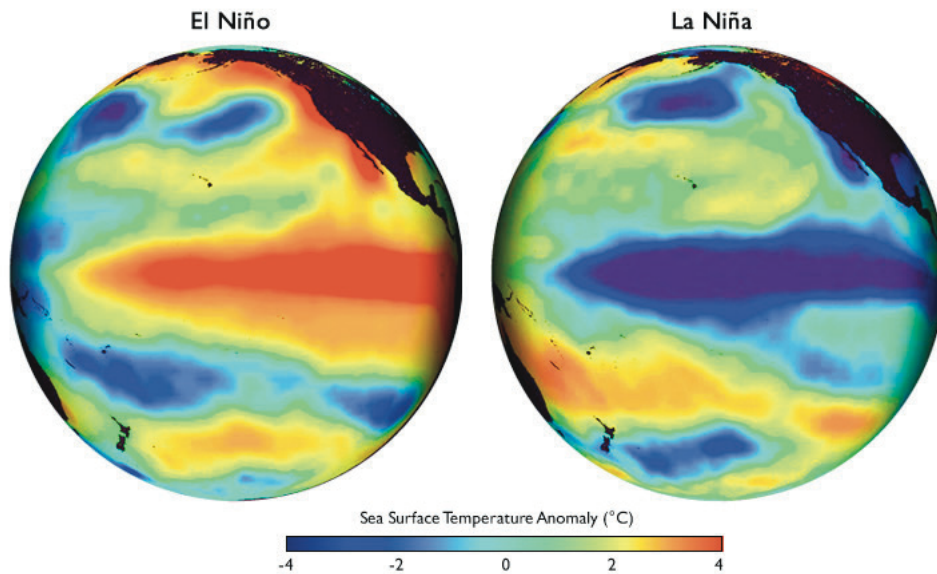
Aquestes dues masses d'aigua, NPIW del nord i AAIW del sud, es troben a la zona equatorial del Pacífic oriental, a unes profunditats d'entre 500 i 1000 m, a on es troba el màxim gradient de propietats físiques i químiques. A aquestes profunditats es localitza una zona amb continguts mínims d'oxigen (OMZ, de l'anglès Oxygen Minimum Zone) degut a la poca ventilació de la NPIW i del consum d'oxigen en la degradació de l'abundant matèria orgànica derivada de l'aflorent equatorial [Wyrтки, 1962; Tsuchiya and Talley, 1998].

Les aigües profundes al Pacífic Equatorial deriven de les aigües intermèdies que entren a la conca de Panamà des del sud, a través d'un estret pas al marge sud de la Conca de Panamà amb una profunditat de 2000-2500 metres [Lonsdale, 1976; Tsuchiya and Talley, 1998; Mix et al., 2003]. Després de transitar cap al nord, acumulant nutrients i perden

oxigen durant el seu camí, l'Aigua Profunda del Pacífic (Pacific Deep Water, PDW) retorna en direcció sud a una profunditat d'entre 1000 i 3000 metres. Gran part de l'exportació advection de fosfats i nitrats del Pacífic es produeix en aquest flux de retorn al Pacífic oriental, on les concentracions d'aquests nutrients són més elevades [Wunsch et al., 1983]. Per tant, els canvis en aquest flux tenen el potencial de canviar el balanç de nutrients a l'oceà Pacífic i l'oceà global [Berger et al., 1997].

### 1.1.3. El Niño-Southern Oscillation (ENSO)

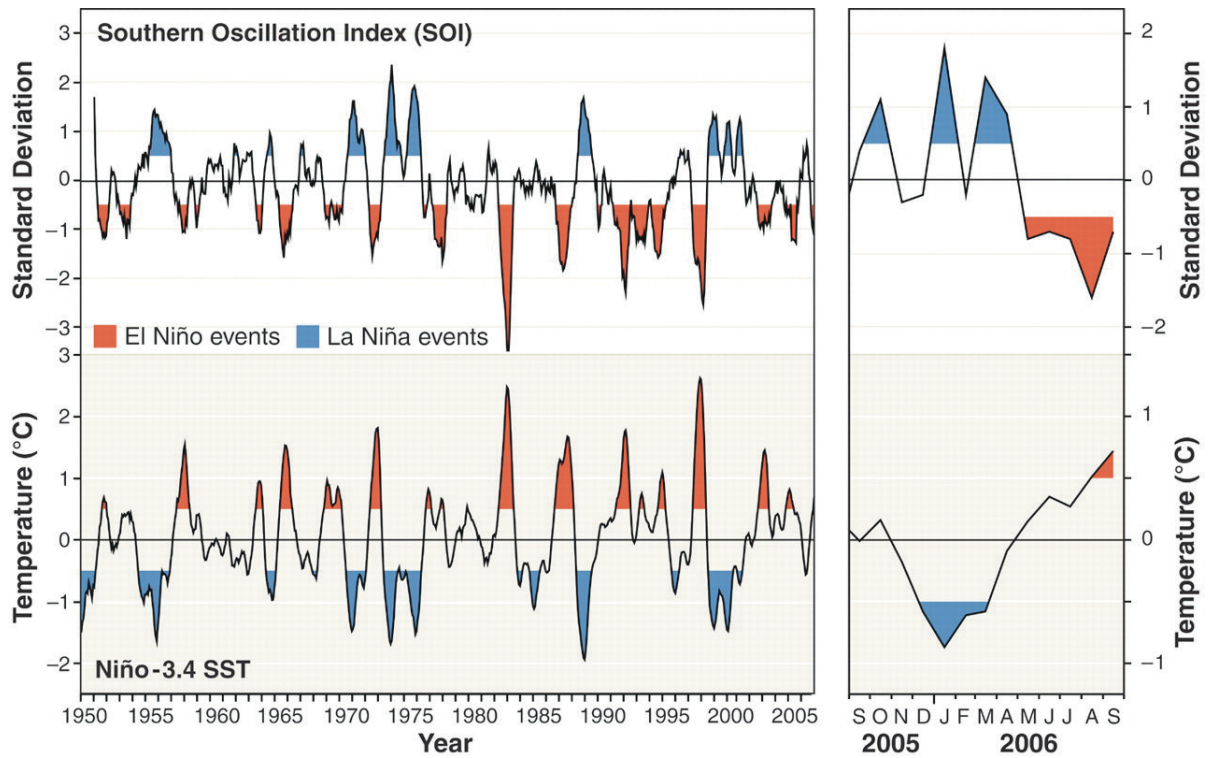
El fenomen ENSO (El Niño-Southern Oscillation) és una fluctuació climàtica, que es produeix cíclicament cada 2-7 anys, entre condicions càlides (El Niño) i fredes (La Niña) de les aigües superficials del Pacífic tropical. Aquest fenomen es desenvolupa en línia amb la seva contrapartida atmosfèrica, la Oscil·lació del Sud (SO, de l'anglès Southern Oscillation), que es defineix com la diferència normalitzada entre la pressió atmosfèrica a nivell del mar de la ciutat de Darwin (Austràlia) i l'illa de Tahiti [McPhaden et al., 2006], i que produeix canvis importants en els sistemes de vents alisis i de les precipitacions. En condicions normal o neutres, els vents alisis del sud-est apilen l'aigua calenta a la part occidental del Pacífic, i alhora afavoreixen l'aflorament d'aigua freda a la regió del Pacífic oriental, produint un gradient de temperatura longitudinal en la superfície oceànica equatorial. Aquest gradient genera al seu torn un gradient de pressions atmosfèriques, sent aquestes més elevades a la part oriental, que donen lloc als vents alisis. Durant esdeveniments del Niño, es produeix un transport d'aigües calentes del Pacífic occidental cap a l'est, produint un escalfament anòmal en aquesta zona (Fig. 10). Aquest fet produeix un bloqueig de l'aflorament i una termoclina més profunda a la part oriental del Pacífic, i al seu torn provoca la reducció del gradient longitudinal de temperatura [McPhaden et al., 2006]. Aquesta reducció produeix alhora una disminució del gradient baromètric en l'atmosfera y per tant un debilitament dels vents alisis. Per contra, durant esdeveniments de la Niña es produeix un refredament de les aigües de la regió oriental del Pacífic i un transport d'aquestes cap a l'oest. Això produeix que el gradient longitudinal de temperatures oceàniques superficials es contregui i es produeixi una intensificació dels vents alisis del sud-est i de l'aflorament equatorial que porta aigües més fredes a la superfície oceànica del Pacífic equatorial oriental (Fig.10).



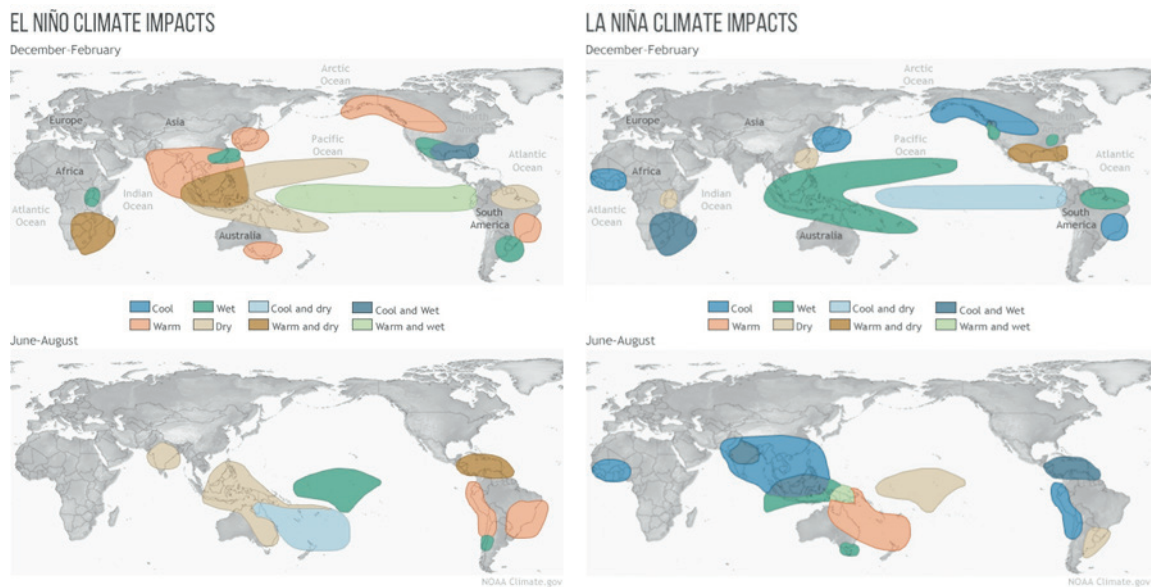
**Fig. 10.** Mapes globals centrats en l'oceà Pacífic on es mostren patrons diferents de temperatures oceàniques superficials, en esdeveniments del Niño i la Niña. Extreta de NOAA Climate.gov

L'índex que s'empra per caracteritzar el fenomen del ENSO es defineix com l'anomalia de temperatures oceàniques superficials SST, que es donen a la regió coneguda com Zona del Niño 3.4, delimitada entre les longituds de 90°W i 150 °W i les latituds entre 5°S i 5°N. Les anomalies positives venen donades per esdeveniments del Niño i les negatives per la Niña. Per altra banda, s'empra l'índex de l'Oscil·lació del Sud (SOI, de l'anglès Southern Oscillation Index), on en aquest cas les anomalies negatives corresponen a esdeveniments del Niño mentre que les positives indiquen condicions de la Niña (Fig. 11).

Tot i que el fenomen ENSO té lloc al Pacífic tropical, també produeix un gran impacte en el clima global. Aquests canvis en el clima afecten directament a l'agricultura i a les pesqueries. Per exemple, durant un esdeveniment de La Niña, el clima de Sud-Àfrica es torna més humit i fred respecte al seu clima habitual, mentre que a l'equador es torna més àrid i fred (Fig. 12).



**Fig. 11.** Índex emprats per caracteritzar el fenomen ENSO durant el període de 1950 a 2005, on s'il·lustren les importants interaccions entre l'oceà i l'atmosfera que donen lloc a variacions del ENSO. Extret de McPhaden, et al., 2006.

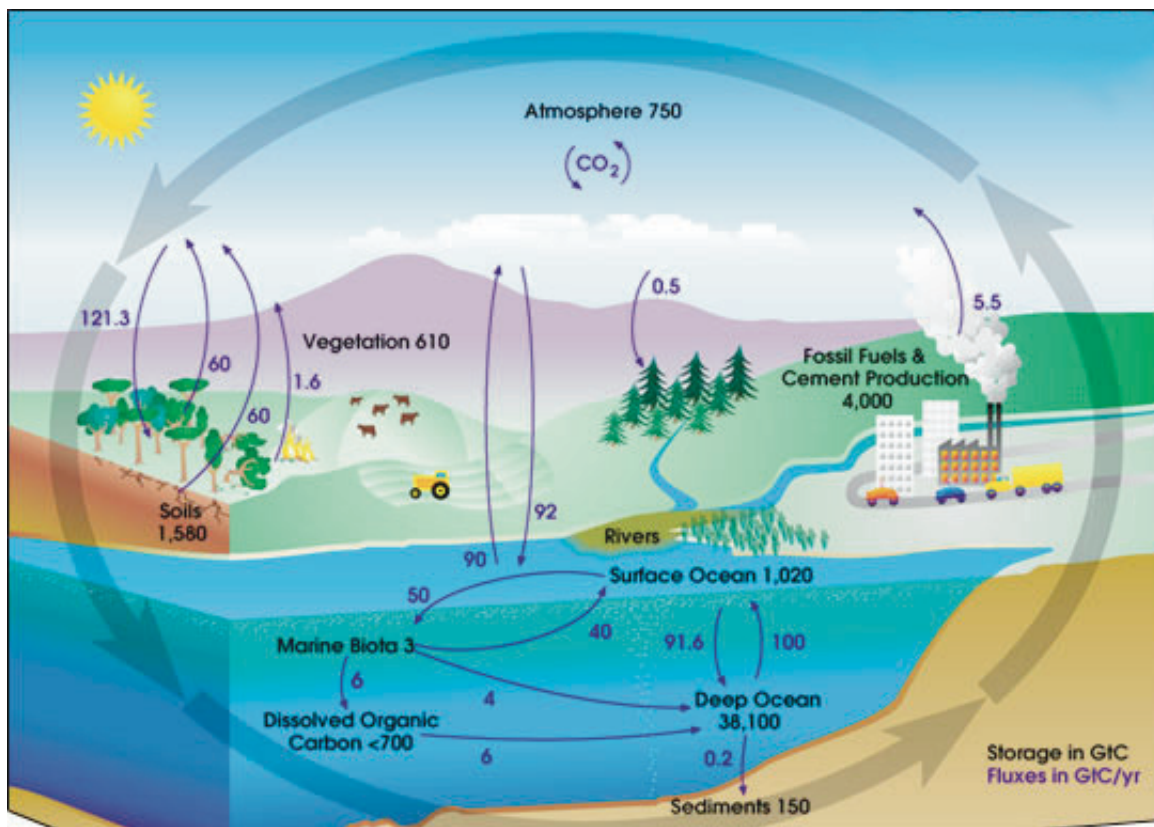


**Fig. 12.** Mapes de distribució dels impactes climàtics derivats d'esdeveniments de "El Niño" i "La Niña". Extret de NOAA Climate.gov.



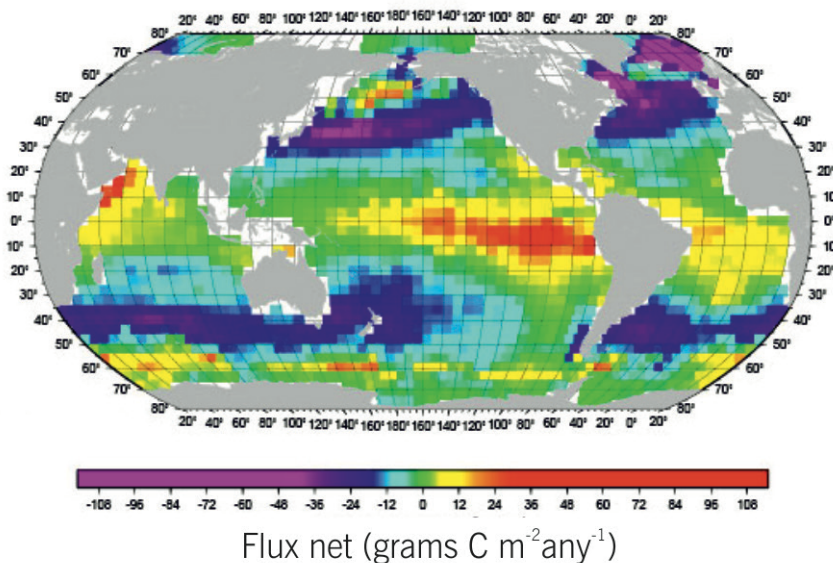
1.1.4. El cicle del carboni i l'emmagatzemament de CO<sub>2</sub> en l'oceà profund

Les concentracions atmosfèriques de gasos hivernacle es troben en uns nivells sense precedents en els últims 800.000 anys. Entre aquests gasos hivernacle es troba el diòxid de carboni el qual presenta una tendència exponencial d'alliberament ràpid a l'atmosfera des de l'inici de l'era industrial amb un increment de 2,0 +/- 0,1 ppm/any. Aquestes elevades concentracions són la causa de la desestabilització del clima terrestre. Aquest augment de CO<sub>2</sub> atmosfèric és el resultat del 40% de les emissions antropogèniques de CO<sub>2</sub> des de 1750, la resta d'emissions han estat incorporades a altres reservoris naturals del carboni (Fig. 13). L'oceà absorbeix gairebé un 30% de les emissions antròpiques de CO<sub>2</sub>, la major part s'emmagatzema a l'oceà profund que constitueix el reservori de CO<sub>2</sub> més important després de la litosfera (Fig. 13). Per tant, l'oceà juga un paper clau regulant la concentració de CO<sub>2</sub> atmosfèric en l'actualitat però també al llarg del Quaternari.



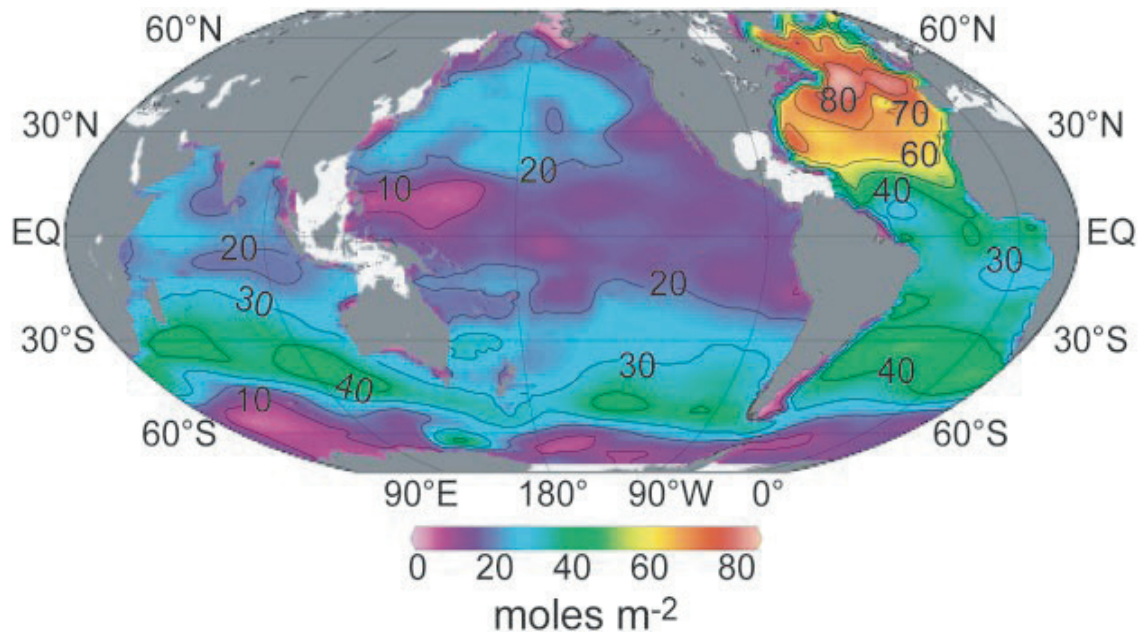
**Fig. 13.** Esquema del cicle del carboni. El volum d'emmagatzematge (en negre) s'indica en giga tones de carboni (1 GT= 1 x 10<sup>9</sup> Tones) mentre que els fluxos (en color púrpura) es troben expressats en Gt de carboni per any. És important notar que l'emmagatzematge més gran de carboni es produeix a l'oceà profund (extret de NASA Earth Science).

Els processos d'intercanvi de  $\text{CO}_2$  entre l'atmosfera i l'oceà que controlen la distribució de carboni són la solubilitat, la bomba biològica i la bomba física. La solubilitat és responsable de l'intercanvi de  $\text{CO}_2$  en la interfase atmosfera-oceà i les bombes biològiques i físiques transporten aquest carboni a profunditat. Seguint la llei de Henry i sota condicions d'equilibri, la concentració de  $\text{CO}_2$  a la superfície oceànica es troba també relacionada amb la pressió parcial de  $\text{CO}_2$  de l'atmosfera [ $\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq.})$ ]. A més, la diferent solubilitat del diòxid de carboni segons la temperatura superficial marina juga un paper important, produint-se una funció inversa; on a menor temperatura superficial es dona una major solubilitat de  $\text{CO}_2$ .



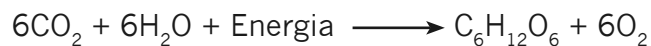
**Fig. 14.** Flux net de  $\text{CO}_2$  mitjà anual entre l'oceà i l'atmosfera basat en tres milions de mesures de  $\text{pCO}_2$  a les aigües superficials des de 1970. L'àrea amb un major alliberament de  $\text{CO}_2$  a l'atmosfera es troba sobretot al Pacífic equatorial, mentre que l'àrea amb un menor intercanvi entre oceà i atmosfera es produeix a l'Atlàntic nord com a conseqüència de la formació d'aigües profundes (extret de Takahashi, et al. 2009).

La circulació termohalina (cf. secció 1.1.2.) juga un paper clau en la bomba física, connectant l'oceà profund i superficial i per tant, es converteix també en una cinta transportadora de  $\text{CO}_2$ . A latituds altes de l'Atlàntic Nord les aigües superficials, fredes, denses i riques en  $\text{CO}_2$ , s'enfonsen i formen les aigües profundes, transportant cap al fons el  $\text{CO}_2$  captat a la superfície oceànica. La bomba física és també activa a l'Oceà Austral, a on la formació d'aigües intermèdies afavoreix el transport de  $\text{CO}_2$  cap a l'interior de l'oceà. Així doncs, es produeix més captació de diòxid de carboni als pols que a la regió equatorial (Fig. 14, 15).

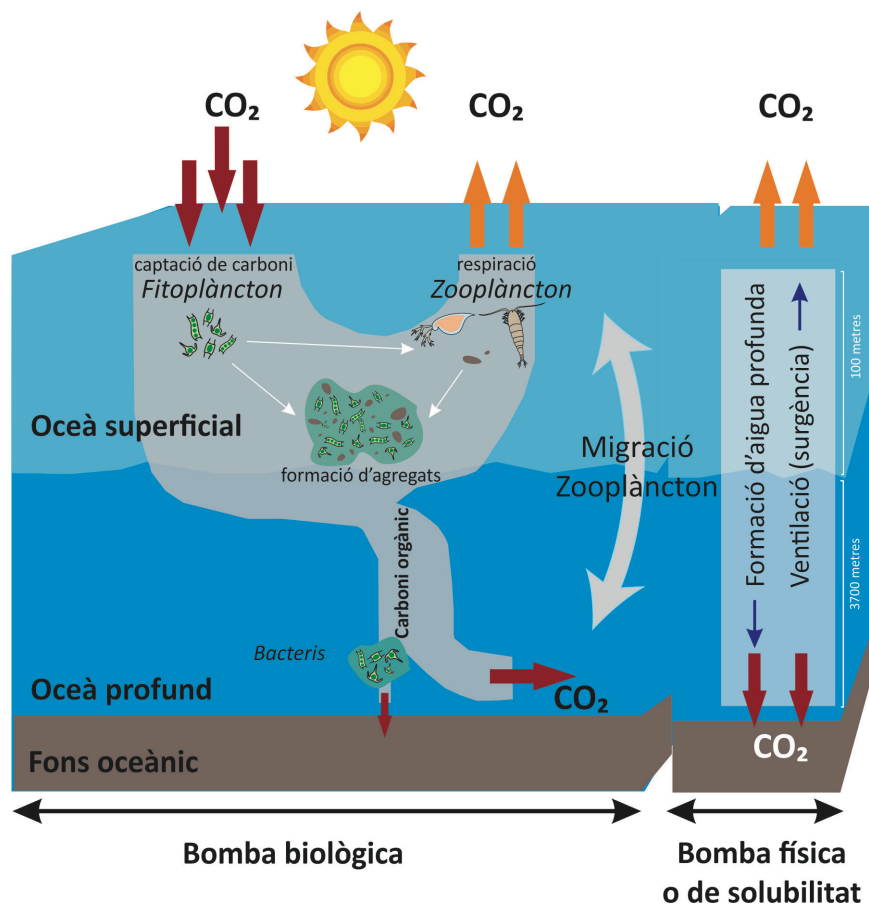


**Fig. 15.** Esquema inventari de CO<sub>2</sub> antropogènic a l'oceà (mol m<sup>-2</sup>). Els inventaris més alts es localitzen entre 30° i 60° N (colors vermells), on es produeix la formació d'aigües profundes de l'Atlàntic nord (colors vermells) (extret de Sabine et al., 2004).

La bomba biològica captura el CO<sub>2</sub> dissolt a les capes superficials de l'oceà transformant-ho en matèria orgànica mitjançant la fotosíntesis (Fig. 16).



Aquest carboni s'incorpora a la cadena tròfica marina, on una gran part del carboni orgànic s'oxida mitjançant la respiració dels consumidors superficials, i forma novament CO<sub>2</sub> que pot retornar a l'atmosfera. Però, una fracció d'aquest carboni orgànic, concretament entre el 20 i el 50%, s'enfonsarà cap a l'oceà profund gràcies a la predació del zooplàncton, la pluja de partícules orgàniques i/o la migració activa de la biomassa. La major part d'aquesta biomassa exportada es remineralitza incrementant el carboni inorgànic en profunditat, i només una petita part queda atrapada als sediments, on es manté aproximadament uns 1000 anys [Chisholm, 2000]. Així doncs, l'estructura de la xarxa tròfica i l'abundància relativa de les diferents espècies té una gran influència en la quantitat de CO<sub>2</sub> que es bombeja cap a l'oceà profund. L'eficiència d'aquesta bomba biològica pot estar també molt lligada a la contribució de la pols atmosfèrica, font principal de ferro, un micronutrient imprescindible per a la productivitat primària oceànica i que és limitant en algunes regions, com és el cas del Pacífic equatorial oriental (cf. secció 1.1.1.3).



**Fig 16.** Esquema del cicle del carboni als oceans. La bomba física (dreta) és impulsada pels moviments verticals de masses d'aigua, molt lligats a la circulació termohalina. En canvi, la bomba biològica (esquerra) es produeix com a conseqüència de la producció primària fitoplànctonica (modificat de U.S JGOFS i Chisholm et al., 2000).

## 1. 2. PALEOCLIMATOLOGIA

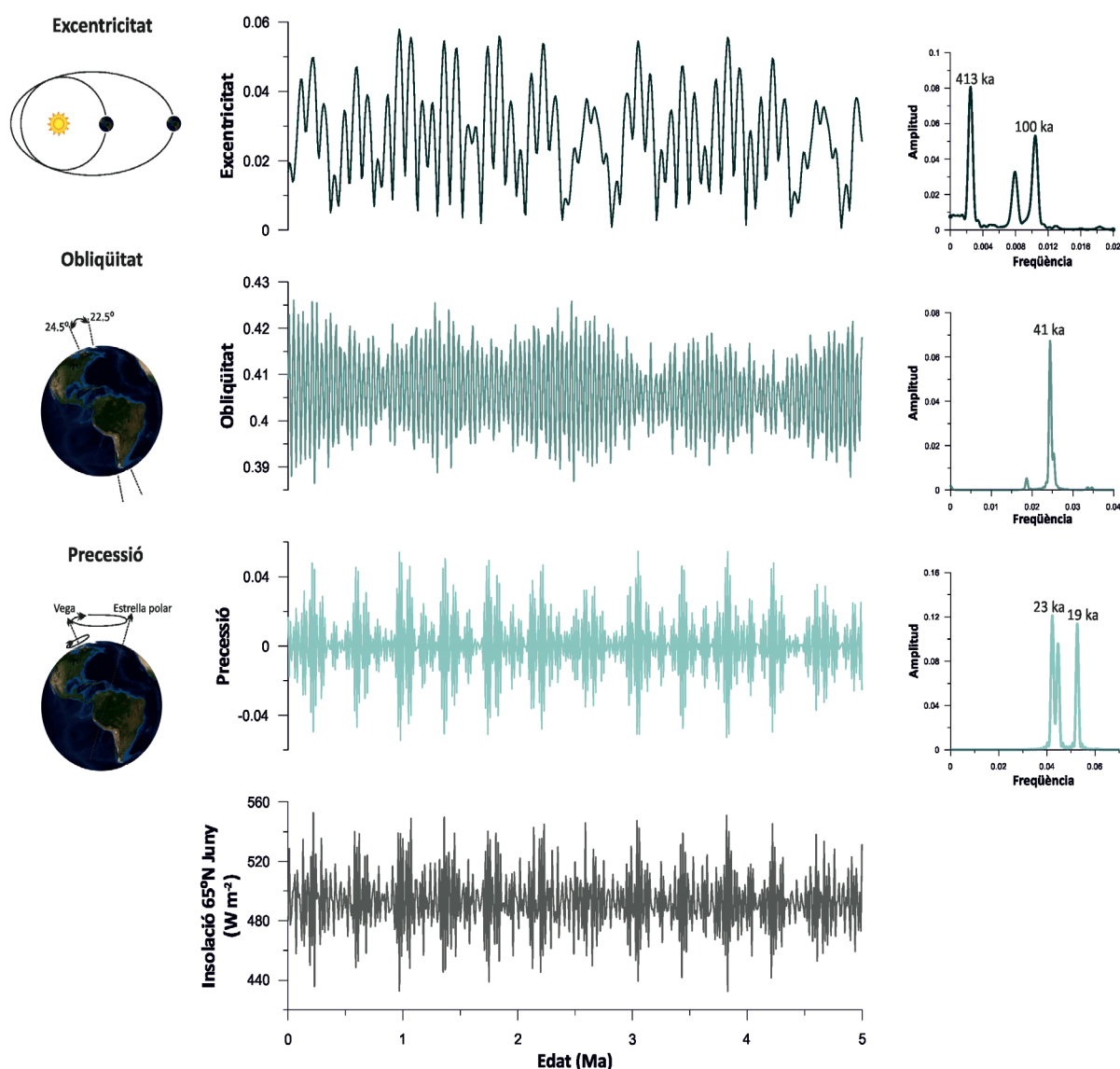
La Paleoclimatologia és la ciència que estudia les variacions climàtiques de la Terra al llarg de la seva història. Aquesta es basa en l'estudi d'una gran varietat d'arxius climàtics, que inclouen sediments marins, lacustres, coralls o gel, dins dels quals es poden trobar multitud d'indicadors paleoclimàtics com és el cas de la flora i la fauna terrestre o marina, o d'altres de caràcter geoquímic o sedimentològic. Les escales temporals en l'estudi de variacions climàtiques poden ser des de multianual, mil·lenàries, escales orbitals o fins i tot de milions d'anys. Així doncs, es poden arribar a identificar des de variacions climàtiques degudes a la influència de l'activitat antròpica, fins a la variabilitat natural del sistema climàtic terrestre.

### 1.2.1. Variabilitat climàtica natural i evolució humana

La variabilitat climàtica natural que es produeix a escala orbital, glacial-interglacial, ve donada com a conseqüència de les variacions en la configuració orbital de la Terra. Aquest fet va ser suggerit pel matemàtic Joseph Adhémar l'any 1842, però no va ser fins a l'any 1941 quan l'astrofísic Milutin Milankovitch va publicar la seva teoria astronòmica, coneguda com a Teoria de Milankovitch. Aquesta teoria es basa en els canvis que presenten tant l'òrbita terrestre al voltant del sol com el mateix eix de rotació de la Terra, i que provoquen fluctuacions cícliques en la distribució de la insolació rebuda per la Terra. Aquests moviments són l'excentricitat, la inclinació de l'eix axial o obliqüïtat, i la precessió. Cada component orbital presenta una ciclicitat característica, on els canvis en l'excentricitat es concentren principalment en dos cicles de 400.000 anys i de 100.000 anys, l'obliqüïtat presenta un cicle dominant a 41.000 anys, mentre que el component de la precessió presenta dos cicles, un de 23.000 anys i un de 19.000 anys (Fig. 17). Cada component orbital presenta una ciclicitat característica, on els canvis en l'excentricitat es concentren principalment en dos cicles de 400.000 anys i de 100.000 anys, l'obliqüïtat presenta un cicle dominant a 41.000 anys, mentre que el component de la precessió presenta dos cicles, un de 23.000 anys i un de 19.000 anys (Fig. 17). A més, Milankovitch va ser pioner calculant els canvis d'insolació que produïen aquests tres moviments sobre la superfície de la terra (Fig. 17).

L'excentricitat de l'òrbita terrestre és la variació de la forma de l'òrbita, que va des de ser gairebé circular fins a lleugerament el·líptica (Fig. 17). Aquesta excentricitat de l'òrbita controla només una petita part de la quantitat de radiació solar incident a la Terra. Per altra banda, l'obliqüïtat ve marcada per les variacions en la inclinació de l'eix de rotació terrestre, dins d'un rang entre 22.2° i 24.5° (Fig. 17).





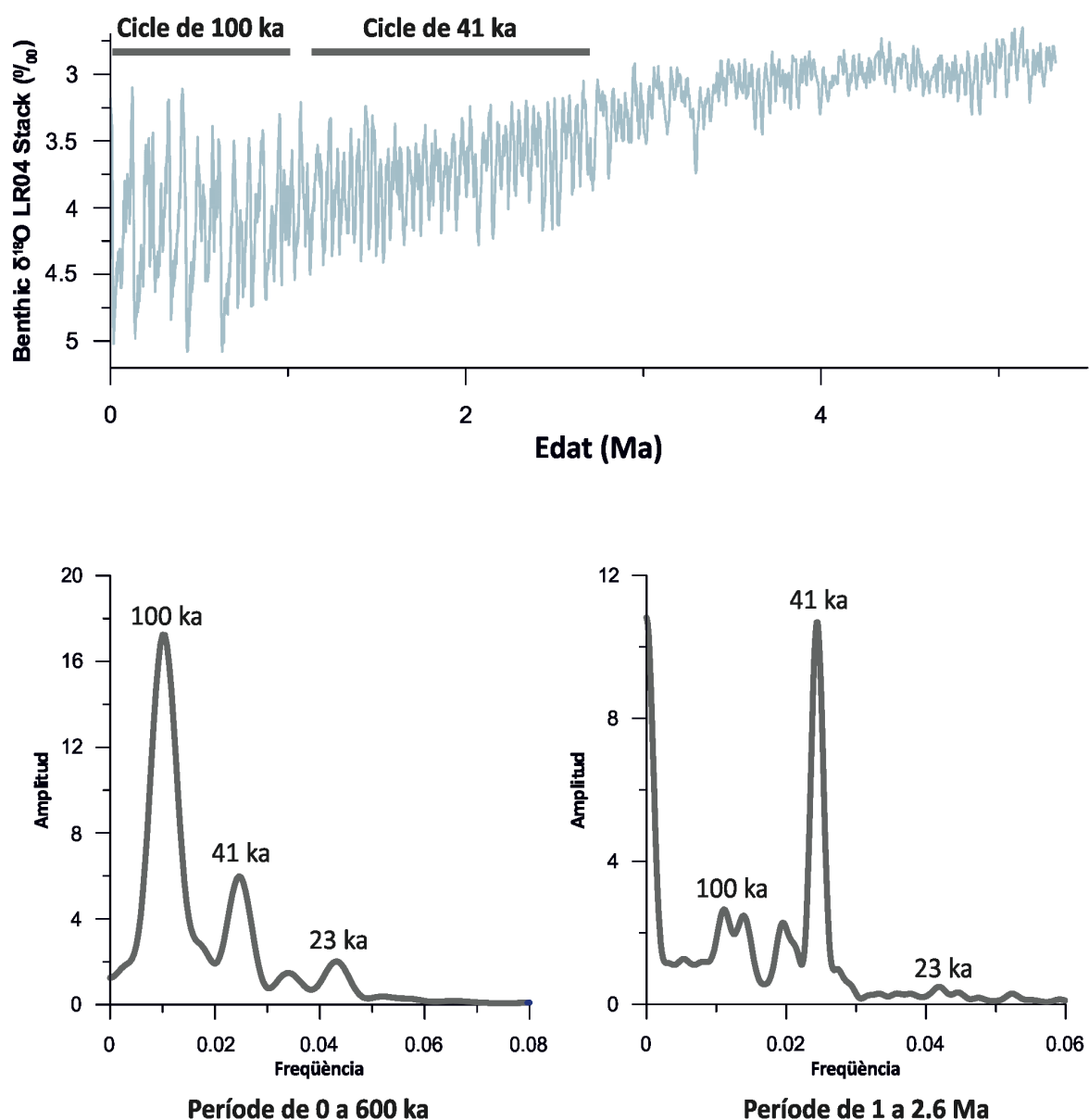
**Fig. 17.** Variacions al llarg del temps dels tres components orbitals: (a) excentricitat, (b) obliquïtat i (c) precessió, indicant amb un anàlisi de freqüència (gràfics de la dreta) quines són les periodicitats dominants per a cada un dels moviments orbitals. (d) Càlcul de la insolació rebuda a 65°N durant el més de juny al llarg del temps [Laskar et al., 2004].

Aquests canvis d'obliquïtat amplifiquen o redueixen les diferències estacionals d'insolació, particularment a altes latituds. Finalment, la precessió dels equinoccis es dona com a conseqüència del canvi gradual en l'orientació de l'eix de rotació terrestre (Fig. 17), i té una influència directa en els equinoccis i els solsticis.

Però, la teoria de Milankovitch no es va poder posar a prova fins que no es va disposar de registres paleoclimàtics continus. El registre d'isòtops de l'oxigen ( $\delta^{18}\text{O}$ ) mesurat a foraminífers constitueix un registre global dels cicles glacials i interglacials, donat que són un reflex del volum dels mantells de gel, a on s'acumula preferentment l'isòtop més lleuger ( $^{16}\text{O}$ ). Aquest registre va permetre analitzar els cicles climàtics, identificant-se les freqüències

dels moviments orbitals i, per tant, donant suport al control dels canvis d'insolació sobre el sistema climàtic terrestre [Hays et al., 1976]. El primer intent d'obtenir un registre global dels cicles va ser a partir de la superposició de registres de  $\delta^{18}\text{O}$  de foraminífers planctònics, aquest va ser el denominat "stack" de SPECMAP (Spectral Mapping Project) [Imbrie et al., 1984; Martinson et al., 1987]. Més endavant, aquesta corba es va millorar mitjançant registres de  $\delta^{18}\text{O}$  de foraminífers bentònics i de més alta resolució (LR04 stack) [Lisiecki i Raymo, 2005], que abasta els últims cinc milions d'anys. Aquest stack és l'eina actual més utilitzada per la realització de models d'edat en registres marins (Fig. 18). L'anàlisi detallada d'aquesta corba patró de bentònics ha permès detectar que les freqüències dominants del registre climàtic canvien al llarg dels últims cinc milions d'anys. Així doncs, la ciclicitat glacial-interglacial de la Terra ha estat dominada per l'obliquïtat en cicles de 41.000 anys, però el clima va passar a estar regit per l'excentricitat durant l'últim milió d'anys, donant lloc al cicle de 100.000 anys. Aquest llindar se'l coneix com la transició del Plistocè mitjà i segueix encara avui en dia sent un misteri sense resoldre [Raymo and Nisancioglu, 2003; Huybers, 2007] (Fig. 18).

Encara que aquestes periodicitats s'han identificat també en altres registres climàtics tant en sediments marins, lacustres, terrestres com de gel, la teoria de Milankovitch avui en dia encara no explica el diferent patró de comportament, que es produeix de forma sobtada en les transicions glacial-interglacial [Raymo, 1992; Ashkenazy and Tziperman, 2004], sent més pausada en les transicions d'interglacial a glacial. Així doncs, es creu que l'excentricitat de l'òrbita terrestre exerceix un forçament petit en la quantitat de radiació solar rebuda per la Terra [Imbrie et al., 1993].



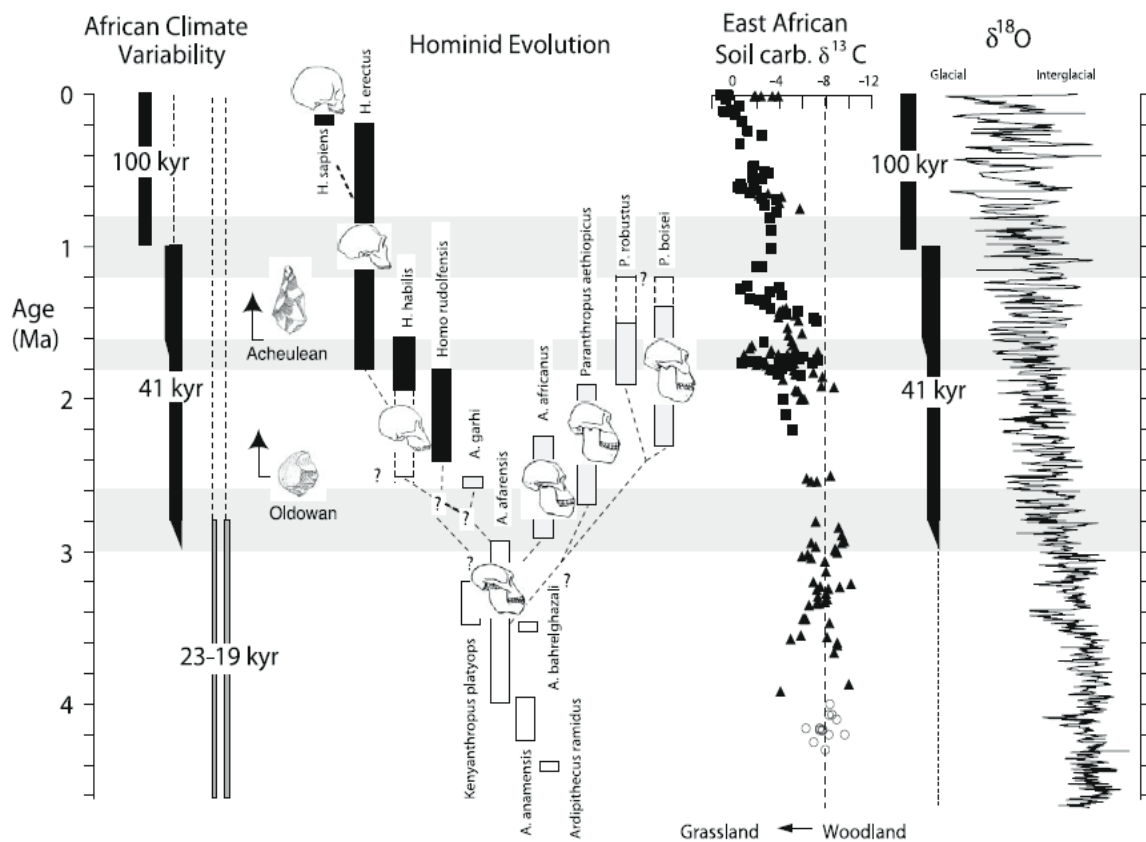
**Fig. 18.** (a) Corba patró d'isòtops de l'oxigen extret de foraminífers bentònics, LR04 [Lisiecki i Raymo, 2005], dels últims 5.5 milions d'anys. (b) L'anàlisi de freqüències realitzat a la corba patró LR04, que revela la influència dominant de l'obliquïtat durant el període de 2.6 a 1 milió d'anys mentre que el període a partir dels 600.000 anys es troba definit pel component de l'excentricitat.

Aquesta variabilitat climàtica natural i les condicions ambientals associades han condicionat, entre altres factors, la història evolutiva de la humanitat, que va començar al continent africà fa aproximadament sis milions d'anys (Fig. 19). Tal com apuntava Charles Darwin l'any 1859 a la teoria de l'evolució [Darwin, 1859], la selecció natural és el procés pel qual les noves estructures adaptatives evolucionen i persisteixen, és a dir, pel qual els organismes canvien en relació amb el seu entorn. Així doncs, els organismes amb característiques menys adaptades moriran i s'extingiran amb major probabilitat que els organismes



més adaptats a aquest canvi. Quan les espècies viuen en ambients estables sense patir la pressió de la selecció natural, amb unes condicions climàtiques invariables de temperatura, humitat, vegetació, aliment disponible, etc., tendeixen a mantenir-se en un nivell estable sense produir-se canvis a escala evolutiva. En canvi, sota unes condicions climàtiques més variables, les espècies es veuen obligades a utilitzar el seu potencial genètic, produint-se canvis en la seva morfologia per adaptar-se a les noves condicions del medi. Un exemple van ser la majoria dels australopithecus que van resistir els canvis en l'ambient i paisatge africà fins fa aproximadament dos milions d'anys.

Els canvis climàtics a llarg termini i els canvis seculars en la variabilitat climàtica són dos senyals ecològiques separades que poden establir oportunitats en la selecció natural [deMenocal, 2004]. L'alternança de cicles glacials-interglacials a partir de 2,6 milions d'anys, controlats per l'obliquïtat, administra la quantitat de radiació solar incident als dos hemisferis. Aquests canvis haurien influït en el clima, provocant una aridesa progressiva i un canvi en el tipus de vegetació associat, des d'un ambient arbori fins a un ambient de sabana del continent africà. Aquesta transició climàtica i ambiental hauria provocat un gran pas a escala evolutiva des de la dominant presència de *Homo habilis* fins a *Homo erectus* (Fig. 19).



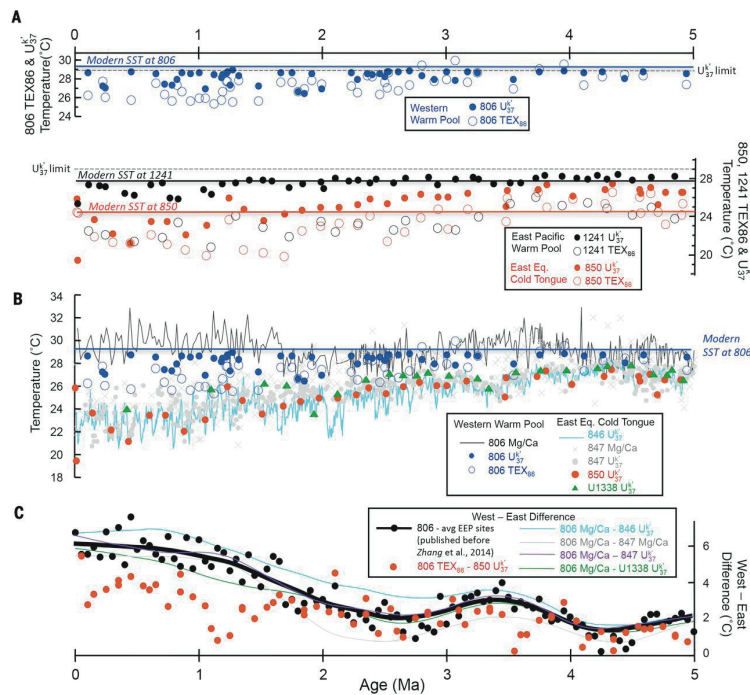
**Fig. 19.** Evolució de la cobertura vegetal africana (Soil carb  $\delta^{13}\text{C}$ ) en relació amb l'evolució dels cicles glacials i interglacials ( $\delta^{18}\text{O}$ ) durant els últims 4,6 milions d'anys, indicant les ciclicitats dominants (41-100 kyr) i els canvis principals en l'evolució dels homínids. Cal remarcar que a partir de l'inici dels cicles de 41.000 anys és quan es produeix la diversificació evolutiva més gran dels homínids al continent africà (extret de deMenocal, 2004).

## 1.2.2. Paleo-ITCZ

La localització latitudinal de la ITCZ al cinturó tropical durant els últims milions d'anys ha estat abordada per diversos estudis basats en diferents registres paleoclimàtics, tant marins com continentals [Hovan, 1995; Philander et al., 1996; Billups, 1999; Chaisson and Ravelo, 2000; Wang, 2001; Koutavas and Lynch-Stieglitz, 2004; Chiang and Bitz, 2005; Broccoli et al., 2006; Hyeong et al., 2006; Sachs et al., 2009]. Les importants migracions latitudinals que ha patit la ITCZ al llarg del temps es creu que podrien estar relacionades amb alteracions del gradient tèrmic entre els pols i l'equador, on la ITCZ es desplaçaria cap a l'hemisferi més càlid [Chiang and Friedman, 2012; Schneider et al., 2014]. Així doncs, segons registres paleoclimàtics i models numèrics aquestes migracions de la ITCZ cap al sud haurien estat més importants durant les fases més fredes de l'hemisferi nord en una gran varietat d'escala temporal, com per exemple durant la Petita Edat del Gel (LIA, de l'anglès Little Ice Age) o durant l'últim màxim glacial (LGM, de l'anglès Last Glacial Maximum), entre d'altres [Koutavas and Lynch-Stieglitz, 2004; Chiang and Bitz, 2005; Broccoli et al., 2006; Sachs et al., 2009]. Els estudis centralitzats en el Pacífic equatorial suggereixen una migració progressiva de la ITCZ cap al sud des del Miocè superior fins a la seva localització actual [Hovan, 1995; Philander et al., 1996; Billups, 1999; Chaisson and Ravelo, 2000; Hyeong et al., 2006]. Concretament, alguns d'aquests treballs han explorat les migracions de la ITCZ a través de l'estudi de canvis hidrogràfics que s'haurien produït al Pacífic equatorial [Philander et al., 1996; Billups, 1999; Chaisson and Ravelo, 2000], i que també suggereixen una migració cap al sud durant el Pliocè inferior. No obstant això, aquests estudis no disposen de la suficient resolució temporal com per poder detectar en detall canvis ràpids durant el Plistocè inferior.

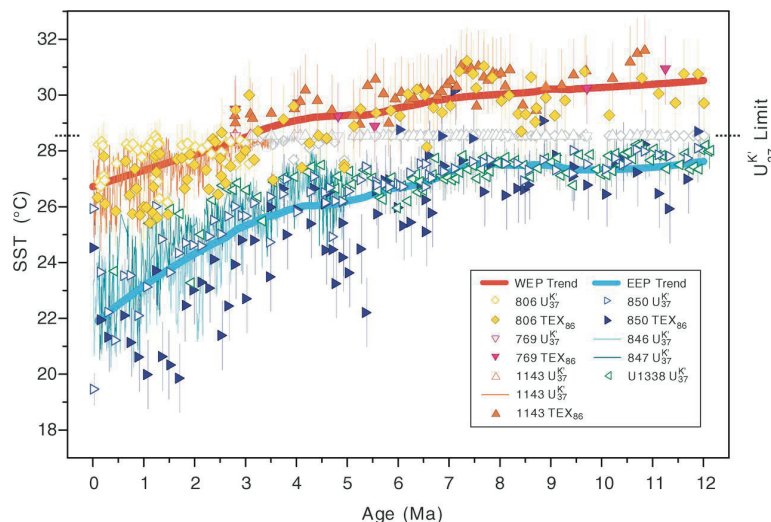
## 1.2.3. Paleo-ENSO durant el Pliocè-Plistocè

L'existència d'una variabilitat climàtica ENSO-like durant la transició Pliocè-Plistocè es troba en un debat ferm en l'actualitat entre la comunitat científica. Alguns treballs basats en l'estudi de les SST suggereixen que el Pliocè hauria estat caracteritzat per unes condicions permanents de El Niño, amb unes temperatures molt homogènies al llarg del Pacífic tropical (Fig. 20) [Ravelo et al., 2004, 2006, 2014; Wara et al., 2005; Fedorov et al., 2006], i que a partir dels 2 Ma s'hauria produït una intensificació de la circulació de Walker i un major gradient oest-est. Aquests treballs han realitzat anàlisis de Mg/Ca en foraminífers planctònics tant en testimonis del Pacífic oriental com de l'occidental.



**Fig. 20.** Temperatures oceàniques superficials (SST) dels últims 5 Ma, extretes de diferents testimonis analitzats al llarg del Pacífic tropical. Extret de Ravelo et al., 2014.

En canvi, Rickaby and Halloran (2005) utilitzen un registre combinat de Mg/Ca i  $\delta^{18}\text{O}$  en tres espècies de foraminífers planctònics, i suggereixen condicions de La Niña durant el Pliocè. A més, nous registres de SST, basats en l'anàlisi d'alquenones ( $\text{UK}^{37}$ ) i  $\text{TEX}_{86}$ , suggereixen un gradient de SST relativament constant al Pacífic equatorial (Fig. 21) durant aquest període de temps amb un aflorament equatorial actiu [O'Brien et al., 2014; Zhang et al., 2014] tant al Pliocè superior com al Plistocè inferior. A més, aquests treballs postulen que els estudis previs presenten limitacions possiblement degudes a canvis en la química de l'aigua, diagènesis i limitacions en el calibratge. Així doncs, el debat segueix actiu i lluny de resoldre's.



**Fig. 21.** Temperatures oceàniques superficials (SST) dels últims 12 Ma, extretes de diferents testimonis analitzats al llarg del Pacífic tropical. Extret de Zhang et al., 2014.

#### 1.2.4. Composició dels sediments marins i el seu interès en Paleoceanografia

Els sediments marins són clau per entendre la variabilitat climàtica al llarg de la història del planeta. L'anàlisi d'aquests sediments i en particular, de la fracció lítica, dóna una informació important sobre els processos de transport que els han dipositat al fons de l'oceà. Mitjançant la seva anàlisi es poden deduir els diferents mecanismes de transport, via atmosfèrica, fluvial o per corrents marins, i aporta a més, informació de la intensitat d'aquests processos així com de les característiques de l'àrea font. Conseqüentment, amb aquest tipus d'estudis es pot obtenir informació rellevant sobre les condicions atmosfèriques en què es van dipositar, com ara la direcció del vent, la seva intensitat o la pluviositat a la zona d'estudi. Aquesta informació pot esdevenir de gran rellevància a l'hora de reconstruir canvis climàtics en el passat.

Els sediments marins estan compostos per quatre tipus de partícules, diferenciades pel seu origen sedimentari. Segons aquest origen les partícules poden ser litogèniques, biogèniques, autigèniques o hidrogèniques, i cosmogèniques, ordenades per ordre d'abundància. Les partícules litogèniques són aquelles que provenen de l'erosió de roques del continent, i que han estat transportades mitjançant transport fluvial, eòlic, icebergs o a causa de l'erosió costanera. Aquesta erosió pot ser deguda a diferents tipus de meteorització, tal com la meteorització física o la química. La meteorització química és la dominant en aquestes zones tropicals a causa de les elevades pluges i temperatures que l'afavoreixen. Per altra banda, es troben les partícules biogèniques formades pels esquelets que construeixen els organismes, i que un cop morts queden dipositats al fons de l'oceà. Les partícules autigèniques o hidrogèniques són formades in situ al fons oceànic, aquestes registren les reaccions, tant biològiques com fisicoquímiques, que es duen a terme durant la deposició i alteració dels sediments del fons marí [Kennett, 1982]. A més, en aquesta regió tropical són particularment importants els òxids de ferro i els nòduls de manganès [Pena et al., 2005]. Per altra banda, les partícules cosmogèniques són les que procedeixen de materials d'origen extraterrestre.

### 1.3. OBJECTIUS DE LA TESI

L'objectiu general d'aquesta Tesi és entendre el paper que juga la interacció entre l'atmosfera i l'oceà durant diferents transicions climàtiques i el seu impacte en els ecosistemes i cicles biogeoquímics marins, i finalment en la captura de carboni al fons oceànic. Per tal d'assolir aquest objectiu s'han examinat en paral·lel els canvis en la dinàmica de vents i la resposta d'un dels sistemes oceànics de producció primària més important del món, com és el Pacífic equatorial, mitjançant l'anàlisi de la fracció lítica i biogènica. Aquest estudi es focalitza en el Plistocè inferior donat la seva rellevància en la reestructuració dels sistemes climàtics tropicals a escala global coincidint a més a més amb un moment clau de l'evolució dels homínids.

Així doncs, els objectius concrets de la Tesi han estat:

- Establir un protocol de tractament dels sediments marins per anàlisi granulomètrics adient a la regió estudiada per tal d'eliminar eficientment la fracció biogènica i autigènica, i per tant assegurar el correcte aïllament de la fracció lítica i garantir la qualitat dels resultats a obtenir. Aquest objectiu neix de la complexitat de l'àrea escollida, donat que les mostres a tractar eren particularment enriquides en material biogènic i autigènic.
- Caracteritzar la fracció lítica a través de l'anàlisi estadística i microscòpica per tal d'identificar els possibles agents responsables del seu transport com la influència directa de les migracions de la ITCZ.
- Analitzar l'evolució temporal dels canvis litogènics amb la fi d'establir relacions amb altres paràmetres, tal com el contingut en ferro, de cara a proposar hipòtesis sobre canvis potencials en la dinàmica atmosfèrica sobre el Pacífic equatorial.
- Caracteritzar la fracció biogènica de l'interval estudiat que proporciona informació de les condicions oceanogràfiques. A partir d'aquesta fracció es pot esbrinar les condicions de la massa d'aigua en la qual s'ha format, aportant informació tant de la temperatura de l'aigua, com dels patrons de productivitat, nutrients i contingut d'oxigen.
- Establir la cronostatigrafia d'alta resolució a partir de l'anàlisi d'isòtops de l'oxigen de foraminífers bentònics i la seva comparació amb la corba patró global.

- Avaluació de les migracions de la ITCZ a través de la comparació dels patrons detallats de la fracció lítica i biogènica, establint les interconnexions atmosfera-oceà durant el Plistocè inferior.
- Anàlisi de la fracció biogènica i litògena del ODP 1238 per a la corroboració de la hipòtesi obtinguda mitjançant l'anàlisi del ODP 1240.
- Comparació de les dades obtingudes en el Pacífic equatorial amb altres registres de la franja tropical, corresponents al mateix període i també sensibles a l'evolució de la ITCZ, per tal d'analitzar l'impacte d'aquesta evolució a escala global.
- Analitzar l'impacte que els canvis de la ITCZ van tenir en la climatologia d'algunes regions de l'Àfrica, i que van ser particularment rellevants en l'evolució dels homínids.

## 1.4. ÀREA D'ESTUDI

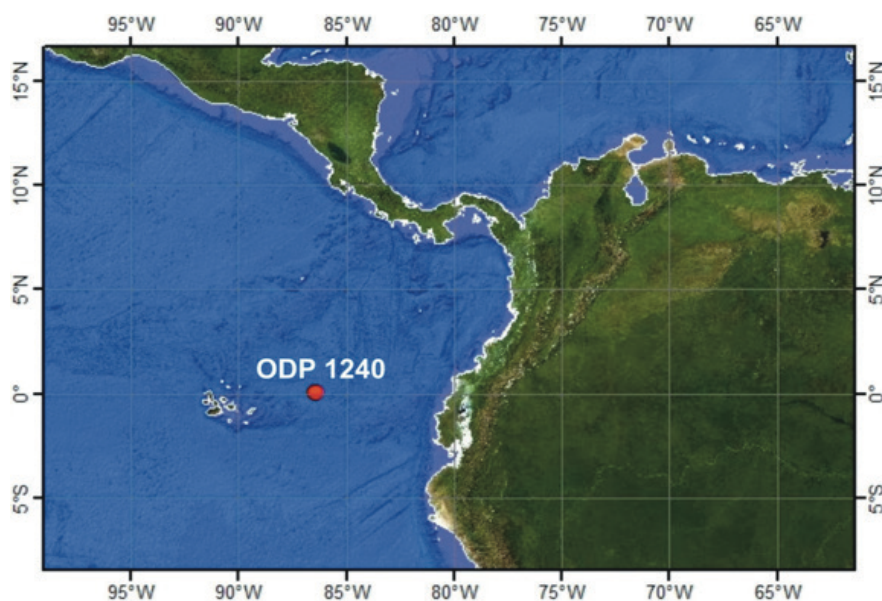
### 1.4.1. Pacífic equatorial

El Pacífic és l'oceà més gran i profund de la Terra, ocupant un 40% de l'àrea de la superfície oceànica global i la tercera part de la superfície terrestre [Tomczak and Godfrey, 2001]. Actualment, la conca del Pacífic es troba sobre un conjunt de plaques tectòniques, concretament sobre la placa Pacifica, Nazca i Antàrtica, a la vora oriental de les plaques continentals Eurasiàtica i Indo-australiana i a la vora occidental de les plaques Nord-americana i Sud-americana. A la subconca del Pacífic sud-oriental es dona la presència de cadenes volcàniques formades pel desplaçament de la placa oceànica sobre un punt calent (en anglès hot spot), entre elles estarien la dorsal de Cocos, de Nazca i la de Galápagos-Carnegie.

### 1.4.2. Ocean Drilling Program (ODP) Leg 202

#### 1.4.2.1. ODP 1240

El Site ODP 1240 (ODP 1240) està situat al Pacífic equatorial oriental ( $0^{\circ}01.31' N$   $86^{\circ} 27.76' W$ ; 2921 metres de profunditat), dins de la conca de Panamà, limitada per les illes Galápagos a l'oest, la costa d'Equador a l'est i al flanc nord de la dorsal de Carnegie [Mix et al., 2003] (Fig. 22). Es tracta d'una fosa de direcció est-oest d'escorça basàltica forma-

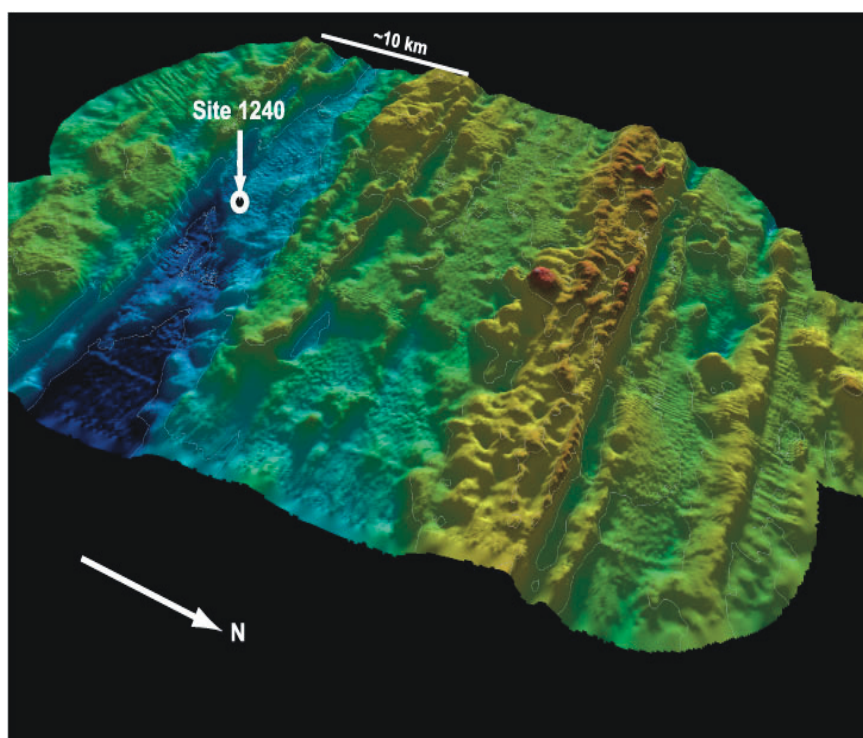


**Fig. 22.** Localització geogràfica del ODP 1240 ( $0^{\circ}01.31' N$   $86^{\circ} 27.76' W$ ; 2921 metres de profunditat).



da en el centre d'expansió Cocos-Nazca fa prop de 3 Ma [Hey, 1977].

Aquest testimoni de sediment, ODP 1240, es va recuperar en una vall abissal a una profunditat de 2921 metres (Fig. 23) prop de l'equador. Els perfils sísmics obtinguts durant el Leg 202 mostren una cobertura de sediments pelàgics en aquest punt relativament gruixuda per a la regió, entre 250 i 280 metres, donada la curta edat de l'escorça. Aquestes elevades taxes de sedimentació suggereixen que les valls abissals actuen com una trampa de sediment que recull la densa pluja de partícules biogèniques sota l'aflorament equatorial, i per tant formen un registre paleoclimàtic d'extraordinària qualitat. Així, el ODP 1240 permet un monitoratge d'alta resolució de les variacions d'aquest aflorament.



**Fig. 23.** Batimetria d'alta resolució corresponent de la regió on es va extreure el ODP 1240. L'àrea coberta corresponent és de 30 km x 30 km (extret de Mix et al., 2003).

La seqüència sedimentaria extreta al ODP 1240 és d'un gruix de 282,9 metres, i està constituïda principalment per fangs amb un elevat contingut fòssilífer de composició variable al llarg de la seqüència [Mix et al., 2003]. Aquest registre fòssilífer està dominat per nanofòssils calcaris, en general ben preservats, tot i que la seva preservació descendeix entre els 20 i els 46 metres de profunditat de sediments compostos (mcd, de l'anglès metres composite depth), i per sota dels 120 mcd. També són molt comuns els foraminífers, amb una conservació bona, excepte entre els 163 i els 194 mcd. Per altra banda, les



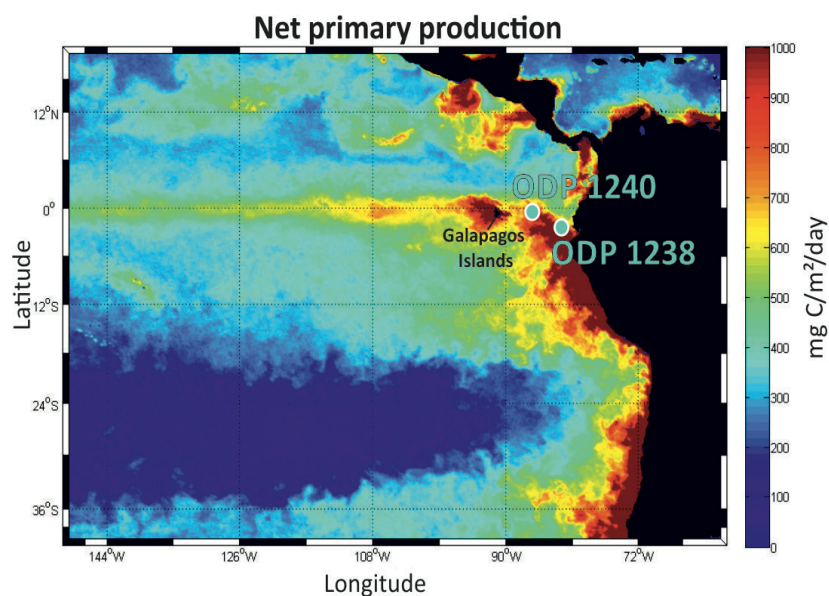
diatomees són abundants a tota la secció, però aquest contingut és sensiblement variable. La seqüència sedimentària ha estat subdividida en tres unitats (1A, 1B i 1C), definides d'acord a les diferents característiques sedimentològiques de cada una d'elles [Mix et al., 2003]. Aquesta tesi s'ha focalitzat concretament en la unitat 1B, en l'interval de profunditat que va des de 135,34 fins a 225,94 mcd.

En aquest site es dona la presència de vuit capes de cendres, que poden estar associades amb el vulcanisme del nord de Sud Amèrica i Centre- Amèrica [Ninkovich and Shackleton, 1975; Mix et al., 2003].

Una característica molt important d'aquest site és la presència de laminacions de diatomees (LDO, de l'anglès Laminated Diatom Oozes,). Aquestes capes són bandes d'un centímetre de gruix que van des de colors oliva fosc fins a oliva i marró-oliva fosc. L'associació de diatomees durant els intervals laminats és dominat per *Thalassiothrix spp.* i *Thalassionema spp.* (cf. secció 1.5.2.) [Mix et al., 2003].

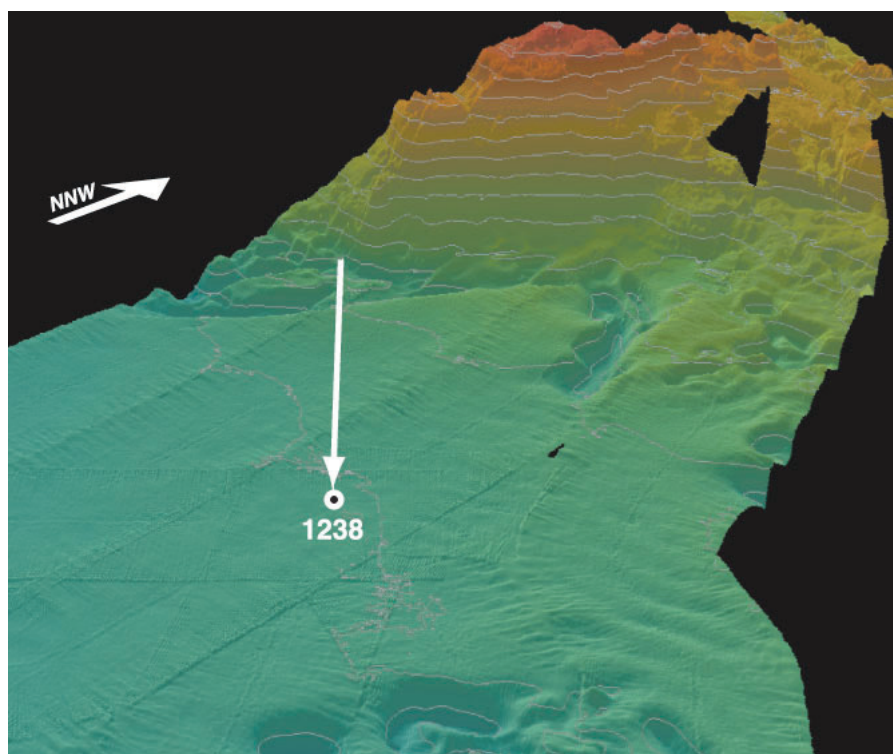
#### 1.4.2.2. ODP 1238

El ODP Site 1238 (ODP 1238) ( $1^{\circ}52.310'S$ ,  $82^{\circ}46.934'W$ ; 2203 metres de profunditat) es troba localitzat també al Pacífic equatorial, a uns 200 quilòmetres de la costa de l'Equador (Fig. 24), en el flanc sud de l'aresta de Carnegie [Mix et al., 2003]. Aquest site es troba sota la llengua freda del sistema d'aflorament equatorial, per tant és una localització perfecta per enregistrar canvis en l'aflorament equatorial i la producció biològica associada (Fig. 24).



**Fig. 24.** Productivitat primària al Pacífic equatorial oriental, amb la localització dels Sites ODP 1240 ( $0^{\circ}01.31'N$   $86^{\circ}27.76'W$ ) i 1238 ( $1^{\circ}52.310'S$ ,  $82^{\circ}46.934'W$ ).

El basament d'aquest site està format per basalt, originat al hotspot de les Galápagos fa 11-13 Ma [Mix et al., 2003]. Els flancs basàltics escarpats de l'aresta de Carnegie són predominantment de roca nua el que suggereix un transport de sediments costa avall (Fig. 25). La seqüència sedimentaria extreta del ODP 1238, té un gruix de 467.3 metres de profunditat composta (mcd) i una edat de 11 Ma (Miocè mig) [Mix et al., 2003], s'ha dividit en dues subunitats (1A i 1B). Els sediments d'aquest site estan caracteritzats per alternances d'escala mètrica de capes de color oliva clar riques en nanofòssils i intervals de diatomees de color oliva fosc. A més, alguns d'aquests intervals arriben a ser molt rics en diatomees [Kemp et al., 1995] i en cendres [Ledbetter, 1985].



**Fig. 25.** Batimetria d'alta resolució de la zona on es va perforar el Site 1238, l'àrea coberta és de 40 km (NW-SE) x 30 km (SW-NE) (extret de Mix et al., 2003).

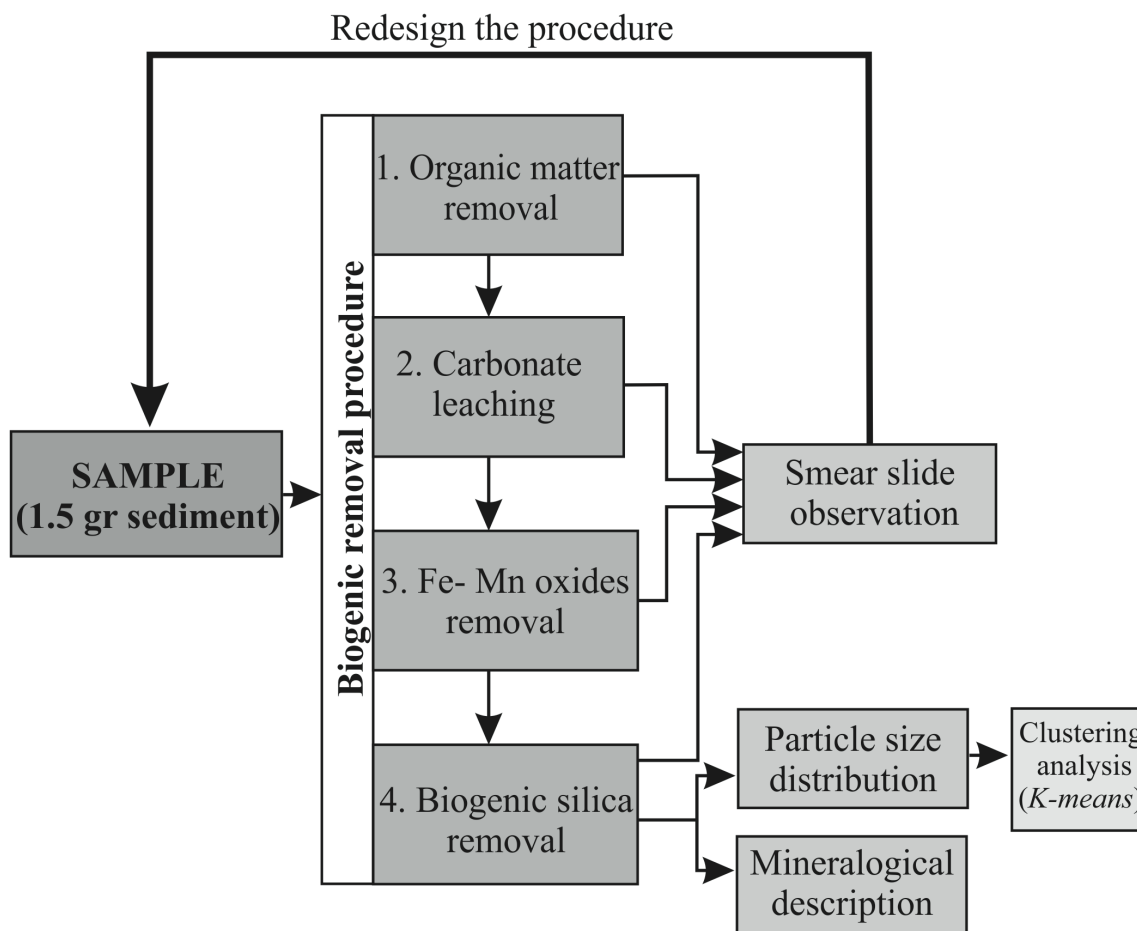
## 1.5. METODOLOGIA EMPRADA

### 1.5.1. Anàlisi de la fracció lítica

Per poder analitzar la distribució granulomètrica del material lític contingut en els sediments marins el primer pas és l'eliminació de les partícules biogèniques (restes fòssils i matèria orgànica) i minerals autigènics (òxids). Donada l'alta productivitat biològica de la zona tractada, aquestes mostres presenten una gran quantitat de restes calcàries (foraminífers i nanofòssils) i restes silíciques (diatomees, radiolaris i espícules d'esponges). En aquest treball s'ha partit d'un protocol estàndard utilitzat usualment en el tractament de sediments marins per a l'anàlisi de granulometries, on s'han aplicat una sèrie de modificacions per tal d'adaptar-los a les característiques de les mostres utilitzades en aquest estudi (cf. secció 2.1.).

#### 1.5.1.1. Protocol per a l'aïllament de la fracció litogènica

El protocol que aquí es presenta és el resultat d'una llarga fase de modificacions i proves de diferents protocols emprats en treballs anteriors, centrats en aquesta i en altres àrees geogràfiques [Chester and Hughes, 1967; Rea and Janecek, 1981; Mortlock and Froelich, 1989; DeMaster et al., 1991; Muller and Schneider, 1993; Hovan, 1995; McCave et al., 1995; Fabres et al., 2002; Lyle and Lyle, 2002]. Aquests protocols van presentar limitacions serioses en l'eliminació d'alguns dels components biogènics, particularment dels fòssils silicatats. El procediment que aquí es descriu és el protocol final emprat en les mostres i que s'ha demostrat que elimina satisfactòriament tots els components autigènics del sediment, però deixant els components litogènics, objecte del present estudi (cf. secció 2.1.). Aquest protocol està compost per quatre fases especialment dissenyades per eliminar la matèria orgànica, la fracció biogènica carbonatada, els òxids de Fe-Mn i la sílice biogènica (Fig. 26).



**Fig. 26.** Esquema del protocol per a l'aïllament de la fracció litogènica i l'anàlisi de la mida de gra.

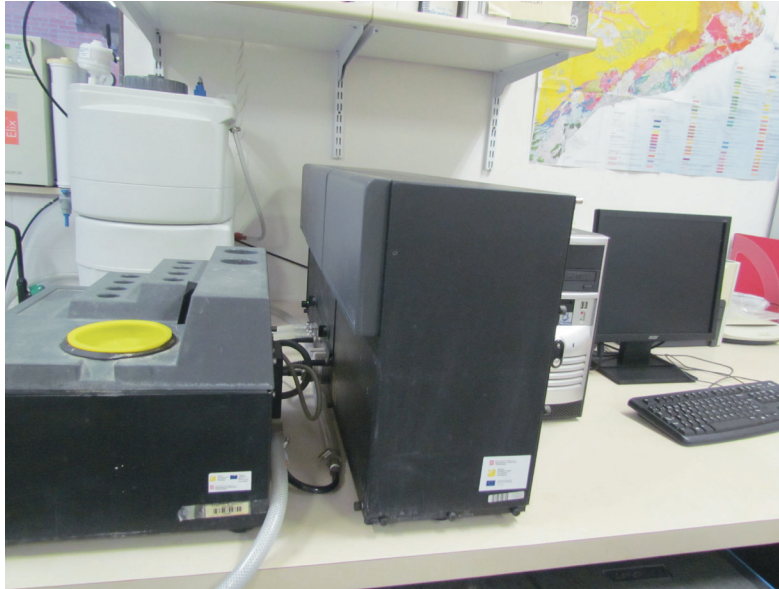
### 1.5.1.2. Contingut en lítics

L'estudi de la fracció lítica del sediment ha resultat ser una eina clau per identificar canvis en els sistemes de transport, així com per detectar canvis en les condicions climàtiques de l'àrea font. Concretament, aquesta eina ha demostrat ser de vital importància com a indicador de les migracions de la ITCZ en aquesta regió. Per tant, una forma de conèixer la quantitat de material que arriba a la zona és calcular el percentatge en lítics que s'obté a partir de pesar la mostra abans i després del protocol d'eliminació de la fracció biogènica (cf. annex I).

### 1.5.1.3. Distribució modal de la mida de gra

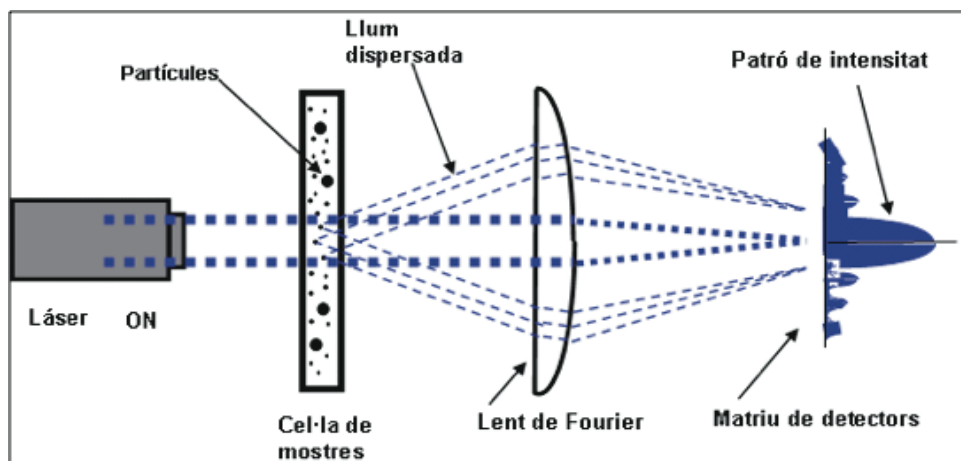
L'anàlisi de la distribució granulomètrica es va realitzar amb un analitzador de mida de partícules per difracció de raigs làser Coulter LS 230® (Fig. 27). El Coulter® LS 230

[Coulter Co., 1994] està constituït per una font de raigs làser, una cel·la de mostres, una lent de Fourier i una matriu de detectors (amb 132 detectors) (Fig. 28). Aquest aparell mesura el percentatge en volum de partícules i els seus límits de detecció es situen entre 0,04 i 2000  $\mu\text{m}$ .



**Fig. 27.** Aparell Coulter LS 230, instal·lat al Departament de Dinàmica de la Terra i de l'Oceà de la Universitat de Barcelona. Aquest aparell consta de dues parts, el mòdul fluid, on es troba la mostra a analitzar i el mòdul òptic, on es realitza la mesura analítica.

El principi bàsic d'aquesta tècnica és analitzar la mida de les partícules segons l'angle de difracció que es produeix en fer passar a través d'elles un feix de llum. Aquest feix de llum monocromàtica es fa passar a través de la cel·la de mostres, on es troba la mostra en solució, i on les partícules en suspensió difracten els raigs que són concentrats a través d'unes lents en els detectors (Fig. 28). Aquests mesuren a diferents intervals de temps la distribució angular de la llum difractada, i per tant s'obté la mida de les partícules (teoria de Fraunhofer) [Hodkinson, J. , 1966].



**Fig. 28.** Esquema de funcionament del Coulter® LS 230 (modificat de Coulter Co., 1994).

Si aquest angle és baix, indicaria que es tracta d'una partícula gran, com es veu a la Figura 29.

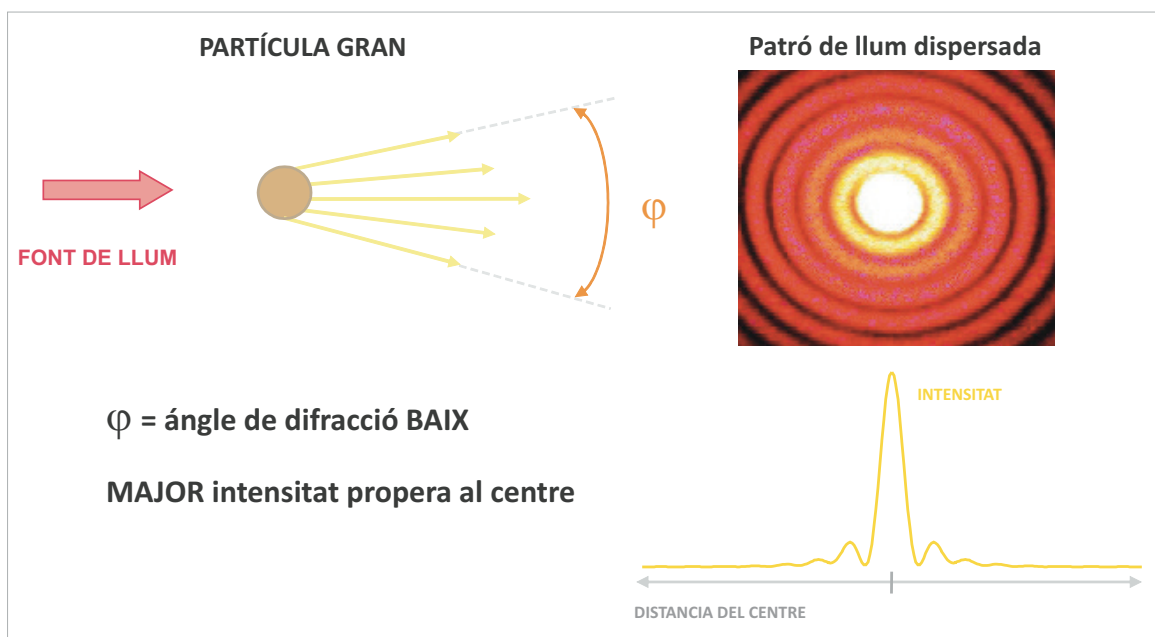


Fig. 29. Patró de intensitat per a partícules grans (modificat de Coulter Co., 1994).

En canvi si l'angle és alt, llavors es tracta d'una partícula petita, com s'indica a la Figura 30.

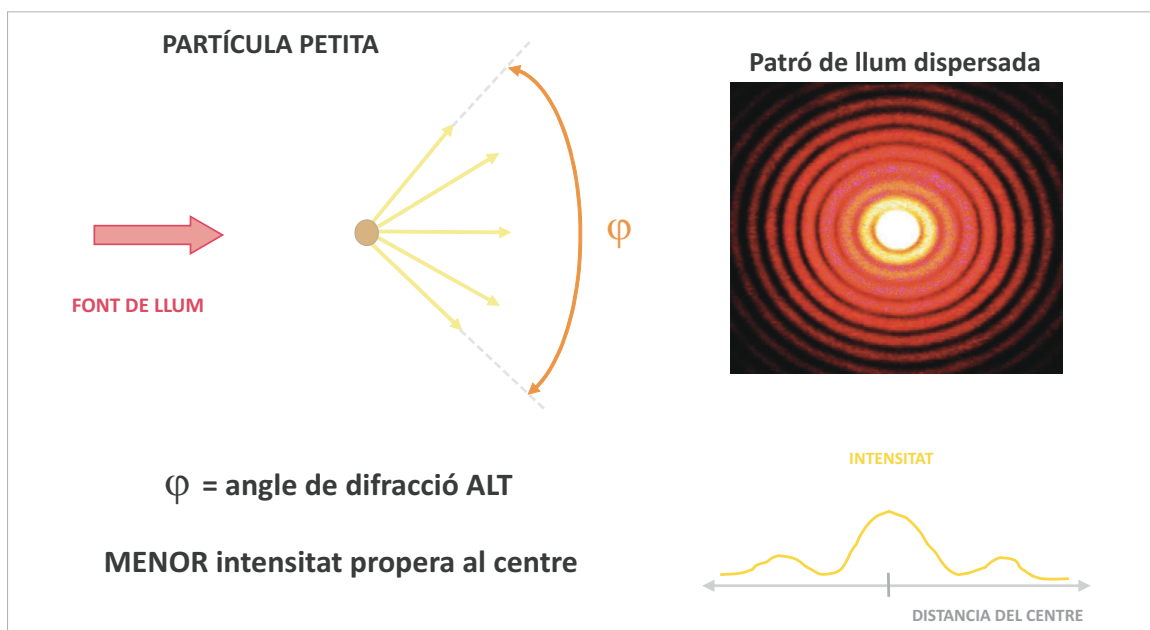


Fig. 30. Patró de intensitat per a partícules petites (modificat de Coulter Co., 1994).



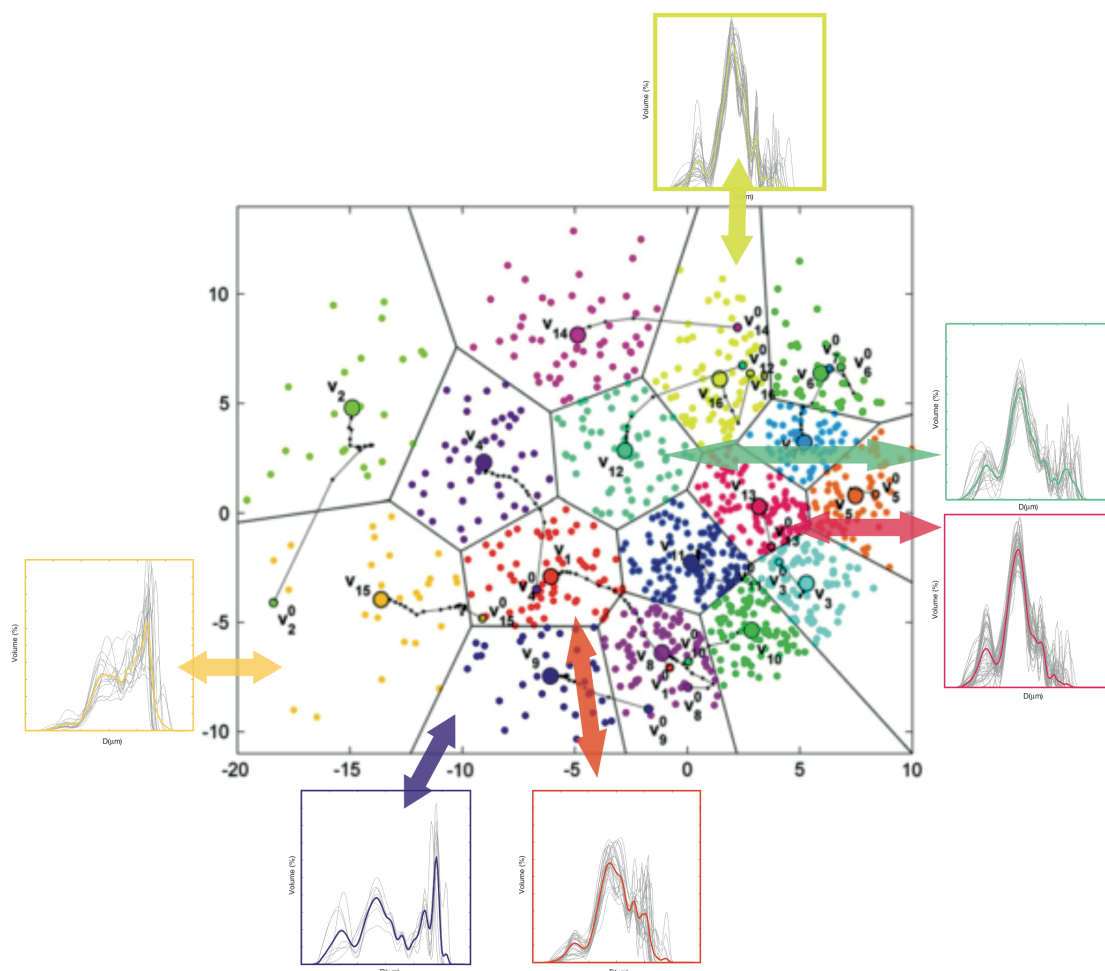
D'altra banda, la intensitat de llum dispersada propera al centre és inversament proporcional a l'angle de difracció, ja que s'observa que en partícules grans la intensitat és elevada, i és menor en partícules petites.

La teoria de Fraunhofer ofereix bons resultats per a partícules grans en relació a la longitud d'ona del làser, però per a partícules més petites és necessari tenir en compte la teoria de Mie [Hodkinson, J. , 1966; de Boer et al., 1987]. Aquesta teoria té en compte els fenòmens que es produeixen quan la llum interacciona amb la partícula: difracció, reflexió i refracció. Per això Beckman Coulter va desenvolupar la tecnologia PIDS (Polarization Intensity Differential Scattering) [Coulter Co., 1994] per obtenir una elevada resolució en un rang submicromètric. Aquesta tecnologia permet diferenciar partícules de mides similars a les del rang submicromètric. Això ho fa mesurant la diferència en la dispersió de la llum polaritzada vertical o horitzontalment, a diferents longituds d'ona i angles de detecció.

#### 1.5.1.4. Anàlisi clúster *k-means*

Un cop realitzat l'estudi de les distribucions modals de la mida de gra i per ajudar a la interpretació de l'àmplia base de dades generada, es va dur a terme una anàlisi clúster per obtenir una classificació objectiva i una millora en la interpretació de les variacions granulomètriques observades.

L'anàlisi clúster té com a objectiu realitzar una classificació objectiva mitjançant l'assignació de les distribucions de mida de gra a grups, on cada grup és similar i diferent dels altres. Una tècnica d'anàlisi clúster que ha estat utilitzada en l'estudi de diferents bases de dades [Serrano et al., 1999; Moreno et al., 2001; Metcalfe et al., 2010], és el mètode *k-means*. Aquesta tècnica divideix l'espai en  $n$  clústers, assignats per l'usuari. Cada clúster és definit per una mostra prototip i per les mostres que més s'aproximen a aquesta [Hastie et al., 2001]. Un cop establert el nombre de clústers i amb els prototips o centroides inicialitzats, a cada nova iteració d'aquesta anàlisi s'identifiquen les dades més properes al centroide de la iteració anterior. Aquest és redefinit com la mitja de les dades corresponents, minimitzant la distància total dins de cada clúster fins que convergeixen i les dades pertanyents a cada grup s'estabilitzen (Fig. 31). A partir d'això es calcula una matriu de similituds entre els  $n$  clústers i les  $N$  observacions, i l'observació més propera queda representada pel clúster més proper. Així, cada clúster es representa pel seu centroide i format per les mostres més properes al centroide [Davis, 2002] (Fig. 31).



**Fig. 31.** Anàlisi clúster k-means aplicada a l'anàlisi de la mida de gra (modificat de Camus et al., 2011). Clústers inicials {v01,...,v016}, actualització i centroides finals de cada clúster {v1,...,v16}. Alguns exemples dels clústers finals han estat marcats amb fletxes, on la línia de color ens indica el centroide de cada clúster.

Tot seguit, s'ha calculat la distància euclidiana entre el centroide de cada grup i les dades N. Aquesta distància comprèn valors de 0 a 1, així una distància de 0 correspon a la mostra centroide i un valor 1 correspon a la màxima distància a aquest centroide. Per tant, aquesta distància permet esbrinar el grau de similitud entre cada mostra i cada clúster, on un valor proper a 0 significa una major similitud a aquell determinat clúster.

#### 1.5.1.5. Observació al microscopi i contingut mineral

En primer lloc, aquest mètode es fa servir com a sistema de certificació de la bona eliminació de la fracció biogènica i autigènica del sediment. Amb aquesta finalitat s'inspecciona exhaustivament al microscopi òptic cada una de les làmines obtingudes de les mostres ja processades. Aquesta revisió ha permès detectar problemes en el protocol durant la fase de prova, com es detalla a l'apartat 2.1.3 del capítol 2. Aquestes làmines es van pre-

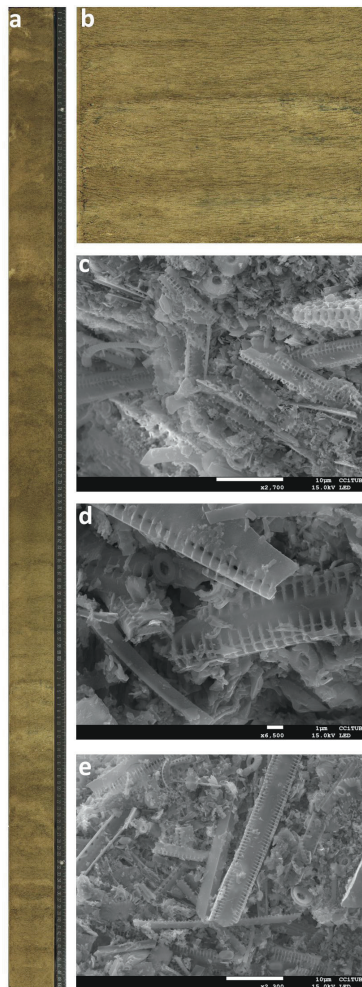


parar agafant mostra diluïda en aigua (de 1 a 2 mm<sup>3</sup>) i expandint-la amb un palet de fusta. Un cop està la mostra ben repartida sobre el porta-objectes es col·loca sota la làmpada de llum ultraviolada i es deixa assecar. Per enganxar el cobreobjectes s'ha utilitzat adhesiu UV i s'ha procedit a l'assecat sota la làmpada de llum ultraviolada [Backman and Shackleton, 1983; Rothwell, 1989].

En segon lloc, aquest mètode es fa servir per a la caracterització de la composició litogènica i autigènica de cada una de les mostres. En aquest cas, l'observació al microscopi s'efectua mitjançant les làmines realitzades a les mostres després del seu tractament. Això ens permetrà establir unes relacions segons el contingut mineral present, la seva mida i el percentatge de cada fase mineral.

### 1.5.2. Laminated Diatom Oozes (LDO)

La caracterització de les capes laminades de diatomees s'ha basat en la identificació visual de bandes de centímetres de gruix que presenten colors que van des de oliva fosc fins a marró oliva i marró oliva fosc (Fig. 32).



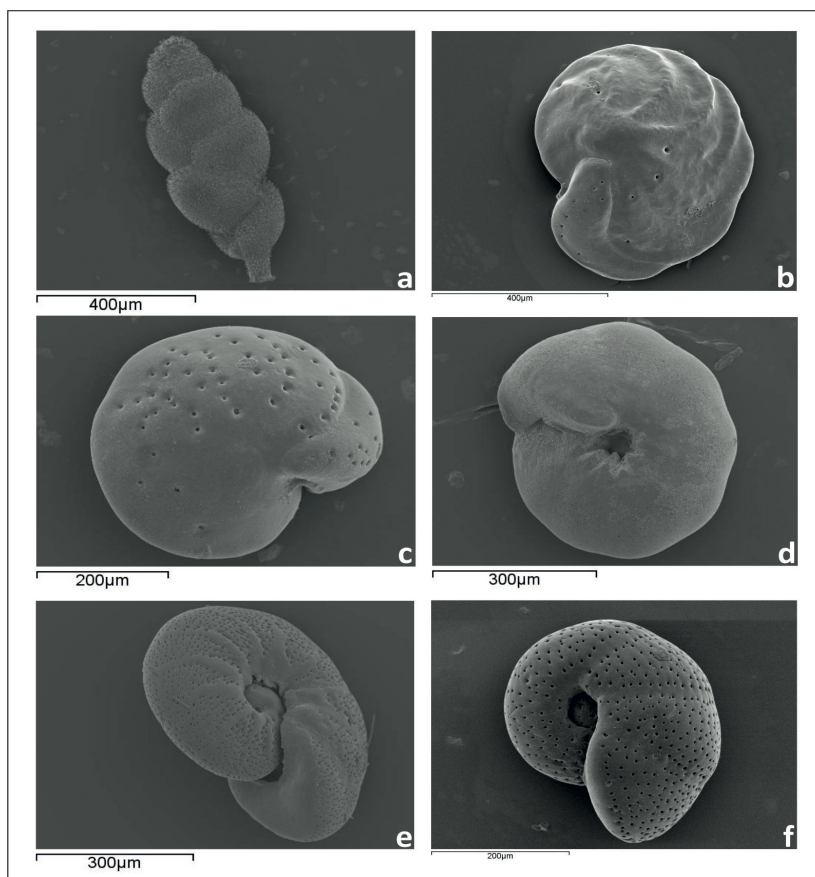
**Fig. 32.** Descripció de les laminacions de diatomees presents al ODP 1240. (a) Secció laminada del ODP 1240, (b) Sediment laminat del ODP 1240, corresponent a la laminació L1 d'aquesta Tesi, (c, d, e) Imatges d'aquests intervals laminats, obtingudes a través del microscopi electrònic, on s'evidencia l'elevat contingut en *Thalassiothrix spp.*

En contrast, el color del sediment en els intervals no laminats alterna colors oliva pàl·lid i gris oliva clar [Mix et al., 2003]. L'associació de diatomees dels intervals laminats i no-laminats s'ha descrit mitjançant la identificació a través d'un microscopi electrònic (SEM) J-7100 FE, que es va dur a terme als Centres Científics i Tecnològics (CCiTUB) de la Universitat de Barcelona (Fig. 32).

### 1.5.3. Abundància de foraminífers bentònics

Les principals espècies de foraminífers bentònics presents a les mostres van ser comptades a fi i efecte d'identificar canvis en la fauna bentònica que podrien ser indicador de canvis de l'oceà profund, i poden aportar informació del contingut de nutrients, oxigen i d'altres variables ambientals.

L'anàlisi en detall de la fauna bentònica es dugué a terme als Centres Científics i Tecnològics (CCiTUB) de la Universitat de Barcelona amb un microscopi electrònic (SEM) Stereoscan S-360. Les principals espècies de foraminífers bentònics analitzades van ser, *Uvigerina* spp., *Cibicides wuellerstorfi*, *Cibicides kullenbergi*, *Giroydina* spp., *Melonis barleanum* i *Melonis pompilioides* (Fig. 33).

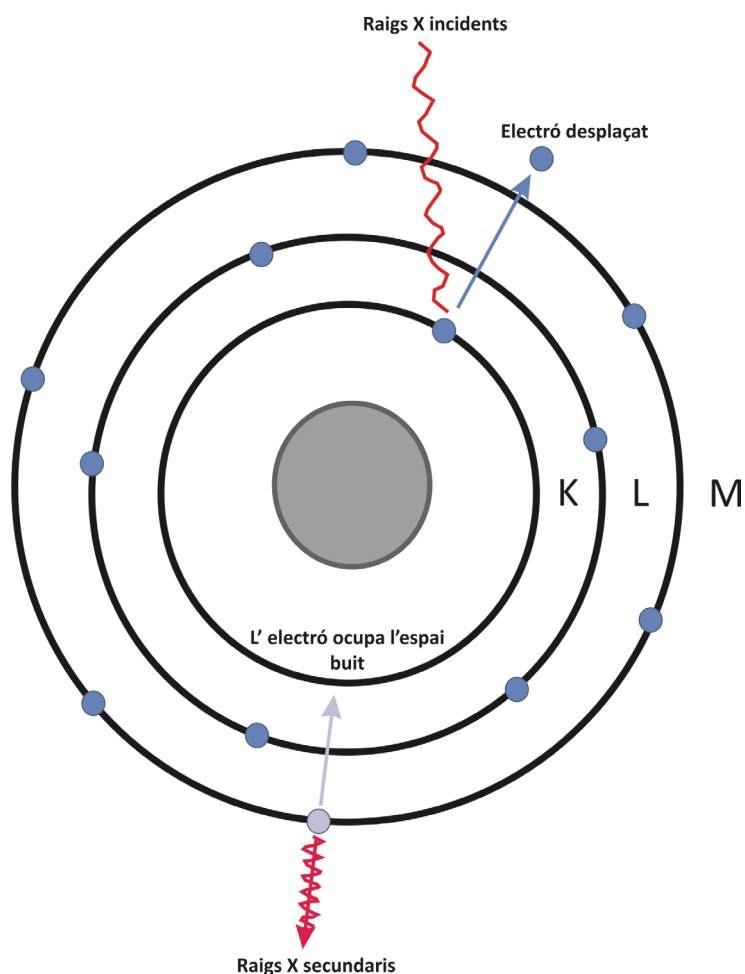


**Fig. 33.** Imatges de microscopi electrònic de les principals espècies de foraminífers bentònics del ODP 1240. a) *Uvigerina* spp., (b) *Cibicides wuellerstorfi*, (c) *Cibicides kullenbergi*, (d) *Giroydina* spp., (e) *Melonis barleanum*, (f) *Melonis pompilioides*.

### 1.5.4. Anàlisi geoquímics

#### 1.5.4.1. XRF Core Scanner

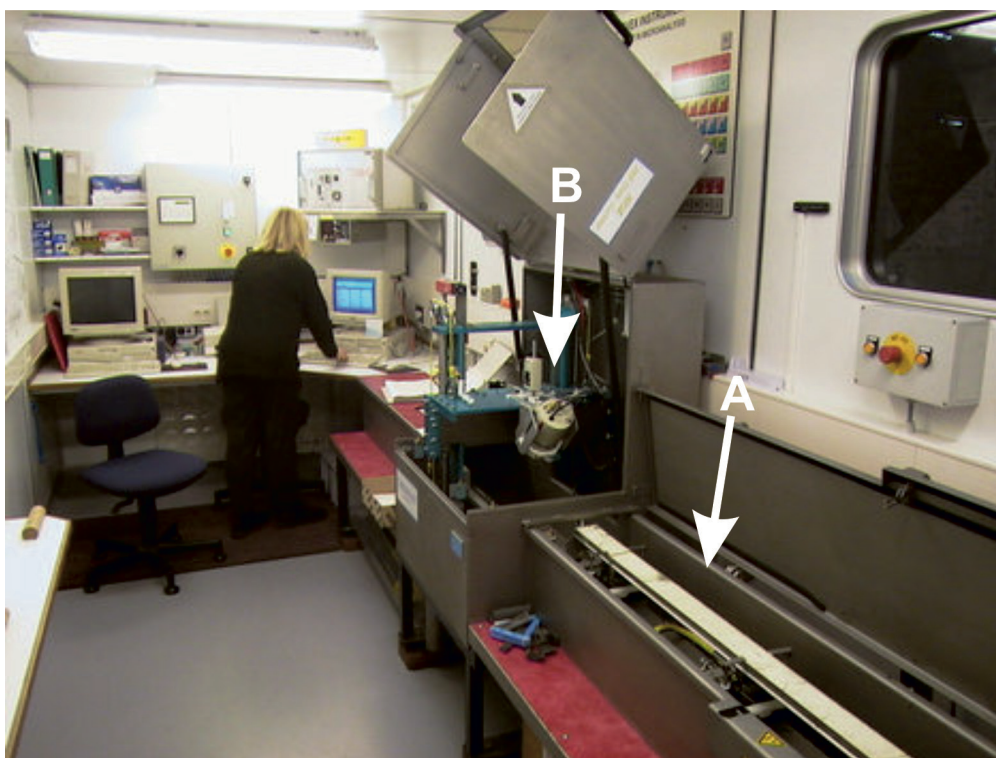
La composició elemental dels elements majoritaris del ODP 1240 ha estat obtinguda mitjançant la tècnica de fluorescència de raigs X, que permet una anàlisi ràpida, continua, no destructiva i d'alta resolució dels sediments marins [Jansen et al., 1998; Rothwell and Rack, 2006; Frigola et al., 2015]. Aquesta tècnica es basa en la detecció de les emissions secundàries produïdes pels diferents elements químics quan aquests són excitats per una font de raigs X. Quan s'exposa el sediment a una font de raigs X s'ionitzen els àtoms que el conformen. Aquesta ionització provoca l'expulsió dels electrons de les capes interiors del àtom, provocant així que els electrons de les capes més externes ocupin els llocs buits (Fig. 34) [Jansen et al., 1998]. En aquesta caiguda es genera energia mitjançant l'emissió d'un fotó. Aquesta energia és l'anomenada radiació de fluorescència de raigs X i dependrà de la diferència energètica entre aquestes dues capes d'electrons, característica de cada àtom.



**Fig. 34.** Principi bàsic de la tècnica de fluorescència de raigs X.

Per tant, donat que la intensitat de la radiació de fluorescència de raigs X es troba relacionada al seu temps amb la concentració de cada element del sediment, es poden calcular les concentracions de cada element per comparació amb estàndards calibrats, realitzant una sèrie de correccions dels errors instrumentals i de l'efecte matriu [Rollinson, 1993].

Amb aquest propòsit s'ha utilitzat un escàner de mesura en continu i no destructiu anomenat CORTEX (Corescanner Texel), el qual és el primer model de la companyia Avaatech instal·lat a la Universitat de Bremen (Fig. 35, 36).

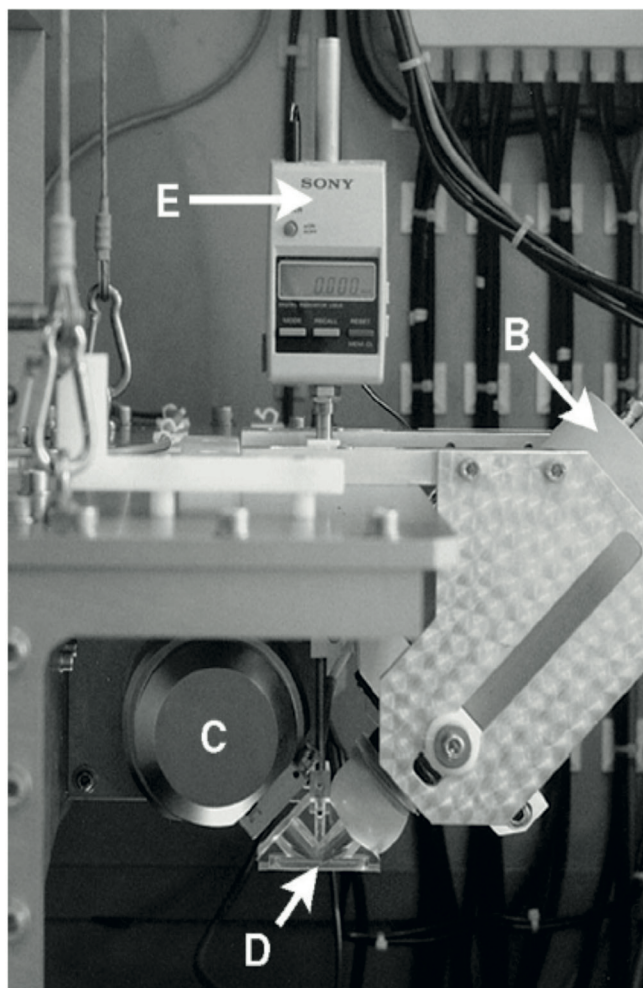


**Fig. 35.** Escàner per fluorescència de raigs X de primera generació CORTEX (Corescanner Texel), fabricat per Avaatech i instal·lat a la Universitat de Bremen ([http://www.marum.de/en/XRF\\_Core\\_Scanner.html](http://www.marum.de/en/XRF_Core_Scanner.html)). A indica la superfície on es situa el testimoni i B el detector XRF [Jansen et al., 1998].

Aquestes anàlisis es van realitzar a la superfície del sediment sobre una àrea d'1 cm<sup>2</sup>, amb un voltatge de 20 kV i un corrent de raigs X de 0.087 mA durant un temps de 30 s. Els elements amb valors estadísticament més significatius obtinguts van ser K, Ca, Fe, Mn, Sr i Ti. Les dades resultants han estat expressades en contes per segon (cps, de l'anglès counts per second). Per convertir aquests valors d'intensitat a concentracions és necessari el calibratge amb mètodes analítics estàndards. Amb aquest objectiu es van analitzar 30 mostres després de la total digestió de 50 mg de mostra seca total. Els elements Mg, Al, K, Ca, Ti, Mn, Fe, Sr i Ba van ser analitzats amb un espectròmetre òptic (Inductively Coupled Plasma Optic Spectrometer, ICP-OES) Perkin- Elmer model Optima 3200 RL, als Centres



Científics i Tecnològics (CCiTUB) de la Universitat de Barcelona, amb una precisió superior al 2%. Les equacions de correlació entre els dos mètodes indiquen una alta correlació i permeten la conversió de les dades de cps a mg/g.



**Fig. 36.** Part central del CORTEX [Jansen et al., 1998]. B indica el detector, C el tub de raigs X, D el prisma de buit de Heli i E el sensor per controlar el descens del prisma.

#### 1.5.4.2. Propietats de color

Les propietats de color dels sediments són una eina ràpida per detectar canvis en la composició i preservació a alta resolució [Mix et al., 1992; Nederbragt and Thurow, 2004; Rogerson et al., 2006; Debret et al., 2011; Frigola et al., 2015]. Així doncs, les dades de color del sediment pels ODP 1240 i 1238 van ser obtingudes mitjançant un espectrofo-

tòmetre Minolta CM-2002, a bord del vaixell oceanogràfic JOIDES Resolution durant el Leg 202. Aquest aparell projecta un feix de llum monocromàtica a través d'una mostra i gràcies a un sensor espectral es mesura la reflectància espectral de superfícies amb un diàmetre de més de 8 mm [Blum, 1997] en funció de la seva longitud d'ona. D'aquesta forma s'obtenen la luminescència ( $L^*$ ) i la reflectància ( $a^*$ ), els quals són els paràmetres de color més utilitzats en Paleoceanografia.

#### 1.5.4.3. Isòtops estables

L'anàlisi d'isòtops estables,  $\delta^{18}\text{O}$  i  $\delta^{13}\text{C}$  es va realitzar en dues espècies diferents de foraminífers bentònics, *Uvigerina spp.* i *Cibicides wuellerstorfi*. L'anàlisi d'*Uvigerina spp.* es va dur a terme en 8-10 individus, mentre que l'anàlisi de *C. wuellerstorfi* es va realitzar en 4-5 espècimens. Un cop seleccionats els individus, es van obrir les seves cambres amb dos porta objectes de vidre i es van netejar amb metanol per tal d'obtenir unes anàlisis més acurades. Aquest procediment consisteix en l'aplicació d'unes gotes de metanol, la sonicació de la mostra durant trenta segons i l'eliminació de la solució amb una micro-pipeta. L'anàlisi instrumental es va realitzar en un espectròmetre de masses Finnigan MAT252 equipat amb un dispositiu de Kiel Carbonat III, als Centres Científics i Tecnològics (CCiTUB) de la Universitat de Barcelona. Els estàndards es van realitzar cada 6 mostres amb una reproductibilitat de 0,06 ‰ per  $\delta^{18}\text{O}$  i de 0.02 ‰ per  $\delta^{13}\text{C}$ . Els valors estan representats com  $\delta^{18}\text{O}$  (‰) i  $\delta^{13}\text{C}$  (‰) respecte al estàndard de Viena Pee Dee Belemnite (VPDB). Per tal de produir la corba integrada de  $\delta^{18}\text{O}$  i  $\delta^{13}\text{C}$ , les dades pertanyents a  $\delta^{18}\text{O}$  *C. wuellerstorfi* es van corregir a l'escala d'*Uvigerina spp.* mitjançant l'addició de 0,64 ‰ mentre que les dades de  $\delta^{13}\text{C}$  de *Uvigerina spp.* es va corregir afegint-li 0.9 ‰ [Shackleton and Hall, 1984].

#### 1.5.4.4. Carboni total, nitrogen total i carboni orgànic

L'anàlisi geoquímica elemental del carboni i del nitrogen s'ha realitzat en un analitzador orgànic elemental Thermo EA Flash 1112, als Centres Científics i Tecnològics (CCiTUB) de la Universitat de Barcelona. Aquesta tècnica es basa en la total combustió de la mostra dins d'un forn a una temperatura de 1000 °C. Els diferents productes d'aquesta combustió, com ara el carboni en forma de  $\text{CO}_2$  i el nitrogen en diferents formes, són transportats pel tub de reducció. Posteriorment passen per un cromatògraf de gasos que permet mesurar  $\text{CO}_2$  i  $\text{N}_2$ , i per tant obtenir finalment el contingut en carboni i nitrogen.

Separadament i amb l'objectiu d'analitzar el carboni orgànic, les mostres van ser ata-

cadetes amb HCl al 25 % abans de l'anàlisi elemental. Es van realitzar dos etapes d'atac de 50 µl de HCl cada un, separades per una etapa d'asseccament a l'estufa de 60 °C [Fabres et al., 2002].

#### 1.5.4.5. Contingut en sílice biogènica

L'anàlisi del contingut en sílice biogènica ha estat realitzat amb la tècnica d'inducció acoblada mitjançant un espectròmetre òptic (Inductively Coupled Plasma Optic Spectrometer, ICP-OES) Perkin- Elmer model Optima 3200 RL, als Centres Científics i Tecnològics (CCiTUB) de la Universitat de Barcelona. La concentració de sílice biogènica fou analitzada en 200 mg de mostra de sediment. El mètode d'extracció ha estat modificat de Povea et al., (2015), i consisteix en una lixiviació en dues etapes amb una solució de NaOH 1,5 M.

### 1.5.5. Anàlisi espectral

El sistema climàtic és un sistema dinàmic tal com s'ha descrit a l'apartat 1.1., per tant els diferents elements i processos que el modulen poden succeir en diferents escales temporals. Així doncs, donades les diferents ciclicitats que es poden observar en un mateix registre paleoclimàtic es fa necessari la realització d'una anàlisi de freqüències de cada registre paleoclimàtic. Aquesta anàlisi permet establir les diferents interconnexions entre els processos i dinàmiques que han modulats aquest sistema climàtic en el passat.

A l'hora de realitzar l'anàlisi de freqüència d'una sèrie temporal s'ha de tenir present que les sèries climàtiques són majoritàriament irregulars en l'espai de les dades, per tant s'ha de realitzar una interpolació de la sèrie. Per dur a terme l'anàlisi espectral s'ha aplicat el periodograma de transformació de Fourier Lomb-Scargle, que pot ser aplicat en sèries no equi-espaiades en el temps, i forma part dels mètodes d'anàlisi espectral per mínims quadrats. A més, aquesta anàlisi s'ha realitzat a través del software comercial Matlab® utilitzant l'algoritme REDFIT de Schulz and Mudelsee, (2002), que permet estimar i corregir el soroll vermell present en les sèries temporals. El soroll és considerat com una pertorbació aleatòria que distorsiona un senyal, sent el soroll vermell el tipus de soroll que solen presentar les sèries ambientals, donat que la intensitat o amplitud espectral disminueix exponencialment a mesura que decreixen les seves freqüències.

Una altra eina molt útil a l'hora de caracteritzar una sèrie temporal és aplicar una anàlisi wavelet [Torrence and Compo, 1998], sobretot en sèries amb esdeveniments transitoris o no estacionals. Aquesta anàlisi permet la descomposició espectral localitzada de la sèrie, determinant els modes dominants de variabilitat i com varien aquests en el temps. En

aquesta Tesi s'ha utilitzat especialment l'anàlisi wavelet amb funció de Morlet, que és una funció exponencial complexa, on la seva amplitud es troba modulada per una funció proporcional a la funció de densitat de probabilitat d'una distribució Gaussiana.







# **CAPÍTOL II**

# **RESULTATS**





## 2.1. A NEW PROCEDURE FOR THE LITHIC FRACTION CHARACTERIZATION IN MARINE SEDIMENTS FROM THE HIGH PRODUCTIVITY AREAS: OPTIMIZATION OF ANALYTICAL AND STATISTICAL PROCEDURES

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### 2.1.1. Abstract

The lithogenic fraction in marine sediments can be a key proxy to reconstruct past changes in atmospheric circulation, river runoff among other sedimentary processes. But accurate isolation of the lithic component within biogenic-rich sediments can be particularly challenging in areas of high marine productivity. We present an experiment to isolate and characterize this lithogenic fraction that ensures the full elimination of biogenic and authigenic components. This experiment demonstrates that standard procedures used in most of the studies of terrigenous fraction in marine sediments, are inadequate to remove efficiently most of the biogenic components in sediments from high productivity regions such as the Eastern Equatorial Pacific. The experiment reviews each of the procedure steps designed for the removal of organic matter, carbonate, Fe-Mn oxides and biogenic silica. The most critical steps were the removal of organic matter incorporated in faecal pellets, and the elimination of the biogenic silica. The continuous monitoring of the grain size distribution of the samples along the experiment steps allows evaluating the impact that an inadequate procedure can induce on the grain size. Finally, lithic grain size distributions were characterized using K-means statistical technique providing objective information for climate interpretation. The proposed approach ensures the quality of the results and allows magnifying the information provided by the lithic fraction in marine sediments.

## 2.1.2. Introduction

Marine sediments contain lithic particles whose study can provide very useful information about different sedimentary processes which ultimately may reflect climate dynamics. This sediment fraction is mostly from terrestrial source and the particles can be transported to the marine environment through the atmosphere or by river runoff. The grain size distribution and composition of the terrigenous fraction has proved to be a proxy for paleocontinental aridity and wind strength in areas such as the Atlantic and Pacific basins [Stuut and Lamy, 2004; Holz et al., 2007] and Mediterranean Sea [Hamann et al., 2008]. Dust fluxes have also been used to estimate the paleoposition of the Intertropical Convergence Zone (ITCZ) in northwest Africa [Tiedemann et al., 1994] and the spatial variability of the Asian monsoon [Nagashima et al., 2007]. Mineralogical and geochemical data can be used as indicator of the source for eolian dust, and the transport mechanisms [Hyeong et al., 2005; Hamann et al., 2009]. According to the sediment core location the lithic fraction can also be a good proxy for river runoff [Lantzsich et al., 2010; Frigola et al., 2012] or an indicator of changes in the intensity of deep water currents [Bianchi and McCave, 1999; Hall and McCave, 2000; Frigola et al., 2007].

This study is focused on the analysis of the lithic fraction and its size distribution in Equatorial Pacific sediments. The samples were collected from ODP Leg 202 Site 1240 in the Eastern Equatorial Pacific, Panama Basin ( $0^{\circ}01.31$  N  $86^{\circ}27.76$  W; 2921 meters depth). This region acts as a sediment trap that collects biogenic particles formed under equatorial upwelling [Mix et al., 2003]. This tropical region is characterized by the convergence of the trade winds at the ITCZ [Pisias et al., 1995]. The ITCZ position has a seasonal fluctuation, being shifted south toward the equator during the Southern Hemisphere summer when the southeasterly trade winds are weaker. During the Southern Hemisphere winter when the southeasterly trades are stronger, the ITCZ it is located further north at about  $8^{\circ}$  N, resulting in maximum equatorial upwelling and eolian transport of the lithic fraction. The sediment at the studied site is dominated by diatom ooze and nannofossil ooze containing diatoms [Mix et al., 2003], this sediment composition is representative of the deep marine sediments that can be found along the Pacific cold tongue, a broad oceanographic region that includes the eastern Pacific coastal and equatorial upwelling systems. Marine sediments rich in siliceous oozes can also be abundant in other upwelling regions of the North Pacific and Indian Oceans and along most of the Southern Ocean [Kennett, 1982].

In this study, we show that most of the standard procedures applied to analyze grain size distribution in marine sediments were not aggressive enough to totally remove the biogenic particles. Due to high content of biogenic particles in the sediments, the standard procedu-

res must be modified to ensure the effective removal of organic (faecal pellets) and siliceous remains (diatoms, radiolaria and sponge spicules). We propose a number of changes to standard procedures for their use under high-productivity areas. Finally, we applied a clustering technique (*k-means*) to the analysis of a large data base of grain size distributions. This allowed us to group the samples using an objective and statistically significant procedure.

### 2.1.3. Materials and procedures

#### 2.1.3.1. Standard procedure

The standard procedure described below and modified from Chester and Hughes (1967), Rea and Janecek (1981), Mortlock and Froelich (1989), Demaster (1991), Muller, et al. (1993), Hovan (1995), McCave, et al. (1995), Fabrés, et al. (2002), and Lyle et al. (2002), is commonly used in the treatment of marine sediments for grain size analysis. This procedure consists of four steps designed to remove the biogenic and authigenic fraction, specifically the organic matter, carbonate, Fe-Mn oxides and biogenic silica fractions.

First step: removal of organic matter. 1.5 gr of dry sediment sample were treated with 35 ml of 5% hydrogen peroxide to oxidize the organic matter. Samples were then agitated and remained for 30 minutes at the oven (60°C) to allow the reaction. The remaining solution was removed after sample centrifugation at 5000 rpm for 10 minutes.

Second step: removal of carbonate bioclasts. The carbonate was leached by the addition of 35 ml of 2.7% acetic acid – 0.34 M sodium acetate solution (pH=4) based in Biscaye, 1965 method (Table 2.2) and placed in the shaker for five hours. After this time, the vials were centrifuged during 15 minutes (5000 rpm) and the solution removed. This attack is repeated twice during the second time the samples were left stirring overnight. At the end of treatment the samples were washed one time with MilliQ water and centrifuged 15 minutes (5000 rpm) to remove the leaching solution.

Third step: removal of Fe-Mn oxides. These oxides produced by authigenic processes, which have been proven to be abundant in this setting [Pena et al., 2005, 2008], were treated with a 0.02 M hydroxylamine hydrochloride and 25% acetic acid to eliminate the Fe-Mn oxides (modified after Chester and Hughes, 1967). These oxides were removed by adding 45 ml of Hydroxylamine hydrochloride solution (Table 2.2) and placed in the shaker during two hours. The solution was then removed by centrifuge for 15 minutes (5000 rpm). The attack was repeated a second time leaving the samples on the shaker overnight. Then, the samples were centrifuged for 15 minutes (5000 rpm) and were washed two times with MilliQ water.

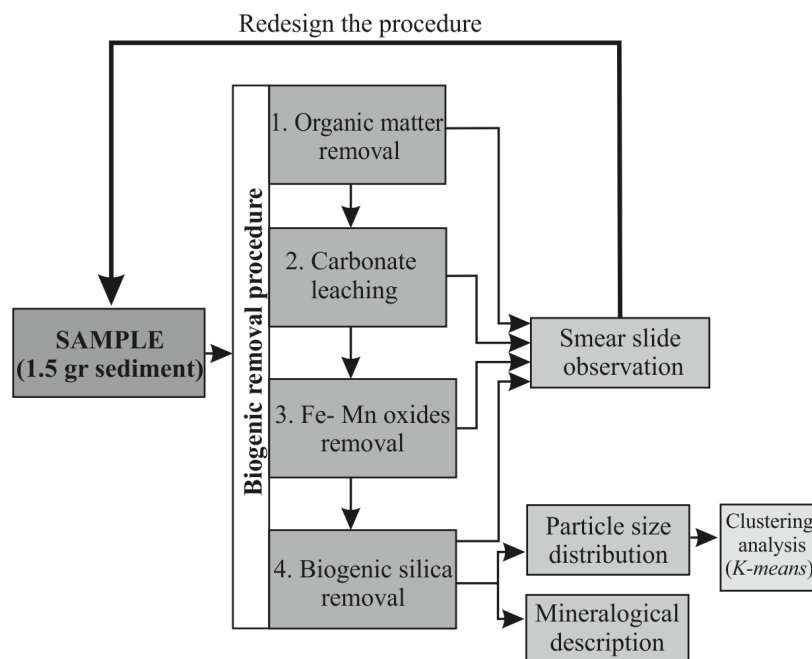
Fourth step: removal of biogenic silica. Removed biogenic silica using a solution of  $\text{Na}_2\text{CO}_3$  2M, from the procedure described by Mortlock and Froelich (1989). This step



consisted on the addition of 35 ml of 2M  $\text{Na}_2\text{CO}_3$  solution. The samples were shaken and left 5 minutes of sonication, the samples stayed in a warm water bath ( $85^\circ\text{C}$ ) for 2 hours. The procedure was later repeated for 2 additional hours. The extracted solution was finally removed after sample centrifugation and the samples were further cleaned adding MilliQ water for two consecutive times.

### 2.1.3.2. Smear slide preparation and microscope observation

Smear slides were prepared systematically during the procedure setup after each chemical step in order to monitor the efficiency of the biogenic and authigenic fraction removal (Fig. 2.1). Smear slides were prepared using a UV curing adhesive and dried under ultraviolet light [Backman and Shackleton, 1983; Rothwell, 1989]. Samples were then observed under the microscope, first to ensure the elimination of the biogenic and authigenic fraction and secondly to broadly characterize the lithic fraction.



**Fig. 2.1.** Diagram of the procedure used to isolate and analyze the lithogenic fraction, including the monitoring for each step of the protocol.

### 2.1.3.3. Grain size distributions and clustering analysis

Grain size analysis were realized after each of the experimental tests to check the effect that the different procedures could have in the grain size distribution and finally, samples

treated with the optimized procedure were analyzed in order to characterize the grain size distribution along time. Prior to the grain size measurements, samples were disaggregated with sodium polyphosphate, sonicated for 15 minutes and shaken overnight. Grain size distributions were characterized using a Coulter LS 230. The basic principle of this device is to analyze the particle size according to the angle of diffraction that occurs when sample grains pass through a light beam. This device measures the percentage volume of particles in 116 size classes, and its detection range is between 0.04 and 2000  $\mu\text{m}$ .

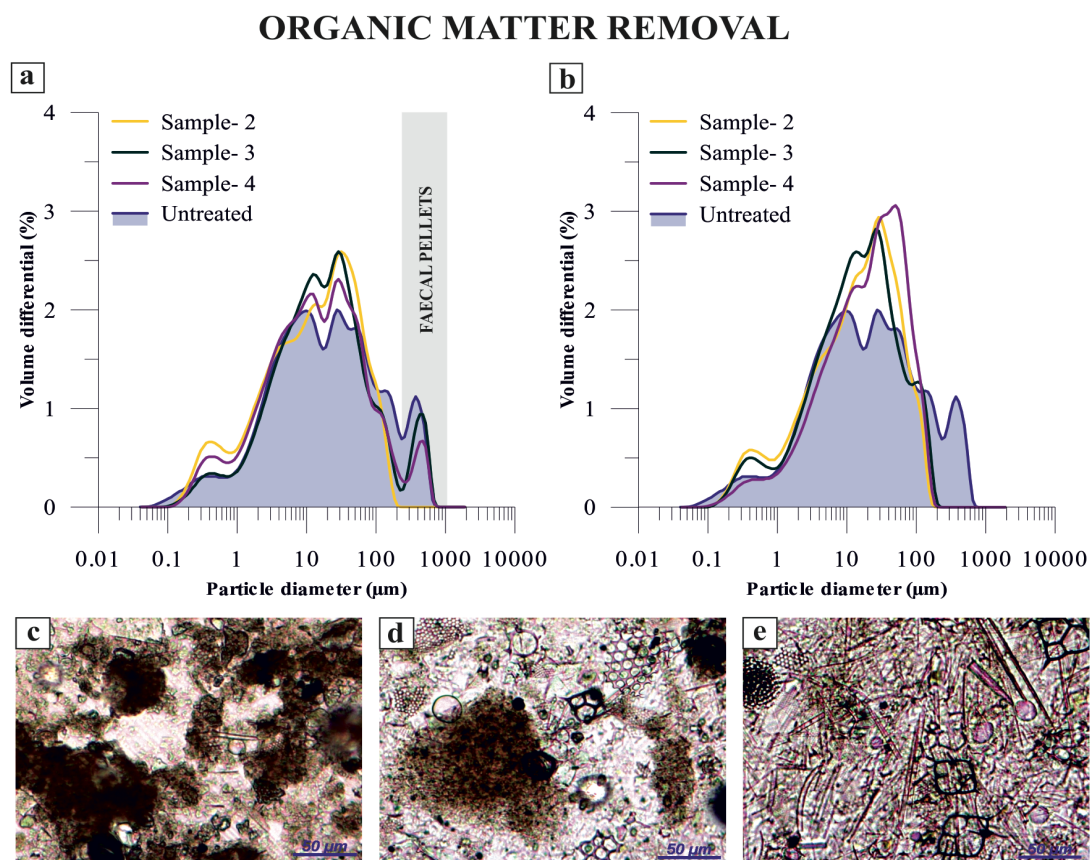
A clustering statistical analysis of grain size distributions was carried out to aid in the interpretation of the main types of grain-size distributions from the measured values. The clustering analysis applied is based in the nonhierarchical *k-means* technique [McQueen 1967], widely used for the analysis of different datasets [Serrano et al., 1999; Moreno et al., 2001; Metcalfe et al., 2010]. This technique divides the  $N$  values of the dataset into  $n$  clusters assigned by the user. The number of clusters is decided after a series of tests with different options, and choosing the minimum that best represent the dataset. The input of the clustering analysis is composed by a matrix with measured samples of grain-size distributions (here,  $N= 164$  grain-size distributions for different core depths and 116 particle diameter percentage values for each measured grain-size laser class). Each cluster is defined by a prototype and includes the samples with a closer distribution to its prototype [Hastie et al. 2001; Davis, 2002]. The maximum-dissimilarity algorithm (MDA) is applied to initiate the prototypes, which guarantees a deterministic classification and the most representative initial subset. The MDA algorithm, which was first described by Kennard and Stone, 1969, permits many variants. In this work, the initial data of the subset is considered to be the vector with the largest sum of dissimilarities relative to the others within the data sample. Once the number of clusters is established, the prototypes (centroids) are initialized, and on each iteration is identified the nearest data to each centroid. Then, the centroid is redefined as the mean of the corresponding data, minimizing the overall within-cluster distance until the iterative reinterpretation of data converges on a single solution, and the data assigned to each group remain constant. A matrix of similarities between the  $n$  clusters and  $N$  observations is calculated, and the closest observation is represented by the nearest cluster. So, *k-means* technique helps us to group the samples into clusters according to their grain-size distribution.

#### 2.1.4. Assessment and discussion

##### 2.1.4.1. Optimization of the organic matter removal procedure

Some of the samples analyzed contained up to 3% total organic content (TOC) [Mix et

al., 2003] (Fig. 2.2c). The observation of the smear slides under the microscope after the treatment with the original procedure showed the presence of brownish particles whose origin was difficult to assert by light microscope observation (Fig. 2.2d). The processed samples were sieved at 63  $\mu\text{m}$  to isolate the coarser fraction and observed under binocular microscope. This confirmed the presence of brown rounded aggregates that were identified as faecal pellets, indicating that the used protocol was not efficient enough to eliminate the organic matter associated to these biogenic aggregates.



**Fig. 2.2.** Efficiency of organic matter removal step. (a) Granulometric distribution from four samples (colored lines) after removal of the organic matter with the standard protocol compared with un-treated sample (shaded area). Vertical grey bar indicates the size distribution (300 – 800  $\mu\text{m}$ ) of faecal pellets. (b) Granulometric distribution of four different samples (colored lines) after removal of the organic matter with the improved procedure proposed that is here compared with un-treated sample (shaded area). Note the disappearance of the terminal mode (300 – 800  $\mu\text{m}$ ). (c) Microscope picture of an untreated sample containing abundant brownish areas often associated to aggregates enriched in organic matter. (d) Microscope picture of a sample after the organic matter removal according to the standard protocol, note the persistence of some brownish areas. (e) Microscope picture of a sample after the organic matter removal according to the modified procedure, note the absence of brownish areas.

Organic matter procedure was then modified increasing the concentration of the hydrogen peroxide solution to 10%. Then, samples were placed in an oven (60 °C) for two days, after additional 50 ml of 10 % hydrogen peroxide were added to replace the evaporated solution. This attack was repeated one more time or even twice, depending of organic matter content of the sample. Continuous monitoring of the samples through smear slides (Fig. 2.2e) and optical microscope (fraction coarser than 63 µm) during each step of the new procedure, confirmed a satisfactory removal of faecal pellets. The comparison of the grain size distribution from un-treated samples and samples processed by the two different protocols (Fig. 2.2. a and b) reveals that the faecal pellets present a dominant mode between 300-500 µm. This mode is present in non-treated samples and in those treated with the standard protocol but it disappears in samples treated by our improved protocol. These observations further prove the efficiency of the new used protocol to remove the organic matter from the marine sediments. Furthermore, analyses of the organic matter content after the application of the new procedure have confirmed that its elimination is greater than 80%. The removal of this biogenic coarse fraction is essential in any grain-size study focused on the lithogenic fraction in order to properly interpret the results.

#### 2.1.4.2. Assessing the carbonate and Fe-Mn oxides removal procedure

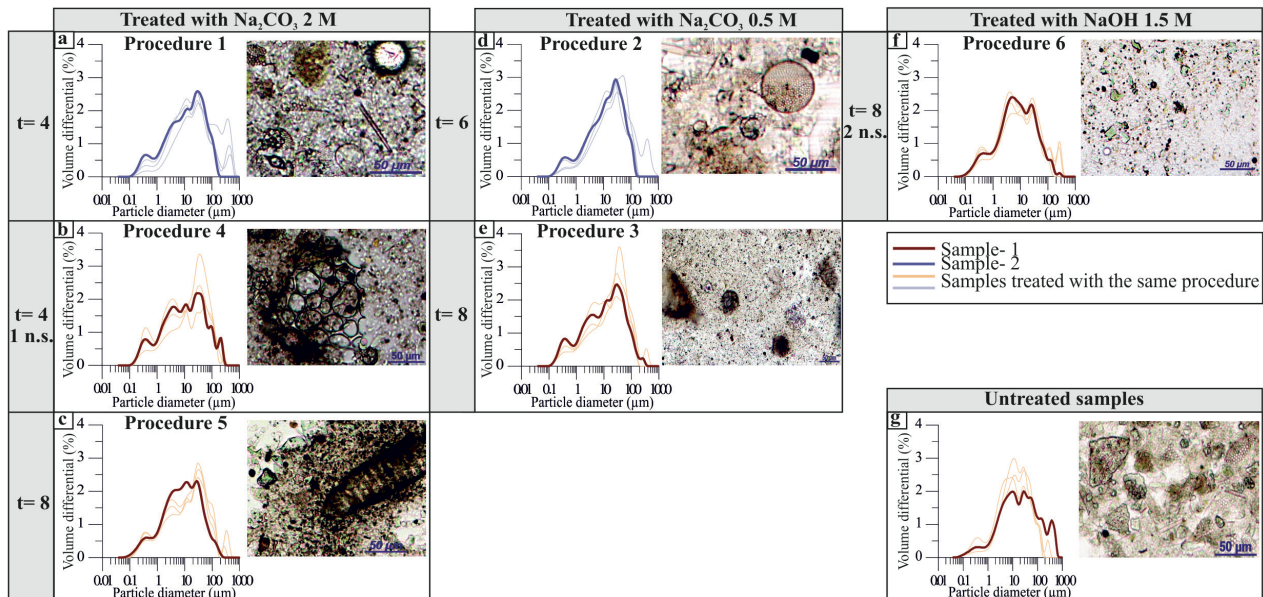
The carbonate component and Fe-Mn oxides were removed adding an acetic acid- sodium acetate solution and hydroxylamine hydrochloride solution, following the standard procedure. After that, each removal step was evaluated by microscope observation of the smear slides, showing the good efficiency of the standard procedure.

#### 2.1.4.3. Optimization of the biogenic silica removal procedure

The biogenic silica component represents a significant fraction of the entire sample, concretely between 5 and 15 % (see section 2.2), and it consists on diatoms and radiolarian remains (Fig. 2.3g). After using the standard protocol, microscope observation of the smear slides revealed the still abundant presence of radiolarian and diatoms remains (Fig. 2.3a). These observations were further confirmed by the visual binocular inspection of the fraction over 63 µm. Consequently, a sequence of further steps was applied in order to increase the removal of biogenic silica without removing lithogenic silica. Six different protocols were tested changing two main variables: (1) the reagent and its concentration and (2) the time and number of extractions (Table 2.1). Both variables were increased progressively in order to ensure the biogenic silica removal but trying to minimize the impact

| Procedure | Reagent                         | Concentration | Time in solution (hours) | Nights in stove (60 °C) | Nights in solution | N° extractions | Effectiveness of treatment |
|-----------|---------------------------------|---------------|--------------------------|-------------------------|--------------------|----------------|----------------------------|
| 1         | Na <sub>2</sub> CO <sub>3</sub> | 2 M           | 4                        | 0                       | 0                  | 2              | no                         |
| 2         | Na <sub>2</sub> CO <sub>3</sub> | 0,5 M         | 6                        | 0                       | 0                  | 3              | no                         |
| 3         | Na <sub>2</sub> CO <sub>3</sub> | 0,5 M         | 8                        | 0                       | 0                  | 4              | no                         |
| 4         | Na <sub>2</sub> CO <sub>3</sub> | 2 M           | 4                        | 0                       | 1                  | 2              | no                         |
| 5         | Na <sub>2</sub> CO <sub>3</sub> | 2 M           | 8                        | 0                       | 1                  | 4              | no                         |
| 6         | NaOH                            | 1,5 M         | 8                        | 2                       | 2                  | 4              | yes                        |

**Tab. 2.1.** Different procedures tested in the biogenic silica removal step. Note that the Na<sub>2</sub>CO<sub>3</sub> was tested with different concentrations and timing. In contrast, when the reagent was changed there was a drastic elimination of biogenic silica as shown in Fig. 2.3f (procedure 6).

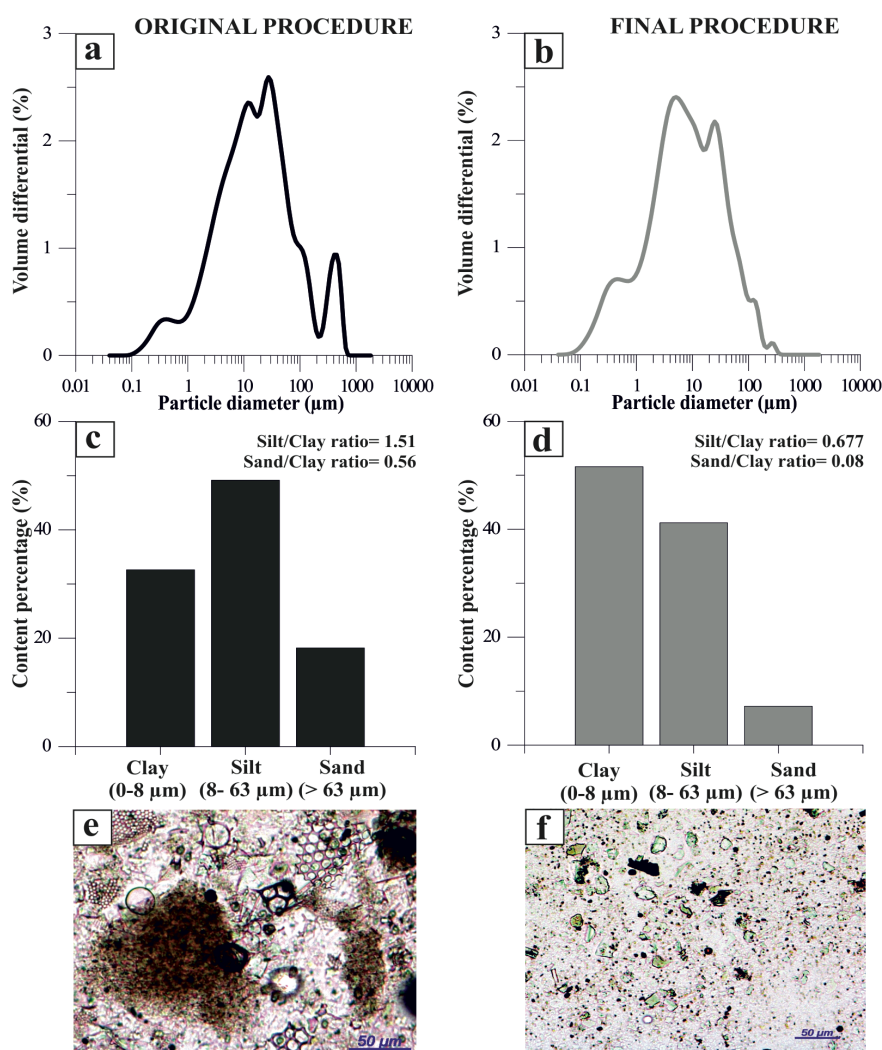


**Fig. 2.3.** Grain size distribution and smear slides pictures after each of the procedures applied for biogenic silica removal. Reagent and concentration are indicated in the upper part of each column and, on the left, it is indicated the number of hours in solution (t) and the number of nights in the oven (n.s.). Note that from (a) to (e) pictures show the presence of biogenic silica remains (diatoms and radiolarian), and grain size distributions show a dominant mode over 10 microns. (f) Correspond to the protocol chosen for the final procedure. The picture shows the only presence of lithic grains and the dominant mode is centered below 10 microns. (g) Grain distribution and picture of a non-treated sample as a reference. Detailed information for each procedures is indicated in Table 2.1.

on silicate leaching. The effectiveness and control of silicate leaching at each step was evaluated through the microscope observation of the processed samples (Fig. 2.3). These observations revealed that the silica microfossils persisted after most protocols with the single exception of protocol 6 (Table 2.1 and Fig. 2.3f). These experiments show that the most efficient reagent for the elimination of the biogenic silica is the NaOH, without the



lithic silica removal. Results of grain size distribution (Fig. 2.3) show that the main mode in protocol 6 (Fig. 2.3) is centered on 3-4 microns, while in the other protocols it is displaced towards larger particles (above 10 microns). These results also indicate that particles above 20 microns are severely reduced in the case of protocol 6 (Fig. 2.3). These different features in the grain size distribution have a large impact in the standard parameters such as Silt/Clay or Sand/Clay, among others, that are often used for paleoceanographic studies (Fig. 2.4).



**Fig. 2.4.** Comparison of the results obtained in Sample 1 after treatment with the standard procedure (a, c, d) and after treatment with the improved procedure (b, d, f) (a, b) Grain size distribution; (c, d) Percentages of clay (laser), silt and sand, expressed in laser size classes; (e, f) Smear slides pictures, where efficient removal of biogenic remains can be observed in (f). Note the disappearance of the coarser mode (300 – 800 µm), and the switch of the median towards finer grain sizes, around 3-4 microns, increasing the percentage of clay fraction.

Samples treated by protocol 1 (Fig. 2.4a, c and e) are dominated by the silt fraction while those treated with protocol 6 (Fig. 2.4b, d and f) are dominated by clay and the sand fraction is severely reduced. Therefore, the most appropriate protocol to remove the biogenic silica is using NaOH 1.5 M solution. The addition of NaOH instead of  $\text{Na}_2\text{CO}_3$  has proven to produce a drastic reduction in the number of diatoms and radiolarian, being thus much more effective than previous standard protocol (Fig. 2.3 and Fig. 2.4).

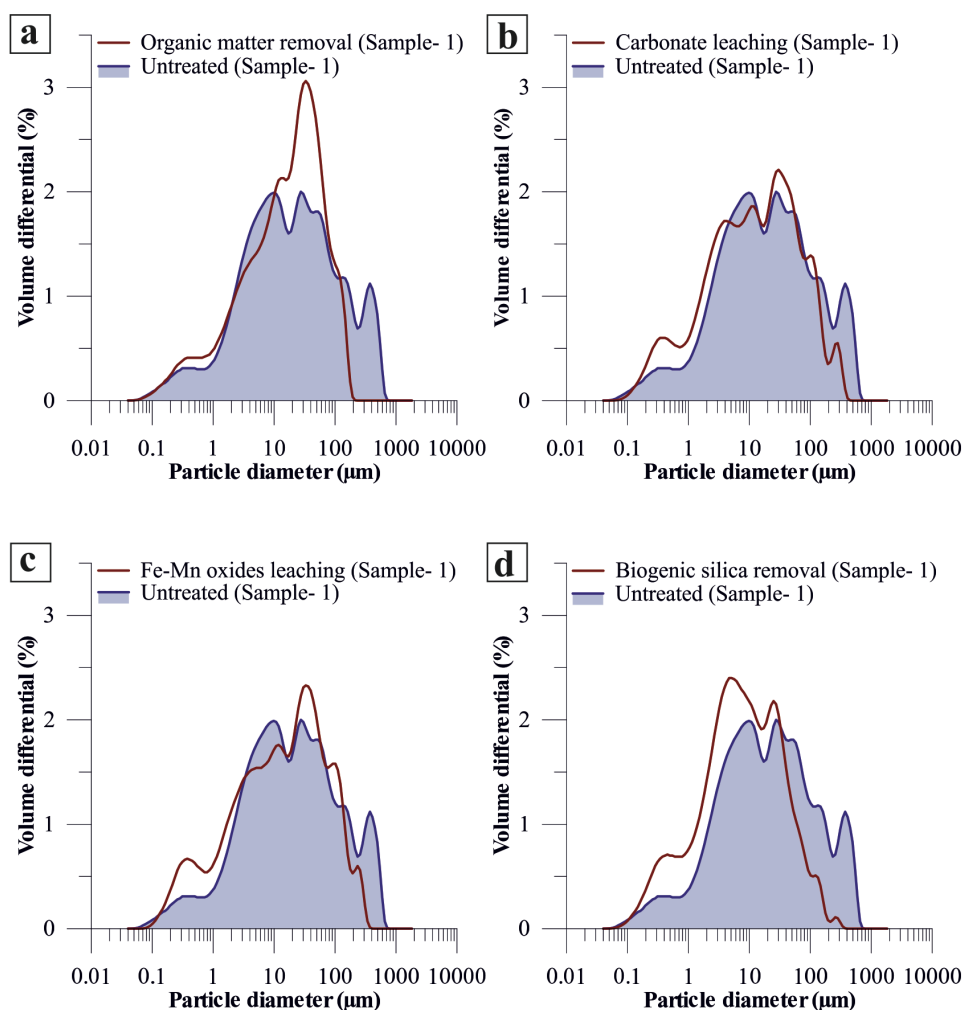
#### 2.1.4.4. Final Procedure

The improved procedure described below includes all modifications suggested to the standard procedure to be used in samples with a high biogenic content (Table 2.2).

Figure 2.5 illustrates the effect of each step in the grain size distribution. In general the biogenic component removal takes out most of the coarse particles corresponding to zooplankton remains, foraminifera and radiolarian as well as faecal pellets. Although the fine silt fraction is also removed corresponding to nanofossils and some small diatoms. This procedure consists of four removal steps, concretely of the organic matter, carbonate bioclasts, Fe-Mn oxides and biogenic silica fractions, described in Table 2.2.

| ORGANIC MATTER                               | CARBONATE COMPONENT  | Fe-Mn OXIDES   | BIOGENIC SILICA   |
|--|--|--|---|
| 50 ml<br>10 % $\text{H}_2\text{O}_2$<br>pH=3 | 35 ml<br>Solution of 2.7 % $\text{CH}_3\text{COOH}$ (27 ml)<br>+ 0.34 M $\text{CH}_3\text{COONa}$ (28 gr) pH=4 | 45 ml<br>HH solution of 25% $\text{CH}_3\text{COOH}$ (250 ml)<br>+ 0.02 M $(\text{NH}_3\text{OH})\text{Cl}$ (1.3893 gr) pH=2 | 35 ml<br>1.5 M NaOH (60 gr)<br>pH= 13                       |
| ↓  | ↓  | ↓  | ↓   |
| Shake the samples                            | Shake the samples for five hours   | Shake the samples for two hours  | Shake and sonicate the samples for 10 minutes               |
| ↓  | ↓  | ↓  | ↓   |
| Left for 2 days                              | Centrifuge the samples for 15 min<br>to remove the solution  | Centrifuge the samples for 15 min<br>to remove the solution  | Remain the solution overnight in an oven (60°C)             |
| ↓  | ↓  | ↓  | ↓   |
| Dry in an oven (60°C)                        | Repeat the extraction,<br>shaking the samples overnight.   | Repeat the extraction,<br>shaking the samples overnight.   | Place the samples in a hot bath for 2 hours (85 °C)         |
|  | ↓  | ↓  | ↓   |
|  | Samples washing with MilliQ water  | Samples washing with MilliQ water<br>two times   | Centrifuge the samples for 15 min<br>to remove the solution |
|  | ↓  | ↓  | ↓   |
|  | Centrifuge samples for 15 min<br>to remove the solution  | Centrifuge samples for 15 min<br>to remove the solution  | Repeat the extraction for 2 hours (85°C)                    |
|  |  |  | ↓   |
|  |  |  | Leave the sample rack in the oven overnight (60°C)          |
|  |  |  | ↓   |
|  |  |  | Centrifuge the samples for 15 min<br>to remove the solution |
|  |  |  | ↓   |
|  |  |  | Repeat two extractions for 2 hours each one (85°C)          |
|  |  |  | ↓   |
|  |  |  | Samples washing with MilliQ water<br>two times              |

**Tab. 2.2.** Description of the improved procedure.

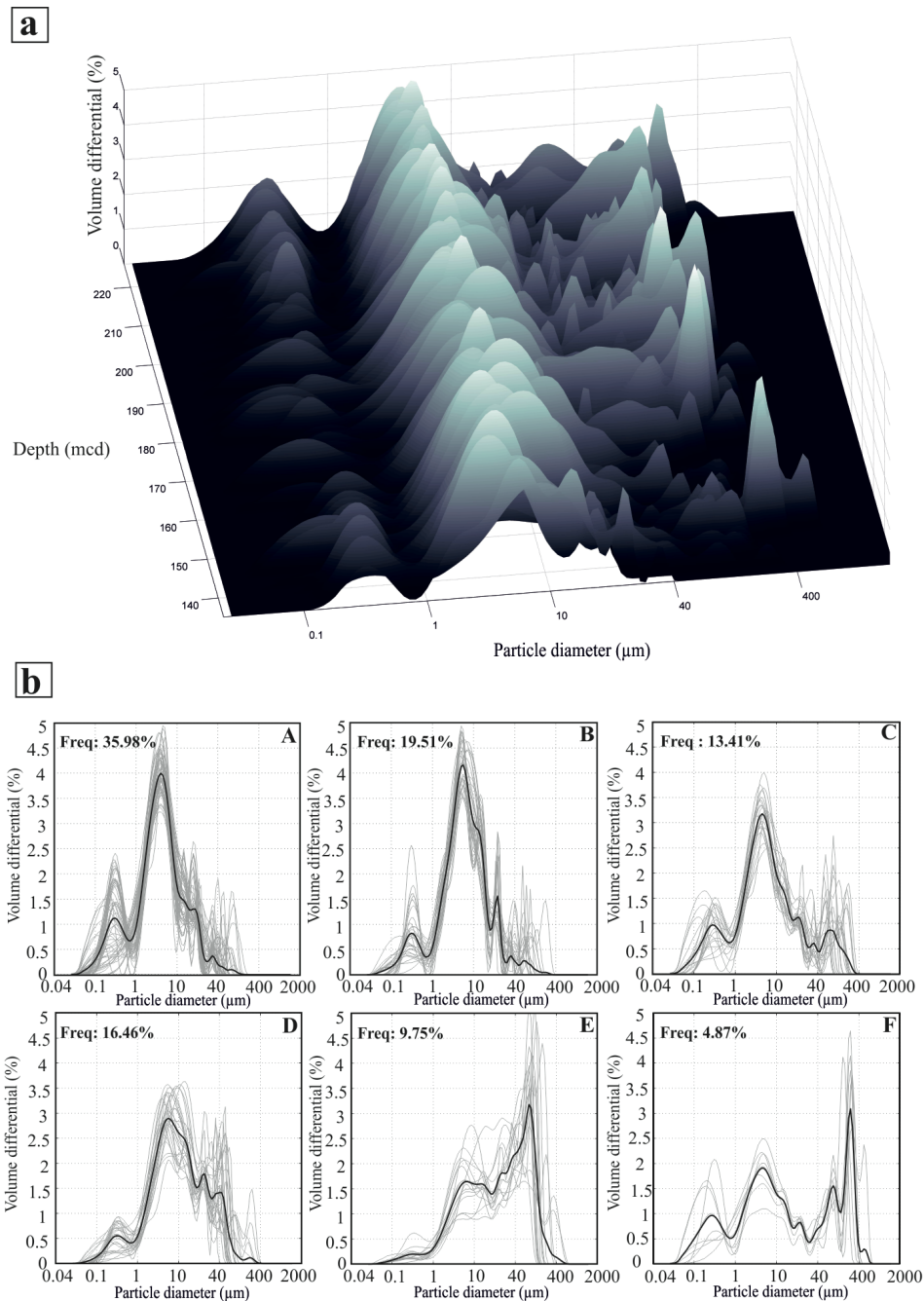


**Fig. 2.5.** Grain size distribution of sample-1 after each extraction step following the improved procedure (line) compared with a non-treated sample-1 (shaded area). (a) Organic matter removal step; (b) Carbonate leaching step; (c) Fe-Mn oxides leaching step; (d) Biogenic silica removal step. Note the gradual reduction of the larger grain sizes, between 150- 800  $\mu\text{m}$ .

#### 2.1.4.5. Grain size distributions and clustering analysis

Grain-size distributions of the analyzed samples through ODP 1240 core depth are shown in Fig. 2.6 (a). The grain-size distribution follows a clear pattern dominated by a mode around 4  $\mu\text{m}$ . Two marginal modes are also discernible: fine mode around 0.7  $\mu\text{m}$  and some random modes on the coarser tail of the distribution. Nonetheless, the grain-size distributions present strong variability. Often these grain size results are expressed as different ratios such as Silt/Clay ratio [Hall and McCave, 2000], Sortable Silt [McCave et al., 1995] or UP10 [Frigola et al., 2007]. These basic representation of the data can reflect the coarser or finer character of the samples, but they do not reflect the modal distribution of the sample or the number of families present in the samples and thus, very valuable information that is still present in the measurements may be missed. Some statistical approaches explored additional information in terms of compositional characterization





**Fig. 2.6.** (a) 3-D plot of grain size distributions of the studied period. The volume differential is expressed in percentage, particle diameter is expressed in  $\mu\text{m}$ , and depth is expressed as composite depth. (b) Clusters defined by *k-means* technique (A- F); particle diameter is expressed in  $\mu\text{m}$  and volume differential is expressed in percentage. Note that the frequency of each cluster is also expressed.

(the so-called “end member modeling”) [Weltje, 1997]. The approach used here divides the samples into a number of clusters according to their grain size distribution similitude. Thus, this method gives us the more representative groups that characterize this high variability and helps to interpret the mechanisms responsible of their transport to the deep sea. In this case, the grain size dataset is composed by a matrix with 19024 values (164 samples for several core depths, expressed in mcd, and 116 size laser classes of particle diameter, expressed in  $\mu\text{m}$ ). After testing with several  $n$  clusters, it is concluded that the

dataset is better characterized using  $n=6$  clusters, as shown in Fig. 2.6 (b). These clusters present distinctive features and have been named as clusters A, B, C, D, E and F. Cluster A is the dominant pattern (36% of the samples) and shows a clear mode around 4  $\mu\text{m}$ . Clusters B (19.51%) and C (13.41%) show certain similarities with cluster A but cluster B has higher percentage of particles in the dominant mode, and cluster C shows a principal mode less abundant and a coarser terminal mode than Clusters A and B. Cluster D (16.46%) shows a distinctive pattern with a coarser principal mode, and higher percentages around 40  $\mu\text{m}$ . Clusters E and F are less frequent but show a pattern totally different with respect to the rest of clusters since coarser sediments become more abundant. The main mode of cluster E (9.76%) is located around 250  $\mu\text{m}$ , while cluster F (4.88%) presents a main mode well classified around 400  $\mu\text{m}$  and the 4  $\mu\text{m}$  mode is more defined than in cluster E.

Cluster analysis brings the opportunity to objectively separate the samples in different families providing very useful information for the interpretation of the processes responsible for the lithic fraction arrival such as eolian and fluvial transport. In this way, this statistical approach offers a powerful tool to further understand past atmospheric changes in wind and/or rain dynamics.

### 2.1.5. Conclusions

This experiment proves that the standard procedures applied to the biogenic removal are too weak in sediments of high productivity areas. These areas required the application of a more aggressive procedure than those normally applied in other studied areas. The final procedure has increased the time and the concentration of the reagents in different steps with respect to previous procedures. Particularly difficult was the biogenic silica removal due to the high content of radiolarians and diatoms remains. In this case  $\text{Na}_2\text{CO}_3$  2M, normally used in other works, was insufficient. NaOH digestions show, instead, a complete biogenic silica removal, without removing the lithogenic silica content.

The continuous monitoring of the grain size distribution after each experimental step reveals that inappropriate procedures for the elimination of the biogenic fraction can induce large biases in the grain size parameters broadly used in paleoceanographic studies.

After obtaining the particle size distributions, *K-means* algorithm has been used to analyze the large grain size data set and characterize sample clusters with distinctive patterns.

### 2.1.6. Comments and recommendations

Our new procedure points to the importance of an accurate protocol to obtain optimal results that allow a careful analysis of the lithogenic particle size distribution in marine sediments from high-productive areas. This method avoids the overestimation of coarser lithic particles due to biogenic artifacts, which is crucial in paleoclimatic reconstructions, such as eolian and fluvial system inputs. This new method can also be useful to separate the lithic fraction and Fe-Mn oxide fraction in studies with radiogenic isotopes.

This procedure can be also used in areas with less productivity, such as the Mediterranean Sea, where, the biogenic silica content represents less than 4% [Rumín-Caparro et al., 2013]. In this case it is recommended to do a few modifications mainly focused on biogenic silica step and in this case it would be enough to apply the method created by Mortlock and Froelick (1989).

The extraction timing control is crucial in the biogenic removal stage to avoid the siliciclastic fraction removal. The cleaning of the samples with MilliQ water in order to remove the remaining NaOH solution is recommended in order to avoid potential damages of grain size analyzer instrumentation.

It is recommended to start the analysis of a specific area testing the effectiveness of each removal stage by monitoring the sample after each step through smear slide microscope observations.

### 2.1.7. Acknowledgments

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## 2.2. ATMOSPHERE-OCEAN LINKAGES IN THE EASTERN EQUATORIAL PACIFIC OVER THE EARLY PLEISTOCENE

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### 2.2.1. Abstract

Here we present a new set of high-resolution early Pleistocene records from the eastern equatorial Pacific (EEP). Sediment composition from Ocean Drilling Program Sites 1240 and 1238 is used to reconstruct past changes in the atmosphere-ocean system. Particularly remarkable is the presence of laminated diatom oozes (LDOs) during glacial periods between 1.85 and 2.25 Ma coinciding with high fluxes of opal and total organic carbon. Relatively low lithic particles (coarse and poorly sorted) and iron fluxes during these glacial periods indicate that the increased diatom productivity did not result from dust-stimulated fertilization events. We argue that glacial fertilization occurred through the advection of nutrient-rich waters from the Southern Ocean. In contrast, glacial periods after 1.85 Ma are characterized by enhanced dust transport of finer lithic particles acting as a new source of nutrients in the EEP. The benthic ecosystem shows dissimilar responses to the high productivity recorded during glacial periods before and after 1.85 Ma, which suggests that the transport processes delivering organic matter to the deep sea also changed. Different depositional processes are interpreted to be the result of two distinct glacial positions of the Intertropical Convergence Zone (ITCZ). Before 1.85 Ma, the ITCZ was above the equator, with weak local winds and enhanced wet deposition of dust. After 1.85 Ma, the glacial ITCZ was displaced northward, thus bringing stronger winds and stimulating upwelling in the EEP. The glacial period at 1.65 Ma with the most intense LDOs supports a rapid southward migration of the ITCZ comparable to those glacial periods before 1.85 Ma.

### 2.2.2. Introduction

The Early Pleistocene climate evolution is marked by the progressive strengthening of the Northern Hemisphere glaciation (NHG), and it has been argued that this situation strengthened trade winds, inducing a cooling in tropical sea surface temperatures (SSTs) by enhanced upwelling activity [Marlow et al., 2000]. Meanwhile, land records indicate an enhanced aridity along the tropical belt with consequences on African faunal evolution [deMenocal, 1995, 2004; Feakins et al., 2005; Trauth et al., 2007]. The obliquity imprint upon tropical proxy records further supports the high-latitude control over tropical regions during this period [Liu and Herbert, 2004; Herbert et al., 2010].

The eastern equatorial Pacific (EEP) is known by its highly productive upwelling system, which has operated with varying intensity across glacial-interglacial cycles [Lyle et al., 1988; Weber and Pisias, 1999; Murray et al., 2000]. During the early Pleistocene, 400 kyr eccentricity cycles seem to have ultimately controlled major changes of SST in the EEP, with abrupt and intense cooling events at 1.7 and 2.1 Ma [Herbert et al., 2010].

Nevertheless, several records from the EEP reveal a rather complex link between SST and primary productivity across the Pleistocene [Lawrence et al., 2006; Dekens et al., 2007; Ma et al., 2015]. In particular, a remarkable period of enhanced EEP primary productivity between 1.6 and 2.9 Ma was reflected in unusually high-alkenone concentrations [Lawrence et al., 2006] without any clear expression of colder SST. Such signal decoupling has been attributed to EEP fertilization due to an increase in nutrient availability finally driven by changes in nutrient utilization in the Southern Ocean [Lawrence et al., 2006; Etourneau et al., 2013]. Nitrogen isotopes support a sharp increase in EEP denitrification but starting later, after 2.1Ma, which is attributed to an enhanced upwelling activity due to strengthened Walker circulation [Liu et al., 2008]. This situation is consistent with a major atmospheric reorganization including an intensification of the Walker circulation and the onset of a strong equatorial west-east gradient at 1.5–2 Ma, as indicated by SST and isotopic records from both western equatorial Pacific (WEP) and EEP [Ravelo et al., 2004, 2014; Wara et al., 2005; Etourneau et al., 2010]. This time period also appears to be critical in Southern Atlantic Ocean where a reinforcement of trade winds and the strengthening of the associated upwelling have been noticed [Etourneau et al., 2009].

Nevertheless, this atmospheric reorganization has been questioned by new long multi-proxy records that suggest a relatively constant E-W equatorial Pacific SST gradient since the Pliocene and, consequently, an essentially rather constant and continuously active EEP upwelling system [O'Brien et al., 2014; Zhang et al., 2014]. The debate is far from being settled [Ravelo et al., 2004, 2014; Wara et al., 2005].

Thus, several records support the occurrence of EEP productivity and atmospheric changes during the early Pleistocene, but their occurrence is not always apparently synchronous and their coupling is still puzzling. The lithic fraction of deep-sea sediments is a proxy that could shed light on atmospheric changes in the EEP. It has been used to track the location of the Intertropical Convergence Zone (ITCZ), which would have migrated southward from the late Miocene to present [Hovan, 1995; Hyeong et al., 2006]. Unfortunately, these studies lack the temporal resolution to evaluate rapid changes that might have occurred during the early Pleistocene. Short-term reconstructions of changes in the average ITCZ location have concentrated on glacial-interglacial cycles of the late Pleistocene and Holocene and are mostly based on SST marine records, humidity terrestrial records, or model assimilations [Koutavas and Lynch-Stieglitz, 2004; Broccoli et al., 2006; Peterson and Haug, 2006; McGee et al., 2014; Schneider et al., 2014].

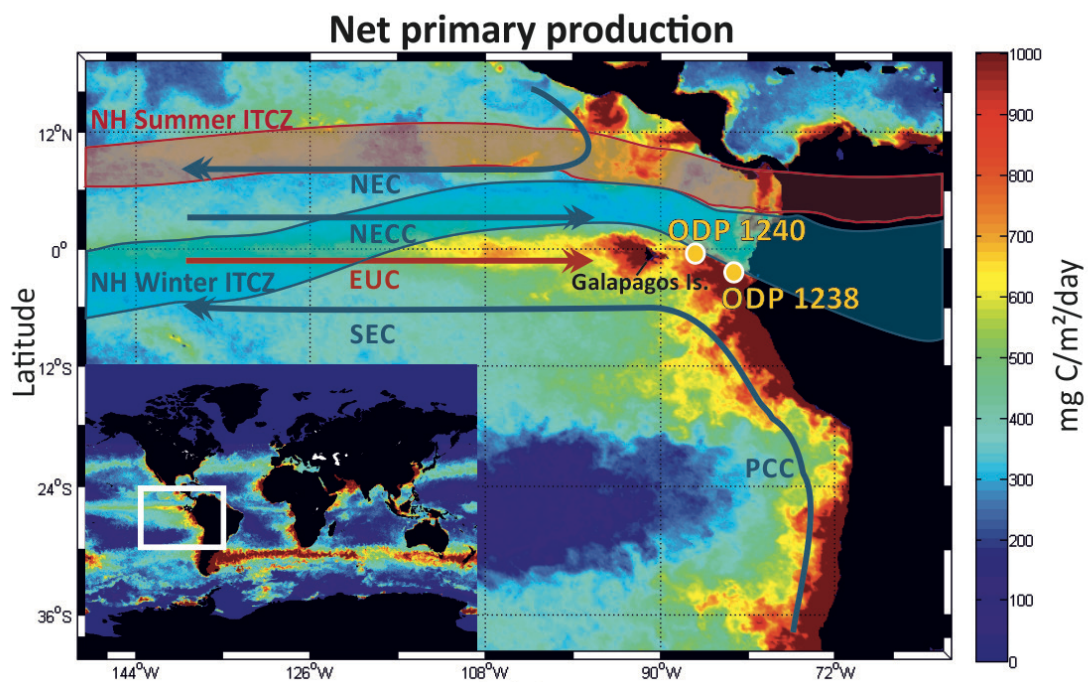
Elucidating the link between any early Pleistocene atmospheric reorganization and productivity changes in the EEP upwelling requires using parallel records of proxies sensitive to both atmospheric and marine conditions. In this paper we present a novel very high resolution multiproxy study over the 1.56–2.26 Ma time interval in the EEP, resulting from the detailed analysis of biogenic and lithogenic components in deep-sea sediments. The study focuses on Ocean Drilling Program (ODP) Site 1240, located at the northern edge of the equatorial cold water tongue (Fig. 2.7) and thus, made this site potentially sensitive to changes in the atmospheric-ocean coupled system [Hovan, 1995; Mix et al., 2003]. Previous results for this ODP site have shown major changes in the sediment composition occurring along the early Pleistocene, which were linked to shifts in the regional atmosphere-ocean system [Mix et al., 2003]. Moreover, ODP 1240 contains sequences of laminated diatom oozes (LDOs), which become a valuable paleoproductivity indicator. In order to ground truth our results and achieve a broader evaluate the geographical extension, the data obtained from ODP 1240 have been compared with data from ODP 1238, located further south and closer to the South American coastline.

Thus, this study offers an exceptional time resolution for the early Pleistocene and demonstrates that the observed changes occurred as rapid transitions related to glacial-interglacial cycles, rather than as progressive long-term change.

### 2.2.3. Oceanographic and Atmospheric Setting

The EEP is one of the most productive upwelling areas in the world controlled by the trade wind systems [Chelton et al., 2001]. This atmospheric convergence near the equator and the ascending branch of the Hadley cell define the position of the ITCZ and control the surface

ocean properties [Koutavas and Lynch-Stieglitz, 2004]. Surface ocean circulation in the EEP is characterized by the north-south asymmetry of the surface currents, as a consequence of the trade winds intensity [Wyrтки, 1974]. ODP Sites 1240 and ODP 1238 locations are both influenced by the South Equatorial Current (SEC), which is the continuation of the Peru-Chile Current (PCC), centered at about 5°S under the southeast trade winds [Wyrтки, 1967; Kessler, 2006]. During the Southern Hemisphere winter, when SE trade winds are strengthened, the SEC is more intense [Wyrтки, 1967]. In the subsurface, the Equatorial Undercurrent (EUC) flows eastward along the equator, and replaces surface water driven westward by the trades [Kessler, 2006], providing nutrients to the EEP that are sourced in the polar regions, mainly from the Southern Ocean [Sarmiento et al., 2004; Calvo et al., 2011; Pena et al., 2013] (Fig. 2.7). Recent studies suggest that Galapagos Islands could influence the flow of EUC east of 95°W, acting as a topographic barrier, although its influence has not been fully characterized yet [Karnauskas et al., 2007, 2010].



**Fig. 2.7.** Regional oceanography and net primary production (NPP) from the Eastern Equatorial Pacific (EEP). Surface and subsurface currents in the EEP; Equatorial Undercurrent (EUC), North Equatorial Current (NEC), North Equatorial Countercurrent (NECC), Peru-Chile Current (PCC) and South Equatorial Current (SEC). NPP in the surface waters of modern EEP is based on the standard v<sub>gpm</sub> algorithm [Behrenfeld and Falkowski, 1997a]. Data was downloaded from the Ocean Productivity site. Northern Hemisphere summer and winter position of the ITCZ have been marked with blue and red bands. ODP Sites 1240 and 1238 are labeled with yellow dots.

The strong southeasterly winds that cross the equator induce an Ekman divergence zone, which allows the upwelling of nutrient-rich and cold waters from the EUC, particularly during the Southern Hemisphere winter (Fig. 2.7) [Wyrtki, 1981]. The extent of the cold tongue created by the upwelling is limited by the equatorial front (EF), the position of which varies seasonally. The EF reaches its most northerly position during the Northern Hemisphere summer [Pak and Zaneveld, 1974; De Szoeko et al., 2007]. In the modern EEP, biological activity does not consume all the macronutrients upwelled to the surface due to limitations in the supply of iron and silicic acid [Brzezinski et al., 2008]. Iron is a micronutrient that limits macronutrient utilization, and thus, it can ultimately control the primary production of the upwelling system [Jickells et al., 2005; Mahowald et al., 2005]. Since the EUC is typically iron depleted by the time it reaches the EEP [Kaupp et al., 2011], the main iron contribution occurs through eolian dust deposition. This induces a strong connection between dust fluxes, iron input, and primary productivity in the EEP [Martin, 1990; Jickells et al., 2005].

At present, the mean ITCZ position is shifted toward the Northern Hemisphere as a consequence of a northward heat transport across the equator by ocean circulation [Marshall et al., 2014]. ITCZ migrations can also be the result of changes in the interhemispheric temperature contrast [Broccoli et al., 2006], responding to seasonal changes in insolation and atmosphere-ocean interactions [Xie and Philander, 1994]. During Northern Hemisphere summer, when the southeasterly trades are stronger [Chelton et al., 2001; Koutavas and Lynch-Stieglitz, 2004], the ITCZ is positioned at about 10°N and both maximum upwelling and significant eolian deposition of dust from South America occur in the EEP [Molina-Cruz, 1977]. The ITCZ migrates southward when the southeasterly trades are weaker [Chelton et al., 2001], between February and April, reducing the dust input and weakening upwelling. Paleoclimate records and numerical models suggest that the southward migration may have been greater during colder phases of the Northern Hemisphere on a variety of time scales, such as the Little Ice Age (LIA), shifting the ITCZ well south of its most southern present position [Koutavas and Lynch-Stieglitz, 2004; Chiang and Bitz, 2005; Broccoli et al., 2006; Sachs et al., 2009].

#### 2.2.4. Materials and Methods

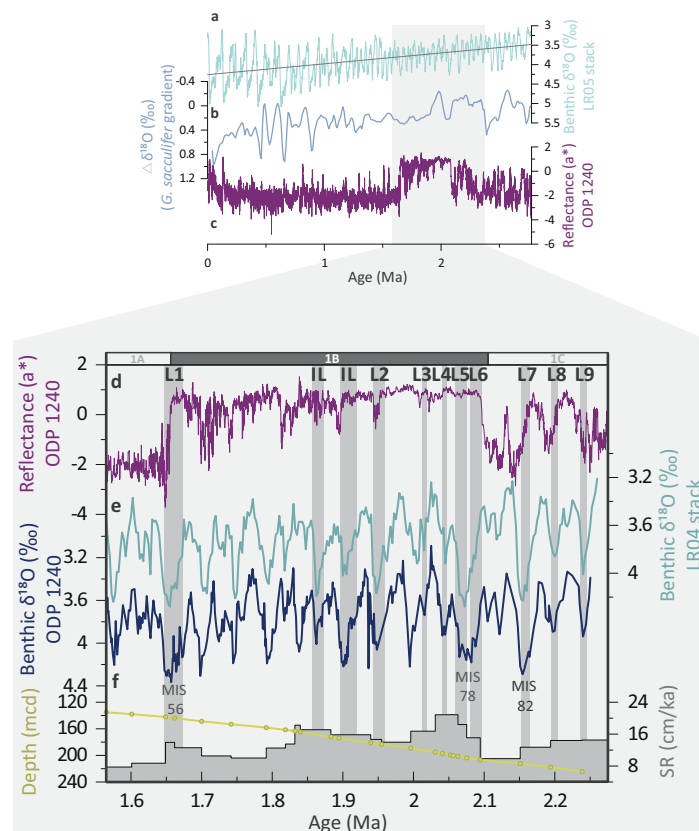
ODP Site 1240 (0°01.31' N, 86° 27.76' W; 2921m water depth) and ODP Site 1238 (1°52.310' S, 82°46.934' W; 2203m water depth) were retrieved in the EEP, from the northern and southern flank of the Carnegie Ridge, respectively, in the Panama Basin during the ODP Leg 202, by JOIDES Resolution in 2002 (Fig. 2.7) [Mix et al., 2003].

The recovered sedimentary sequence of ODP 1240 is a fossil-rich mud with variable



composition [Mix et al., 2003]. Three subunits (1A, 1B, and 1C) were defined according to their dominant sedimentological characteristics [Mix et al., 2003]. In this work we focus on subunit 1B, in the depth interval from 135.34 to 225.94 meters composite depth (mcd), between 1.65 and 2.1 Ma, which presents higher reflectance ( $a^*$ ) values (Fig. 2.8). It was initially proposed to reflect an intensification of atmospheric circulation, based on the preliminary results of grain density, biogenic silica, total organic carbon (TOC) content, and the shipboard stratigraphic description presented in Mix et al. [2003]. Eleven LDOs were described mainly within subunit 1B (1.65–2.2 Ma) [Mix et al., 2003] (see section 2.2.6.1). They are composed largely of pennate diatoms, such as *Thalassiothrix spp.*, that tend to form large grids of strongly intertwined cells.

The sedimentary sequence from ODP 1238 is mostly formed by diatom nannofossil ooze and bioturbated nannofossil oozes with a variable abundance of clay and foraminifera [Mix et al., 2003]. The analyzed sequence is centered from 79 to 99 mcd, in interval of 1.6–1.75Ma.



**Fig. 2.8.** Chronological framework for ODP 1240. (a) Global benthic  $\delta^{18}O$  stack (LR04 stack) [Lisiecki and Raymo, 2005], (b) Oxygen isotope difference (*G. sacculifer*) between ODP 851 (Eastern Pacific) [Cannariato et al., 1997] and ODP 806 (Western Pacific) [Berger et al., 1993; Jansen et al., 1993], (c) ODP 1240 reflectance ( $a^*$ ) for the last 2.7 Ma [Blum et al., 2005], shows abrupt variations in sediment composition for the studied interval, (d) ODP 1240 reflectance ( $a^*$ ) for the studied period [Blum et al., 2005], showing three subunits clearly marked and represented as a white and grey bar (1A, 1B and 1C), (e) Age model from ODP 1240, developed by comparison of high resolution ODP 1240 benthic  $\delta^{18}O$  and global benthic  $\delta^{18}O$  stack, (f) Tie points and linear sedimentation rates from ODP 1240 for the studied interval. Grey shaded vertical bars indicate the position of the observed and the interpreted LDOs, labeled as L1-L9 and IL, respectively. Marine Isotopic Stages (MIS) 56, 78 and 82 are also shown.

#### 2.2.4.1. Oxygen Isotope Record

In order to establish robust chronology, we measured benthic foraminifer  $\delta^{18}\text{O}$  from ODP 1240, which was based in the analysis of two different species of benthic foraminifera, *Uvigerina spp.* and *Cibicidoides wuellerstorfi*. Each measurement of *Uvigerina spp.* was made on eight to ten individuals. Measurements of *C. wuellerstorfi* were performed on four to five individuals ( $>212\ \mu\text{m}$ ). Samples were crushed to open the foraminiferal chambers and then cleaned with reagent grade methanol in order to remove attached clay particles. All measurements were made with a Finnigan-MAT252 mass spectrometer fitted with a Kiel Carbonate Device I in the Scientific and Technological Center of the University of Barcelona (CCiT-UB). Values are reported as per mille with respect to the Vienna Peedee belemnite standard. For the duration of the analyses, external reproducibility was always better than  $0.06\text{‰}$  for  $\delta^{18}\text{O}$ . In order to produce the composite  $^{18}\text{O}$  record, the *C. wuellerstorfi* results were corrected to the *Uvigerina spp.* scale by adding  $0.64\text{‰}$  [Shackleton and Hall, 1984].

#### 2.2.4.2. Biogenic Fraction: Total Organic Carbon, Nitrogen Content, Opal Content, and *Uvigerina spp.* abundance

EEP biogenic fractions (TOC, total nitrogen (TN), opal, and *Uvigerina spp.* abundance) were analyzed to monitor past changes in the ocean productivity system. TOC and total nitrogen (TN) content were analyzed at the CCiT-UB using an elemental organic analyzer Thermo EA Flash 1112. TOC was measured in 25% HCl-treated sediment samples [Fabres et al., 2002].

Biogenic silica concentrations were measured in 200 mg samples of bulk sediment. The extraction method is modified from Povea et al. [2015] and includes a two-step leaching with a 1.5M NaOH solution. Si concentration in both leachates was determined through inductively coupled plasma optic spectrometer (ICP-OES), using a Perkin Elmer model Optima 3200 RL at the CCiT-UB. Biogenic opal concentrations were determined from Si concentrations multiplying the obtained values by 2.4 [Mortlock and Froelich, 1989].

The main benthic foraminifera genera present in the samples were counted to identify any major change in the assemblage, which could be indicative of changes in the deep ocean nutrient content and oxygen concentration. The principal benthic foraminiferal assemblage is formed by *Giroydina spp.*, *Uvigerina spp.*, *Melonis spp.*, *Cibicides wuellerstorfi*, and *Cibicides kullenbergi* in order of abundance. After a preliminary low-resolution counting (107 samples with a 6.5 kyr average time resolution) considering these five genera, *Uvigerina spp.* was selected to generate high-resolution counts over the whole sequence because it showed the greatest variability.

### 2.2.4.3. XRF Core Scanner Measurements

XRF core scanner was used in order to achieve at high resolution the elemental composition of the EEP sediments. Sampling for XRF core scanner analyses was done at the Gulf Coast ODP repository at Texas. U-channels were collected by pushing rigid u-shaped plastic liners ( $2 \times 2$  cm cross section, 1.5m in length) into the core sections to collect narrow continuous samples of core. XRF core scanner analyses were done at the University of Bremen (Germany). The XRF analyzes the very top of the sediment surface over  $1\text{cm}^2$  area, using 30s count time, 20kV X-ray voltage, and an X-ray current of 0.087mA to obtain statistically significant Fe counts. A detailed description of the applied X-ray fluorescence analysis and the system configuration of the XRF core scanner at the University of Bremen are given in Jansen et al. (1998) and Röhl and Abrams, (2000). The resulting data represent element intensities in counts per second, and all the intensities are above the detection limits [Richter et al., 2006]. Intensity values were converted to concentrations through calibration with absolute elemental concentrations obtained from 30 sediment samples selected along this section (see section 2.2.6.5). Sediment samples were analyzed by ICP-OES at the CCiT-UB after total digestion of 50mg of dried bulk sediment material in a pressure digestion system with a mixture of 3mL  $\text{HNO}_3$  65%, 2mL HF 40%, and 2mL HCl 32%. After decomposition, the samples were heated to dryness, redissolved in 5mL of 6.5%  $\text{HNO}_3$ , and homogenized in the microwave. Fe element was analyzed by ICP-OES in a PerkinElmer Optima 3300 RL with a precision better than 2%. The accuracy of element determinations was checked using standard reference materials. The ICP-OES obtained values were used to transform the XRF data into concentration values (mg/g). Correlation equations with  $r^2 = 0.79$  indicate a high correlation between both methods, thus allowing the data conversion (Figure S2.1 in the supporting information).

### 2.2.4.4. Grain Size and Mineralogical Analyses

Grain size analysis and mineralogical description have been conducted to characterize the lithic fraction that reached the eastern equatorial Pacific. Prior to the grain size analysis, samples were processed with a protocol specifically designed to ensure the complete removal of all the biogenic (organic matter, carbonate, and biogenic silica) and authigenic components (diagenetic oxides), leaving only the lithogenic components [Povea et al., 2015]. After this procedure, smear slides were prepared for each sample using a UV curing adhesive and dried under an ultraviolet light [Backman and Shackleton, 1983; Rothwell, 1989]. They were then observed with a microscope to ensure the quality of the procedure

as well as to determine the percentages of the main mineralogical components of the lithic fraction [Povea et al., 2015]. Mineral abundance was estimated using the comparison chart for visual percentage estimation [Terry and Chilingar, 1955]. Grain size distributions were determined using a Coulter LS 230 on the lithic fraction. In addition, the lithic percentage was calculated for the studied interval (1.56–2.26 Ma). Bulk dry samples were weighed before the removal of the biogenic fraction. After the application of the biogenic removal procedure, the samples were lyophilized and weighed. The difference between these weights gives the biogenic fraction removed. Thus, the lithic percentage was obtained after subtracting the biogenic percentage from the total percentage (lithic percentage =  $100\% - \% \text{ biogenic fraction}$ ). To aid in the interpretation of the large grain size data set, a statistical method using a k-means clustering algorithm was applied [Povea et al., 2015]. This method divides the data set into  $n$  clusters, which are represented by its centroid and formed by the data for which the centroid is the nearest [Hastie et al., 2001]. The degree of representation of each cluster in each sample is obtained by calculating the Euclidean distances between each cluster centroid and the  $N$  data.

### 2.2.5. Chronological Framework

The age model is based on visual alignment of the high-resolution benthic  $\delta^{18}\text{O}$  isotopic record from ODP 1240 with the LR04 stack [Lisiecki and Raymo, 2005], including tie points every  $\sim 27$  kyr on average ( $r^2 = 0.76$ ; Fig. 2.8). Our sequence corresponds to the time interval between 1.56 and 2.26 Ma, comprising the early Pleistocene from marine isotopic stage (MIS) 52 to MIS 86. Sedimentation rates vary through this interval, with values oscillating between 7.7 and 20.9 cm/ka. These sedimentation rates are relatively high for this area and can be attributed both to the high particle flux from the equatorial upwelling system and to the basin morphology, an abyssal valley which acts as natural sediment trap [Mix et al., 2003]. The studied interval provides a time resolution of 4 kyr on average for the lithic and biogenic records and 170 years for the XRF scanner data.

Mass accumulation rates for the biogenic and lithic records were calculated based on linear sedimentation rates and dry bulk density (DBD). This density has been estimated from a linear correlation ( $r^2 = 0.92$ ) between gamma ray attenuation bulk density and the available DBD discrete measurements (Fig. S2.2 in the supporting information) [Mix et al., 2003].

## 2.2.6. Results

### 2.2.6.1. Laminated Diatom Oozes

Lithology from ODP 1240 is mostly dominated by diatom-nannofossil ooze or diatom-bearing nannofossil ooze. The identification of the laminated diatom oozes is based on the visual identification of centimeter-thick color bands from dark olive to olive and dark olive brown. In contrast, the sediment color in the nonlaminated intervals alternates between pale olive and light olive gray and presents frequent bioturbation marks of *Zoophycos* burrowing [Mix et al., 2003]. Diatom assemblage during the laminated layers is dominated by *Thalassiothrix spp.* and *Thalassionema spp.*, while the nonlaminated layers are dominated by *Azpeitia nodulifera* (Fig. S2.3 in the supporting information). The observed LDOs (labeled as L1 to L9) have been defined based on the visual identification due the dark olive brown color. The interpreted LDOs (labeled as IL) have been determined since exhibiting the same pattern of the observed LDOs, based on the highest concentrations of biogenic silica and lithic contents, albeit its visual identification is not so clear.

### 2.2.6.2. Oxygen Isotope Record

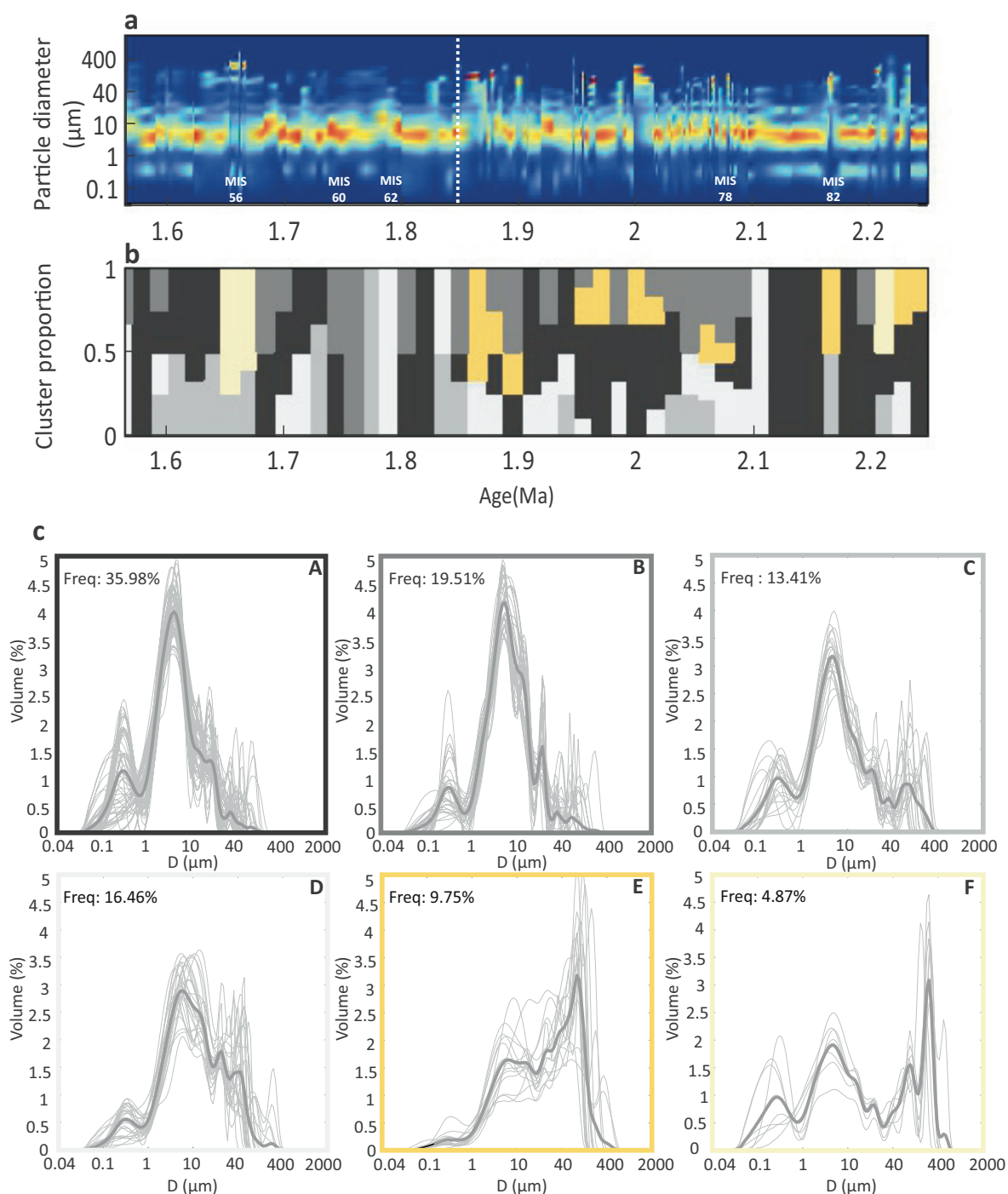
The benthic  $\delta^{18}\text{O}$  record has values that range from 3.2 to 4.5‰ with oscillations corresponding to glacial/interglacial cycles (Fig. 2.8). The data reveal very sharp transitions between interglacial and glacial phases. Three remarkable glacial periods are recorded as presenting the highest  $\delta^{18}\text{O}$  values and the longest durations, MIS 56 (1.65–1.67Ma), MIS 78 (2.07–2.09Ma), and MIS 82 (2.15–2.17Ma).

### 2.2.6.3. Grain Size Distribution and Clustering Analysis

Particle size distributions reveal that most of samples are trimodal, with one initial mode around 0.5  $\mu\text{m}$ , followed by a principal mode centered at 6–7  $\mu\text{m}$ . After this principal mode, a high variability of grain size modes is observed between 100 and 400  $\mu\text{m}$  (Fig. 2.9). However, in certain time intervals, mainly before 1.85 Ma, the main mode is displaced to coarser grains (>60  $\mu\text{m}$ ) and the samples are overall poorly sorted.

According to the obtained modal distribution, k-means clustering analysis characterizes the grain size data set into six clusters (cluster A to cluster F), previously presented in Povea et al. (2015). Clusters A, B, and C are the most dominant patterns, reaching almost 69% of the frequency (Fig. 2.9c). These clusters show a well-defined main mode around 6–7  $\mu\text{m}$ , a finer mode around 0.5  $\mu\text{m}$ , and a more variable last mode. Clusters E and F

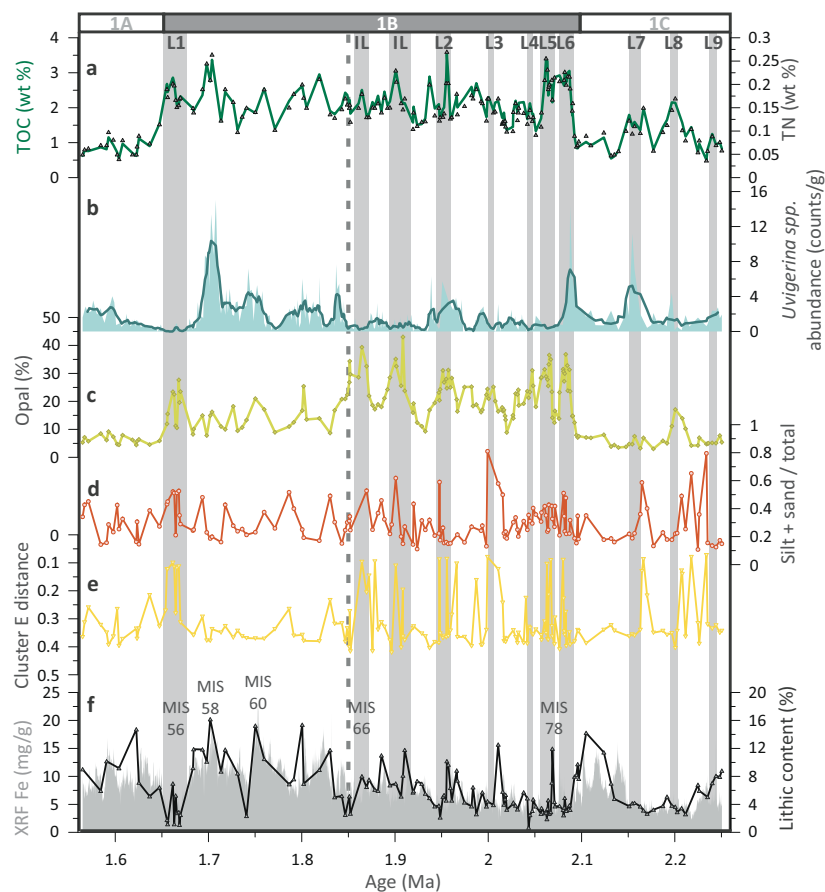
are less abundant, with a combined frequency of 15%, and clearly different from the rest, presenting a main mode shifted to coarser sizes (Fig. 2.9c). Cluster D seems to be the intermediate and transitional pattern between the well-sorted (clusters A, B, and C) and the poorly sorted and coarser (clusters E and F) clusters (Fig. 2.9c), with the mode around 6–7  $\mu\text{m}$  less defined and a terminal mode more abundant.



**Fig. 2.9.** Clustering analysis of ODP 1240 particle size distribution. (a) Particle size distribution of the entire studied period, (b) Proportion and distribution of six clusters along the studied period, note that each color corresponds to each cluster of the next caption, (c) Cluster classification based on their particle size distribution [Povea et al., 2015]. Frequency distribution is noted for each cluster. Marine Isotopic Stages (MIS) 56, 60, 62, 78 and 82 are also shown.



In order to better understand the time distribution of these distinct clusters, cluster E distance is estimated. This value reflects the degree of similarity between each sample and this cluster, where the lower value (close to 0) means the greater similarity to cluster E. Cluster E has been chosen for its most distinct modal distribution, displaying a coarser-main mode, and its frequent presence during colder phases, especially during LDO deposition (Fig. 2.10e). The comparison with the abundance of the coarse fraction represented by the silt+ sand/total ratio (Fig. 2.10d) shows a generally good agreement between these two parameters that both peak during glacial periods. However, cluster E practically disappears during glacial times without LDOs. While the silt-clay parameter does not differentiate between these two groups of glacial periods, the absence of cluster E indicates that the lithic fraction during the non-LDO glacial phases had a distribution closer to A, B, C, and D clusters (e.g., MIS 58 and MIS 60 in Fig. 2.9 and 2.10).



**Fig. 2.10.** Biogenic and lithogenic fraction characterization from Eastern Equatorial Pacific (ODP 1240). (a) TOC (solid line) and TN (grey triangles) contents(%), (b) *Uvigerina spp.* abundance (counts/g), note that the green dark line shows the running average of 5 points, (c) Opal (%), (d) Grain size parameter showed as (Silt+ sand)/total, (e) Euclidean distance of cluster E to each sample, (f) XRF Core scanner Fe (mg/g) and lithic content (%). Grey shaded vertical bars indicate the position of the observed and the interpreted LDOs, labeled as L1-L9 and IL, respectively. White and grey bar on the top show the three sedimentological units (1A, 1B and 1C). Vertical dashed line marks the 1.85 Ma transition. Marine Isotopic Stages (MIS) 56, 58, 60, 66 and 78 are also presented.

#### 2.2.6.4. Paleoproductivity Proxies

TOC and TN records show substantial variability over the studied time interval, with generally higher values during the glacial intervals when LDOs occurred (Fig. 2.10a). These records exhibit three distinct intervals, consistent with previously defined subunits [Mix et al., 2003], with higher TOC and TN mean values during subunit 1B (Table 2.3) and very sharp boundaries between subunits. The upper part (1.56–1.65Ma) presents the minimum values of all the sequence, while the middle interval (1.65–2.09 Ma) shows the maximum values of TOC, TN, and opal (Table 2.3). The biogenic fluxes of TOC and opal also show the highest values during subunit 1B (Fig. 2.11e and 2.11g), with maximum values during the LDO intervals.

*Uvigerina spp.* abundance oscillates from 0 to 80% of the total benthic assemblage (Fig. 2.10b). High *Uvigerina spp.* abundances typically occur in phases of relatively high TOC percentages with some exceptions, when peaks in TOC% correspond to low *Uvigerina spp.* abundance, and these events mostly correspond to the LDOs (Fig. 2.10a and 2.10b).

| Record<br>(wt %) | Unit 1A |      |         | Unit 1B |       |         | Unit 1C |       |         |
|------------------|---------|------|---------|---------|-------|---------|---------|-------|---------|
|                  | Min.    | Max. | Average | Min.    | Max.  | Average | Min.    | Max.  | Average |
| TOC              | 0.5     | 1.5  | 0.86    | 0.84    | 3.5   | 2.16    | 0.5     | 2.15  | 1.2     |
| TN               | 0.04    | 0.11 | 0.069   | 0.06    | 0.27  | 0.15    | 0.03    | 0.17  | 0.09    |
| Opal             | 4.41    | 9.19 | 6.24    | 7.81    | 43.03 | 21.12   | 3.02    | 17.10 | 6.51    |

**Tab. 2.3.** Biogenic contents from Eastern Equatorial Pacific (TOC, TN and opal). Note that are divided in the three sedimentological subunits (1A, 1B and 1C).

#### 2.2.6.5. Lithic Fraction and Iron

The record of lithic percentage mimics, at lower resolution, the iron content profile measured by the XRF scanner for the whole studied period (Fig. 2.10f). This relationship ( $r^2 = 0.63$ ), together with the absence of fluvial runoff to the studied basin, supports their common origin and thus the eolian deposition of the measured iron. In contrast to the biogenic proxies, these terrigenous source proxies do not differentiate the three sediment subunits (Fig. 2.10f) but show a general increasing trend toward the top of the studied period also shown in the lithic and iron fluxes (Fig. 2.10f, 2.11j, and 2.11k and Fig. S2.5 in the supporting information).



Interestingly, the higher values occurred during the glacial periods between 1.68 and 1.85 Ma, when the cluster E and silt + sand/total parameter did not agree. On the contrary, the minimum values occurred during the glacial periods previous to 1.85 Ma when cluster E was better represented. The pronounced minimum in both iron and terrestrial content associated with MIS 56, corresponding to the last and very pronounced LDOs (L1).

The mineralogical composition of the lithic fraction is dominated by six main mineral phases that remain constant in composition over the studied period (1.56–2.26 Ma; Fig. S2.6 and Table TS2.1 in the supporting information). The most abundant phases are feldspar (42.15%), opaques (25.45%), and quartz (19.43%), and the minor mineral components are epidote (6.50%), volcanic glass (4.52%), and amphibole (1.95%).

## 2.2.7. Discussion

### 2.2.7.1. Changes in Atmospheric Transport

Since terrigenous sediment comes to the studied location primarily through the atmosphere, its characteristics should reflect the ITCZ position and intensity of the wind belt system, as well as changes in the aridity of the source area. Previous studies have found that eolian dust in the EEP comes from the arid areas of western South America [Nakai et al., 1993], mostly from the Atacama desert [Molina-Cruz, 1977] or from the Andean region [Janecek and Rea, 1985; Chuey et al., 1987; Rea, 1990]. Moreover, Atacama desert became hyperarid in the Pliocene as a consequence of a global climate cooling [Hartley et al., 2002]. This episode of hyperaridity produced a sedimentary hiatus in the Atacama region from 3.37 Ma, which would be coeval to a major development of Antarctica ice sheets and to an enhancement of the cold ocean upwelling in the eastern Pacific during the Pliocene-Pleistocene transition [Sáez et al., 2012]. Thus, these cooling stages could trigger the extreme hyperarid conditions in the Atacama region with an absence of sediment production and accumulation [Sáez et al., 2012].

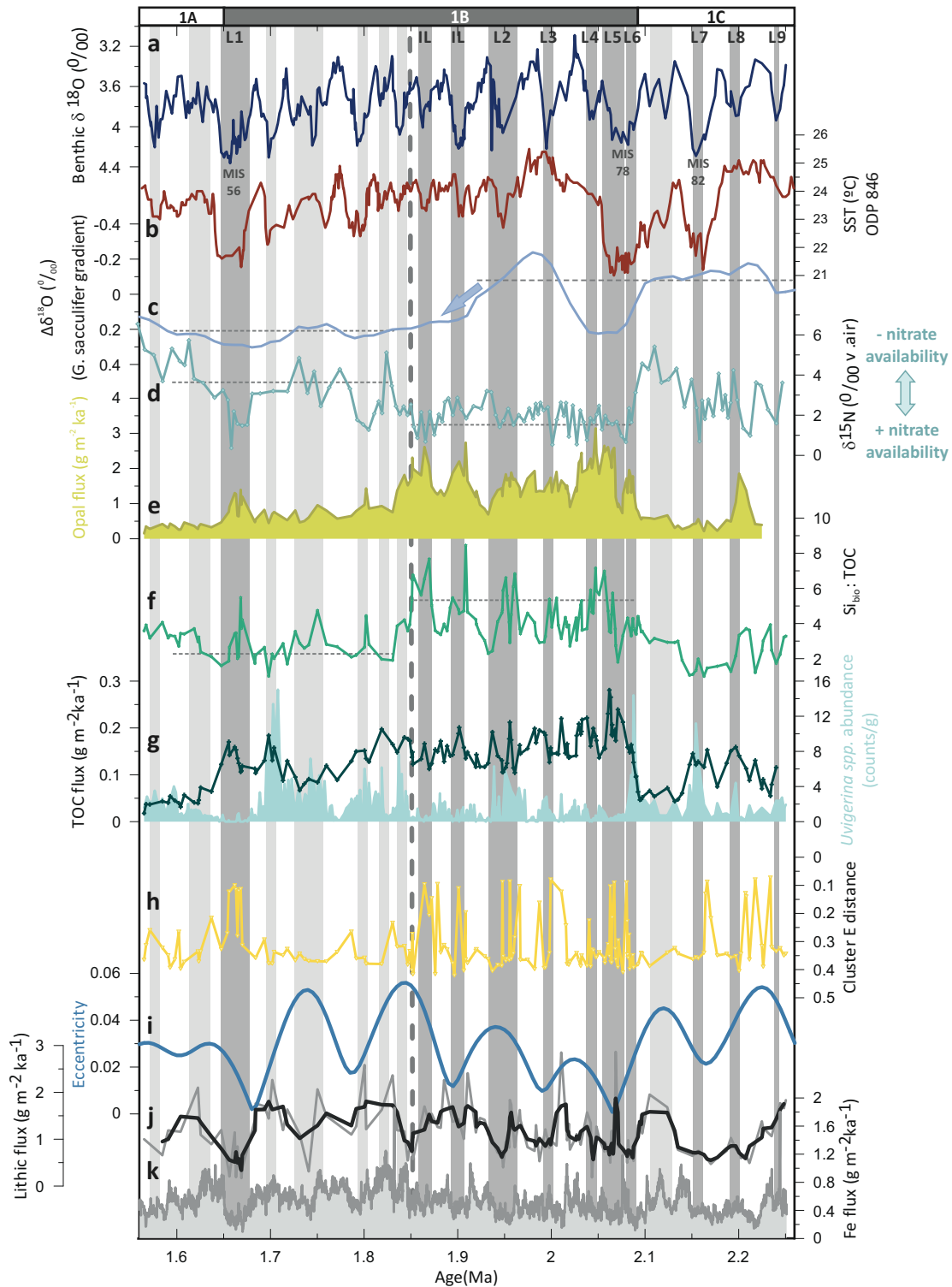
Deposition of lithic material, including iron, was relatively low during the time interval prior to 1.85 Ma (Fig. 2.11j and 2.11k). During this period, the grain size distribution results at ODP 1240 show the dominance of giant (>60  $\mu\text{m}$ ) and relatively poorly sorted coarse grains (Fig. 2.9c, clusters E and F). In some extreme cases, within the period previous to 1.85 Ma, the fine dominant mode between 4 and 6  $\mu\text{m}$  completely disappears or become very scarce. These are the samples represented by a low cluster E distance, which means a higher similarity with this cluster (Fig. 2.11h), and happen particularly during glacial periods and coinciding with LDOs and also during the strong event at MIS 56. In

contrast, after 1.85Ma, the samples displayed a characteristic trimodal distribution with a principal mode between 6 and 7  $\mu\text{m}$ , indicating the dominance of better sorted fine grains and low variance, particularly during the glacial times (MISs 58, 60 and 62; Fig. 2.9a, 2.11j and 2.11k 60 and 62; Fig. 2.9a). These glacial intervals also record an increased arrival of lithic grains and iron.

The size of dust particles transported over hundreds of kilometers is generally below 10  $\mu\text{m}$  [Tegen et al., 1996]. However, the presence of eolian giant particles ( $>10 \mu\text{m}$ ) has also been documented in previous studies [Glaccum and Prospero, 1980; Betzer et al., 1988; Moreno et al., 2001; Jeong et al., 2013].

These particles can be transported over long distances if strong upward advection of air masses lifts these dust particles to higher altitudes [Windom, 1985; Pye, 1995] or a midtropospheric wind belt induces a rapid dust transport [Jeong et al., 2013]. An additional factor controlling grain size distribution is the relative contribution of wet and dry deposition [Guerzoni et al., 1997]. The range of grain size particles of dust deposition by a wet event has been explored through the analysis of a series of Saharan dust samples collected in Iberia during rain events (mean Saharan dust wet deposition; Fig. S2.7 in the supporting information), showing that a wide size range of particles can be transported and deposited but always with a strong presence of the coarser mode.

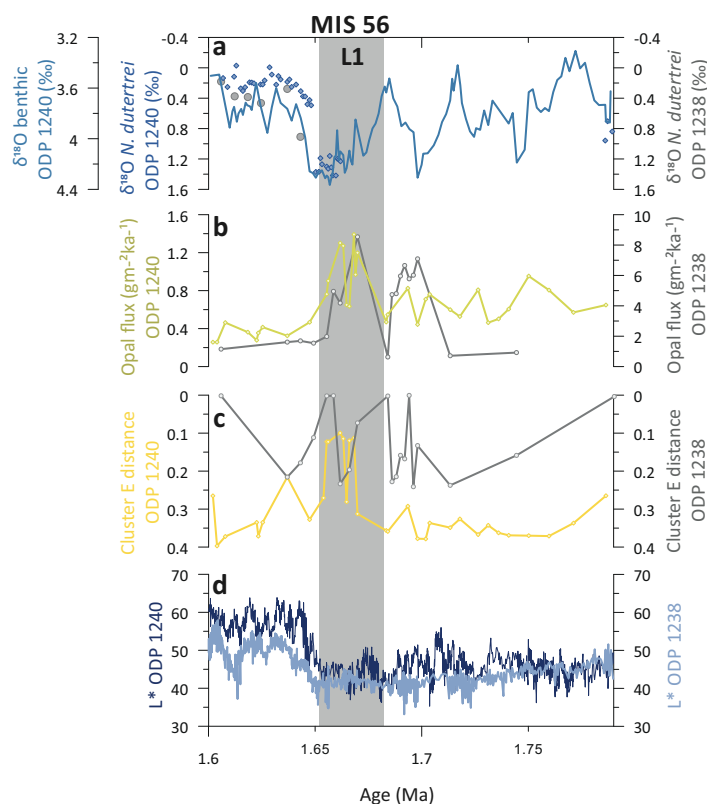
These observations would suggest that most of the samples result from a mixture of wet and dry deposition processes. Nevertheless, when samples get closer to the cluster E, deposition is dominated by wet deposition, consistent with the proximity to the particle size distribution from the Saharan dust (wet deposition; Fig. S2.7 in the supporting information). These changes in the grain size distribution reflect the position of the ITCZ. Strong southeasterly trade winds occur south of the ITCZ, while within the ITCZ, the trade winds become weaker and wet deposition dominates [Hovan, 1995]. Consequently, it appears that during glacial periods with the occurrence of the LDOs, mostly before 1.85 Ma, the ITCZ was located at its southernmost position, just above ODP 1240. The presence of coarser grains, even giant particles ( $>200 \mu\text{m}$ ), and scarcity of lithic and iron contents, indicates the dominance of weak southeasterly winds and increased rainfall or wet deposition events. The lithic fraction presents a coherent trend with eccentricity [Laskar et al., 2004], with minimum values at eccentricity minima (Fig. 2.11i–2.11k). Low eccentricity in the glacial periods previous to 1.85 Ma would have reduced seasonal contrast, and thus ITCZ seasonal migration, anchoring it in a southerly position. This is particularly evident in glacial stages MIS 78 and 56 when intense and long glacial conditions are observed, highlighting the previously proposed relevance of the 400 kyr eccentricity cycle in the EEP for this time period [Herbert et al., 2010]. In contrast, when eccentricity was higher (with



**Fig. 2.11.** Interpreted ITCZ migrations and distinctive fertilization mechanisms associated to atmosphere-ocean connections over the Eastern Equatorial Pacific during the studied period. (a) Benthic  $\delta^{18}\text{O}$  record ( $\text{‰}$ ), (b) SST ( $^{\circ}\text{C}$ ) ODP 846 [Herbert et al., 2010], (c) Oxygen isotope difference (*G. sacculifer*) between ODP 851 (Eastern Pacific) [Cannariato et al., 1997] and ODP Site 806 (Western Pacific) [Berger et al., 1993; Jansen et al., 1993], (d)  $\delta^{15}\text{N}$  ( $\text{‰}$  v. air) [Etourneau et al., 2013], (e) Opal flux ( $\text{g m}^{-2}\text{ka}^{-1}$ ), (f)  $\text{Si}_{\text{bio}}/\text{TOC}$  ratio, (g) TOC flux ( $\text{g m}^{-2}\text{ka}^{-1}$ ) and *Uvigerina* spp. abundance (expressed as counts/grams dry bulk weight), (h) Cluster E distance, (i) Eccentricity [Laskar et al., 2004], (j) Lithic flux ( $\text{g m}^{-2}\text{ka}^{-1}$ ), (k) Fe flux ( $\text{g m}^{-2}\text{ka}^{-1}$ ). Dark grey shaded bars indicate the position of the observed and interpreted glacial LDOs, labeled as L1-L9 and IL, respectively. Light grey shaded vertical bars indicate glacial periods without LDOs. White and grey bar on the top show the three sedimentological units (1A, 1B and 1C). Vertical dashed line marks the 1.85 Ma transition. Marine Isotopic Stages (MIS) 56, 78 and 82 are also shown.

an upward increase after 1.85 Ma), Earth's seasonality increased causing greater latitudinal migration of the ITCZ. Thus, the ITCZ may have been located further north, closer to its current position, with a reinforcement of the local winds and decreased rainfalls. This situation would have allowed a higher lithic input, including iron, well sorted around a finer mode. Furthermore, the overall increase in lithic contributions across the studied period, with a greater content from 1.85 Ma, also indicates more arid conditions of the source regions. This enhanced aridity has been also detected in other regions like the African continent during this time period [deMenocal, 2004]. Finally, the invariant mineralogical composition along the whole record, including glacial and interglacial phases (Fig. S2.6 and Table TS2.1 in the supporting information), suggests that there were no noticeable changes in the source area of the lithic material in relation to these ITCZ migrations.

In order to better characterize the geographical impact of the discussed ITCZ displacements, ODP 1238, located further southeast (1°52.310'S, 82°46.934'W) in the EEP, was also examined for the time period of the most intense LDOs (1.6–1.79 Ma), which occurred during glacial MIS 56. If these events occurred during a weakening of the southeasterly trade winds, it should also be reflected in ODP 1238 (Fig. 2.12).



**Fig. 2.12.** The imprint of a major southward ITCZ migration during L1 (1.6-1.79 Ma), registered further south over ODP 1238. (a) ODP 1240 benthic  $\delta^{18}\text{O}$  record ( $^{\circ}/_{\text{oo}}$ ) (blue line), ODP 1240 *N. dutertrei*  $\delta^{18}\text{O}$  record ( $^{\circ}/_{\text{oo}}$ ) (blue diamonds) and ODP 1238 *N. dutertrei*  $\delta^{18}\text{O}$  record ( $^{\circ}/_{\text{oo}}$ ) (dark grey circles), (b) Opal flux ( $\text{gm}^{-2}\text{ka}^{-1}$ ) from ODP 1240 (green line) and ODP 1238 (dark grey line), (c) Cluster E distance from ODP 1240 (yellow line) and ODP 1238 (dark grey line), (d) Luminescence ( $L^*$ ) from ODP 1240 (dark blue line) and ODP 1238 (light blue line) [Blum et al., 2005]. Grey shaded bar shows the location of L1 and MIS 56.

Thus, the recorded signal in ODP 1238 with high fluxes of opal, coarse grains with a similar distribution to cluster E (Fig. 2.12), even with an increased signal due to the shorter transport distance for the lithic material, supports this southward shift of the ITCZ and illustrates the wide geographical extension of the L1.

#### 2.2.7.2. Atmosphere-Ocean Coupling

Primary productivity in the EEP is controlled by the availability of nutrient inputs in the system which in turn is influenced by the atmosphere-ocean coupled system. Thus, it is also sensitive to the ITCZ or equatorial front (EF) migration and the associated equatorial upwelling system. Highest values of export production occurred during glacial periods between 1.85 and 2.1 Ma and glacial time located at 1.65 Ma (MIS 56; Fig. 2.11e–2.11g), when the LDOs were formed. The lithic fraction data (section 2.2.7.1) suggest that during these glacial periods, the ITCZ was located over the equator (ODP 1240 location) likely at its most southward position over the entire record. The dominance of the cluster E occurred primarily during periods when opal and TOC were high; thus, the interpreted weak trade winds could not stimulate this high-productivity system (Fig. 2.11). In addition, this high productivity could not be explained through an iron fertilization process as could be expected in an iron-limited ocean region [Martin, 1990; Jickells et al., 2005], since iron values are relatively low before 1.85 Ma. A comparison with a sedimentary  $\delta^{15}\text{N}$  isotope record from the same marine core [Etourneau et al., 2013] also reveals low  $\delta^{15}\text{N}$  values especially during this interval prior to 1.85 Ma transition (Fig. 2.11d). Etourneau et al. (2013) interpreted this as a reflection of enhanced nitrate availability in the eastern equatorial Pacific system, suggesting that nutrient consumption was low relative to nutrient supply. Thus, the low  $\delta^{15}\text{N}$  values when export production was high indicate a significant supply of nutrients, including silicic acid and nitrate [Billups et al., 2013], to the eastern equatorial Pacific between 1.85 and 2.1 Ma. Since the EEP is Si and iron colimited [Brzezinski et al., 2008, 2011], diatoms tend to deplete surface waters of silicic acid before nitrate, reducing the  $\text{Si}(\text{OH})_4:\text{NO}_3$  ratio in the surface ocean [Hutchins and Bruland, 1998]. This major silicic acid uptake promotes more silicified diatoms, with heavier and larger frustules [Franck et al., 2000; Beucher et al., 2007], thus allowing for faster sinking and the formation of the LDOs during these periods prior to 1.85 Ma. The *Thalassiothrix spp.* diatoms, typical of these LDOs, have been associated to the dominance of stratified surface waters in the vicinity of the EF [Kemp et al., 2000, 2006; Pike and Stickley, 2007]. The occurrence of these laminations has also been associated to major cooling events in the eastern equatorial Pacific [Kemp et al., 1995]. This seems to be confirmed by excursions toward cooler

SST during LDO deposition as evidenced by alkenone derived SST record (Fig. 2.11b) [Liu and Herbert, 2004; Herbert et al., 2010]. This is not true for two laminations (L3 and L8) that record higher SSTs. This may be explained by the seasonality of the coccolithophorid population. The inferred stratified conditions are consistent with the interpreted ITCZ location over equator. But, the stimulated diatom productivity also requires an extra arrival of silicic acid to the EEP, likely through advection of nutrient-rich intermediate waters feeding the EUC. Previous studies have identified strong connections between high and low latitudes, mainly through advection of Southern Ocean intermediate water to the Equatorial Undercurrent (EUC) [Kessler, 2006; Pena et al., 2013]. This Antarctic component would have provided Si-rich waters to the tropical thermocline [Calvo et al., 2011], stimulating diatom production (Fig. 2.11e) and a consequent increase in nitrate availability [Sarmiento et al., 2004]. This high-latitude forcing is confirmed by the strong obliquity signal on the opal record during the interval previous to 1.85 Ma (Fig. S2.8 in the supporting information). Consequently, prior to the 1.85 Ma transition, we interpret that the fertilization of the EEP occurred through an enhanced EUC nutrient supply, potentially of Southern Ocean origin, as also published in Etourneau et al. [2013].

After 1.85 Ma, according to the lithic fraction interpretation, the ITCZ changed its mean position toward a more northern location, particularly during glacial times. This situation would have triggered enhanced equatorial upwelling, less stratified surface waters, a thermocline shoaling, and a greater equatorial E-W Pacific gradient (Fig. 2.11c), consistent with the enhancement in Walker circulation proposed in previous studies [Ravelo et al., 2004; Wara et al., 2005; Ford et al., 2012]. The productivity proxies indicate a decrease but still relatively high values in export production (Fig. 2.11e and 2.11g) and a clear change in the phytoplankton community, supported by a lowering in the  $\text{Si}_{\text{bio}}:\text{TOC}$  ratio and the disappearance of the heavy silicified diatoms that formed the LDOs (Fig. 2.11f). This evidence and the parallel increase nitrate consumption (Fig. 2.11d) suggest a change in the  $\text{Si}(\text{OH})_4:\text{NO}_3$  ratio consistent with a reduction in the availability of silicic acid and/or enhanced iron fertilization. The reinforcement of the upwelling system by southeasterly trade winds produced SST slightly lower after 1.85Ma and also increased the atmospheric dust transport as is supported by the relatively high lithic and iron fluxes (Fig. 2.11j and 2.11k). The exception to this situation occurred during the glacial MIS 56 (1.65Ma), when conditions returned to those of glacial previous to 1.85 Ma, but with a more extreme expression. This southward displacement of the ITCZ may be a consequence of the extreme glaciation triggered by 400 kyr minimum eccentricity at 1.65 Ma, as already seen it in numerical models [Masunaga and L'Ecuyer, 2011]. The ITCZ displacement reached further south, to the position of ODP 1238, confirming the severity of the glacial MIS 56 period.



On the other hand, although the most marked and important changes are observed during glacial periods before and after 1.85 Ma, the interglacial phases also show a different pattern of behavior between these two marked periods, such as TOC and opal fluxes (Fig. 2.11e and 2.11g). These evidence support a tight coupling between the atmospheric changes and the upwelling system and highlight the high dynamism of the equatorial system during the studied period.

### 2.2.7.3. Implications for carbon fluxes to the deep-sea floor

The TOC record (Figure 2.11g) shows the highest fluxes during the period covering lithological subunit 1B (1.65–2.08Ma), supporting an enhanced C export to the deep ocean. Nevertheless, C fluxes appear to be slightly higher prior to the 1.85 Ma transition and, particularly, during those glacial periods with LDO formation. *Uvigerina spp.* is a detritivore and infaunal benthic foraminifera, typical of environments with a high organic carbon flux and low oxygen content [Seiglie, 1968; Murray, 1991; Rathburn and Corliss, 1994]. In general, *Uvigerina spp.* abundances parallel the TOC variability, with maximum percentages of *Uvigerina spp.* occurring during maxima in TOC. However, this relationship is not satisfied during most of the LDOs (Figures 2.10a, 2.10b, and 2.11g). These time intervals of maximum TOC fluxes toward the deep ocean did not stimulate the proliferation of *Uvigerina spp.*, theoretically prone to high carbon fluxes. This very distinctive response of the benthic system to two primary productivity scenarios suggests different mechanisms of carbon sinking to the deep ocean. LDO layers are formed by pennate-type diatoms, such as *Thalassiothrix spp.* [Mix et al., 2003]. These diatoms tend to form large grids of twisted cells, which could drag down large amounts of organic carbon and other particles to the deep-sea floor. These high fluxes of TOC would have occurred in rapid events, probably as seasonal cycles (especially during fall or early winter) [Kemp et al., 2000] rather than as a continuous and homogeneous rain, and apparently prevented the development of *Uvigerina spp.* owing to the extremely high contents of TOC. These results highlight the role of vertical particle transport controlling the benthic population and also document the high efficiency of the LDOs in the deep transfer and storage of carbon and their potential to increase the storage of atmospheric CO<sub>2</sub> in the deep ocean [Kemp et al., 2000, 2006; Dugdale and Wilkerson, 2001].

### 2.2.8. Conclusions

The integrated study of both lithic and biogenic components from EEP sediments allows the identification of coupled changes in atmospheric and oceanic dynamics that occurred along the early Pleistocene (from 1.56 to 2.26 Ma) indicating major meridional shifts in the main position of the ITCZ. Glacial periods from 1.85 to 2.26 Ma present lower iron and lithic contents, dominated by coarse and unsorted lithic particles, interpreted to reflect a southerly position of the ITCZ, approximately over the equator (ODP 1240). This would result in a weakening of the trade winds over the region and increasing wet dust deposition associated with more frequent rainfall events below the ITCZ. This situation is consistent with the dominance of the heavy silicified diatom that formed the LDOs, typical of stratified surface waters in the vicinity of oceanic frontal zones. The increased N availability (low  $\delta^{15}\text{N}$  values) [Etourneau et al., 2013] and opal fluxes, particularly after 2.1 Ma, support a change in the nutrient availability likely induced by a greater input of silicic acid-rich waters, potentially from Antarctic origin. The high-latitude origin of these Si-rich waters is supported by the detected obliquity pacing in the biological Si record. The almost absence of *Uvigerina spp.*, a benthic species that usually takes advantage of high TOC fluxes, supports a high and rapid flux of carbon toward the deep ocean that overwhelmed the benthic ecosystem during LDO formation.

Glacial periods after 1.85Ma present higher deposition of finer and better sorted lithic particles and also enhanced iron fluxes. These conditions could reflect the dominance of eolian dry deposition as a result of a northward migration of the ITCZ. This interpretation is supported by the evidence of high primary productivity but with remarkable differences in the nutrient balance (less N availability) consistent with conditions of enhanced upwelling and iron fertilization in the region. This situation would have enhanced the E-W gradient in the equatorial Pacific in agreement with the previously proposed strengthening of the Walker circulation after 1.85 Ma. The high resolution of the new ODP 1240 records at this time frame has allowed to characterize an abrupt shift in the system located at 1.85 Ma rather than a progressive and smooth long trend change. During this time, carbon flux toward the deep ocean was also high but occurred as a more homogeneous rain that efficiently stimulated the development of *Uvigerina spp.*

The glacial period centered at 1.65 Ma (MIS 56) was an exception to this 1.85 Ma boundary and became a major breakdown to this northward shift of the ITCZ. MIS 56 and also MIS 78 are characterized by the best developed LDOs and also the coldest glacial phases coincident with eccentricity minima paced by the 400 kyr cycle. The seasonal changes derived from this distinctive astronomical configuration combined with the growing ice of the



North Hemisphere ice sheets are suggested to have lead the recorded migrations in the ITCZ position.

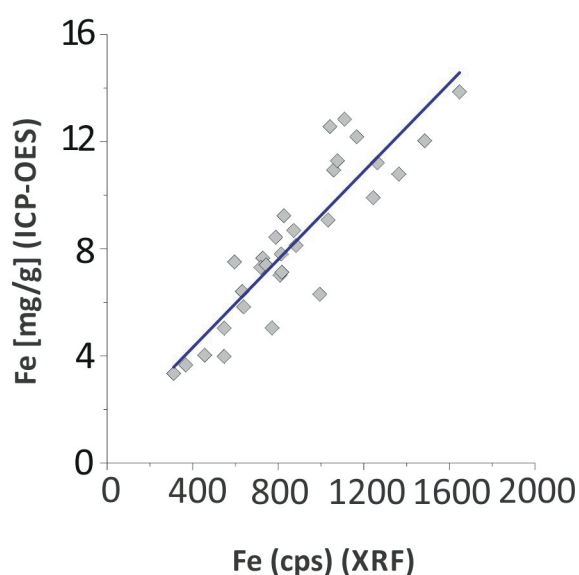
### 2.2.9. Acknowledgments

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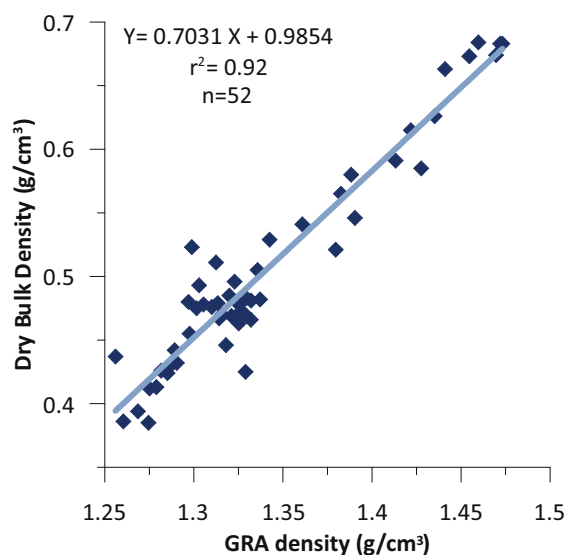
Net primary production data was downloaded from the Ocean Productivity site (<http://www.science.oregonstate.edu/ocean.productivity/index.php>). Data will be available at the Scientific Earth Drilling Information Service (SEDIS; <http://sedis.iodp.org>), Pangaea website (<http://www.pangaea.de>) and NOAA Paleoclimatology (<https://www.ncdc.noaa.gov/data-access/paleoclimatology-data>).

### 2.2.10. Supplementary material

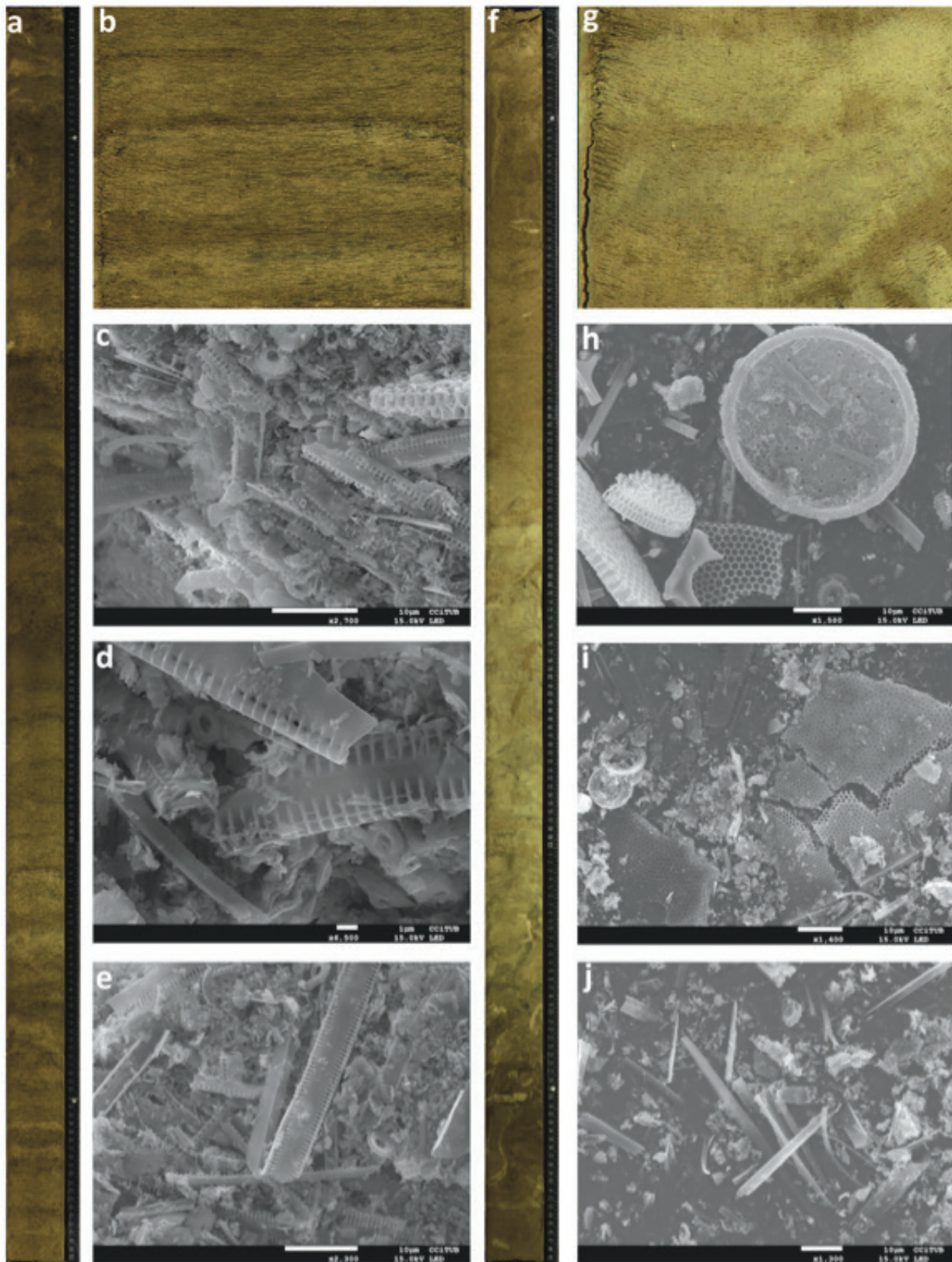
This supporting information provides additional figures with extended methodological data, useful for the calibration between Fe content measured with XRF Core Scanner and ICP-OES (S2.1), and the estimations of Dry Bulk Density (DBD) (S2.2). Besides, we have also provided additional figures for the Laminated Diatom Oozes description (S2.3) and the mineralogical composition from ODP 1240 (TS2.1, S2.6). Fig. S2.4 provides additional biogenic results as  $C_{org}:N$  ratio from ODP 1240, which is compared with ODP 1240 biogenic silica content and SST from ODP 846 alkenone-derived ( $^{\circ}C$ ) [Liu and Herbert, 2004; Herbert et al., 2010]. Fig. S2.5, S2.7 and S2.8 offer extended data to complement the discussion.



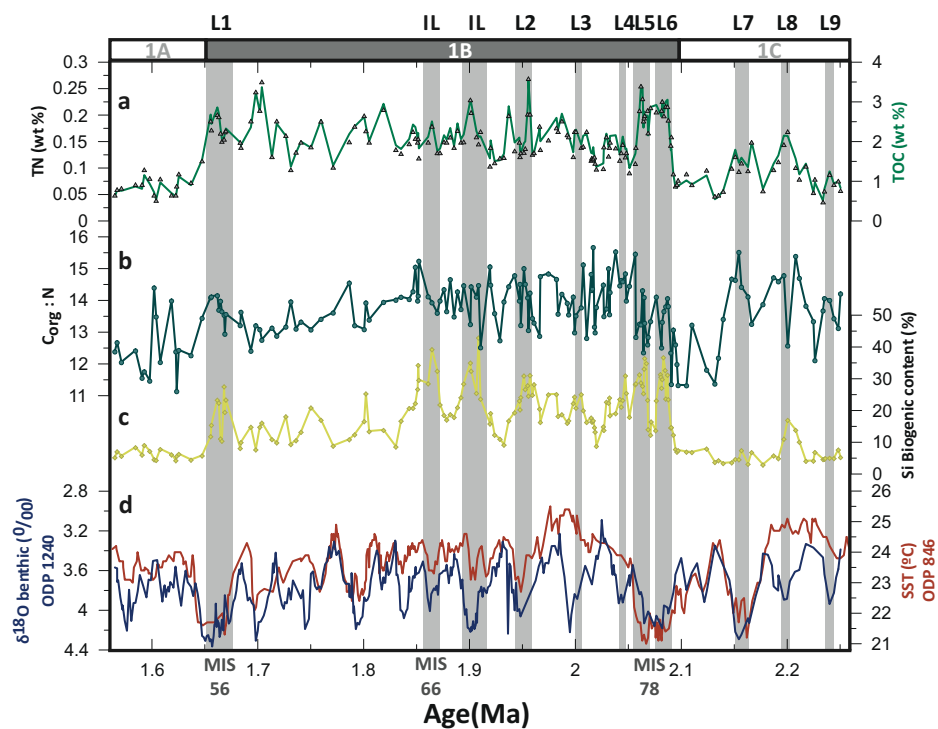
**Fig. S2.1.** Correlation analysis between Fe values obtained with XRF Core Scanner method (x) and with ICP-OES (y) method, with a correlation coefficient of 0.79.



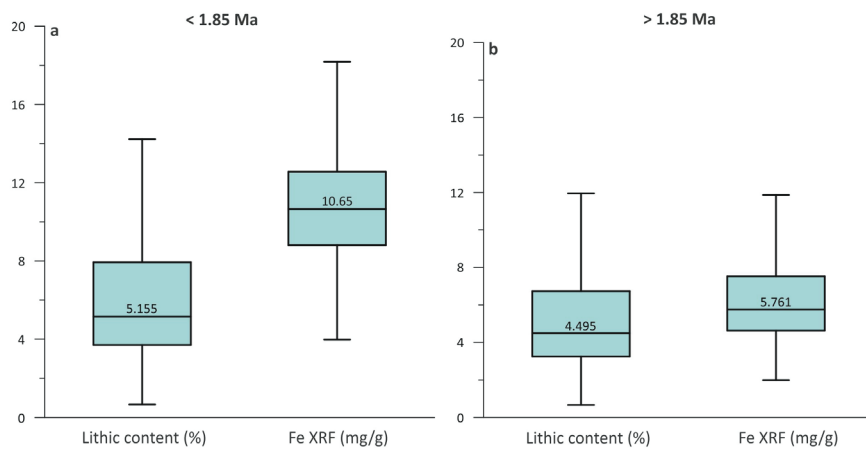
**Fig. S2.2.** Linear regression between GRA Density and discrete Dry Bulk Density (DBD) measurements.



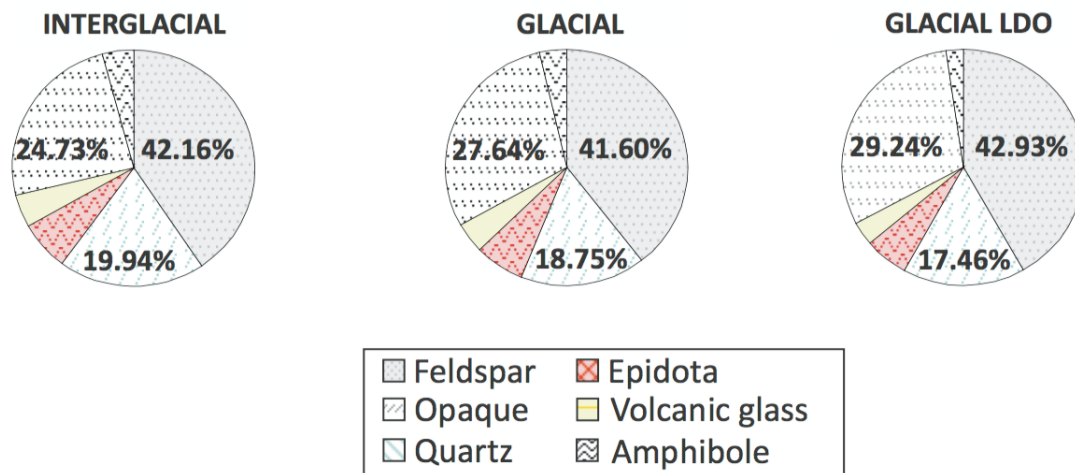
**Fig. S2.3.** Laminated Diatom Oozes (LDO) description. (a) Picture of ODP 1240 laminated section, (b) ODP 1240 laminated sediment, corresponding to L1 of the present study, (c, d, e) Electronic microscope pictures from this laminated sediment, note the high content of *Thalassiothrix spp.*, (f) Picture of ODP 1240 non-laminated section, (g) ODP 1240 non-laminated sediment, (h, i) Electronic microscope pictures from the non-laminated section, note the major presence of centric diatoms as *Azpeitia nodulifera*, (j) Electronic microscope pictures from the non-laminated section, note the minor abundance of *Thalassiothrix spp.*



**Fig. S2.4.** Extended data Fig. 2.10. Comparison between SST, productivity proxies and LDOs occurrence. (a) ODP 1240 TN (wt %) and TOC (wt%), (b) ODP 1240  $C_{org} : N$  ratio, (c) ODP 1240 Biogenic silica content (%), (d) ODP 1240 Benthic  $\delta^{18}O$  record (‰) and ODP 846 SST alkenone-derived (°C) [Liu and Herbert, 2004; Herbert et al., 2010]. Dark grey shaded bars indicate the position of the observed and interpreted glacial LDOs, labeled as L1-L9 and IL, respectively. White and grey bar on the top show the three sedimentological units (1A, 1B and 1C). Vertical dashed line marks the 1.85 Ma transition. Marine Isotopic Stages (MIS) 56, 66 and 78 are also shown.

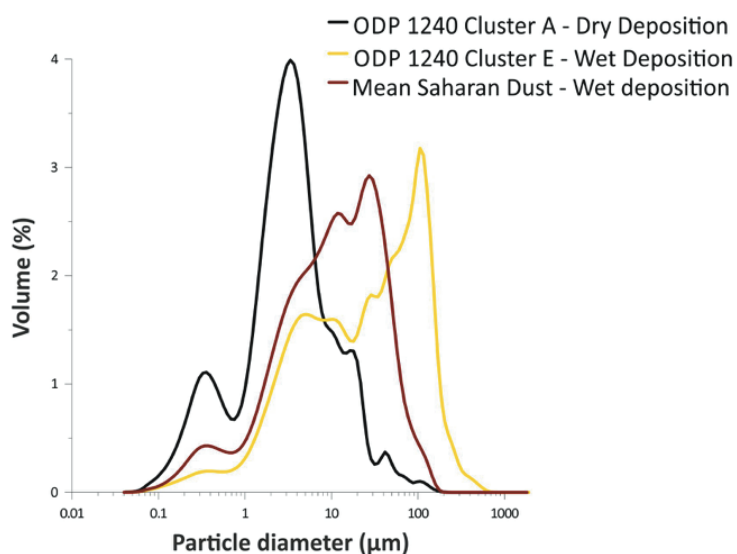


**Fig. S2.5.** Extended data Fig. 2.10 and 2.11. Box-plot showing the difference between iron and lithic contents, (a) after and (b) prior 1.85 Ma. Note that the median shows higher values after 1.85 Ma transition (a). L1 (MIS 56) data has been included in the box plot prior to 1.85 Ma (b).

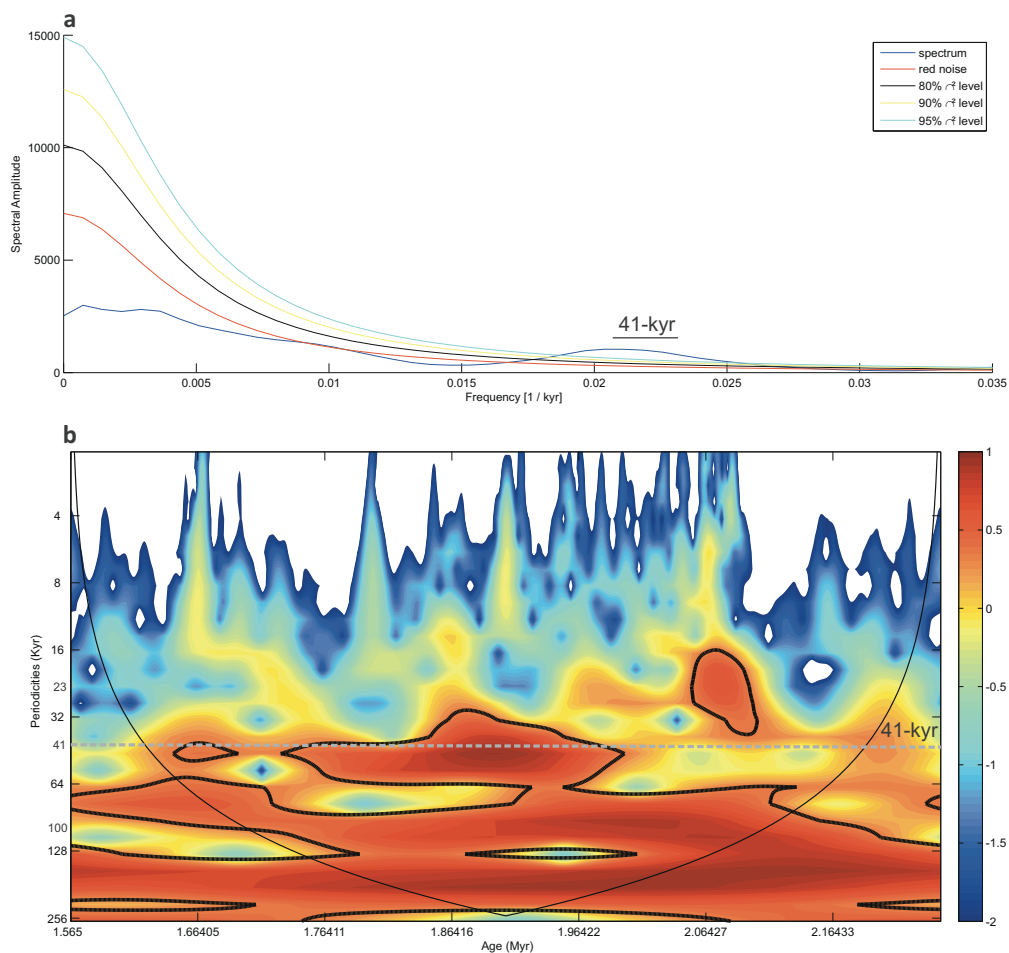


**Fig. S2.6.** Extended data Fig. 2.10 and 2.11. Mineralogical composition from ODP 1240. Note that the main mineralogical phases have been counted separately for interglacial, glacial and glacial LDOs periods.





**Fig. S2.7.** Extended data Fig. 2.11. Comparison between Particle Size Distribution (PSD) of clusters A – dry deposition (black line) and E – wet deposition (yellow line) with mean PSD of Saharan dust - wet deposition (garnet line).



**Fig. S2.8.** Extended Data Fig. 2.11. Spectral analysis (a) and wavelet analysis (b) of the opal record from ODP 1240. 41-kyr cycle can be observed in both analyses as the dominant frequency.

|                                | Feldspar | Opaques | Quartz | Epidote | Volcanic glass | Amphibole |
|--------------------------------|----------|---------|--------|---------|----------------|-----------|
| <b>TOTAL<br/>(N=142)</b>       |          |         |        |         |                |           |
| <b>Min</b>                     | 10       | 0       | 9.43   | 0       | 0              | 0         |
| <b>Max</b>                     | 62.5     | 50      | 40.32  | 20      | 19.51          | 15.38     |
| <b>Mean</b>                    | 42.15    | 25.45   | 19.43  | 6.50    | 4.52           | 1.95      |
| <b>Std dev</b>                 | 7.95     | 9.81    | 5.66   | 4.28    | 3.56           | 3.14      |
| <b>GLACIAL<br/>(N=30)</b>      |          |         |        |         |                |           |
| <b>Min</b>                     | 24.19    | 0       | 10     | 0       | 1.56           | 0         |
| <b>Max</b>                     | 62.5     | 50      | 40.32  | 16.67   | 16.67          | 8.06      |
| <b>Mean</b>                    | 41.60    | 27.64   | 18.75  | 6.14    | 4.55           | 1.31      |
| <b>Std dev</b>                 | 7.42     | 11.16   | 6.30   | 4.02    | 3.75           | 2.18      |
| <b>GLACIAL LDO<br/>(N=37)</b>  |          |         |        |         |                |           |
| <b>Min</b>                     | 27.78    | 12.5    | 9.43   | 0       | 0              | 0         |
| <b>Max</b>                     | 62.5     | 50      | 27.78  | 15.63   | 9.23           | 4.35      |
| <b>Mean</b>                    | 42.93    | 29.24   | 17.46  | 5.92    | 3.41           | 1.04      |
| <b>Std dev</b>                 | 7.22     | 9.04    | 3.96   | 3.63    | 2.01           | 1.37      |
| <b>INTERGLACIAL<br/>(N=75)</b> |          |         |        |         |                |           |
| <b>Min</b>                     | 10       | 0       | 9.43   | 0       | 0              | 0         |
| <b>Max</b>                     | 62.5     | 46.87   | 40.32  | 20      | 19.51          | 15.38     |
| <b>Mean</b>                    | 42.16    | 24.73   | 19.94  | 6.51    | 4.49           | 2.15      |
| <b>Std dev</b>                 | 8.41     | 8.82    | 5.89   | 4.43    | 3.39           | 3.32      |

**Tab. TS2.1.** Mineralogical composition and main statistic parameters from ODP 1240. Note that it has been calculated for the entire period, and then for the glacial LDOs, glacial and interglacial periods. *N* means the number of samples for each period.

### 2.2.11. References

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## 2.3. MAJOR ATMOSPHERIC REORGANIZATION IN THE TROPICAL BAND DURING KEY JUNCTURES IN HOMININ EVOLUTION

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Manuscript *in preparation*

### 2.3.1. Abstract

The connection between Early Pleistocene climate changes in the tropical band and appearance and/or disappearance of some of our hominin ancestors has long been proposed [deMenocal, 1995, 2004a; Bobe et al., 2002; Cameron, 2003; Wynn, 2004; Trauth et al., 2005, 2007; Pickering et al., 2007]. However, the absence of high resolution paleoclimate records, from one side, and the difficulty to obtain accurate absolute chronologies to precisely locate some hominin remains, from the other, has prevented a more detailed understanding of this apparent climate-human joint history. Here we review some high resolution paleoceanographic records from ODP Site 1240 in the Eastern Equatorial Pacific (EEP) that reveal a series of abrupt atmospheric reorganization transitions dominated by Intertropical Convergence Zone (ITCZ) migrations throughout the Early Pleistocene [Povea et al., 2016]. Among all these records, 1.8 Ma appears to be a key transition event towards an ITCZ more anchored in northern positions, ending a wide period of high instability. This is further supported by new radiogenic isotope data from the lithogenic sediment fraction at ODP 1240, which indicate a change in lithic source region towards South America after 1.85 Ma. A review of available paleoclimatic records from the equatorial Atlantic Ocean [Tiedemann et al., 1994], the Arabian Sea [deMenocal, 1995, 2004b; Clemens et al., 1996, 2008] and the Chinese Loess [Clemens et al., 2008], all sensitive to ITCZ changes, support this as a global ITCZ reorganization event. Interestingly, new high precise chronologies from South African flowstones [Pickering et al, in prep] allows, first, to identify a series of extreme wet events before 1.8 Ma. These enhanced rainfall conditions resulted from a complex interplay between specific orbital configuration conditions and the main state of the ITCZ, which allowed the occurrence of more extreme La Niña-like events. These South African flowstones chronology also allow to accurately place in the paleoclimatic record the first appearance of *Australopithecus sediba* revealing that these climatic conditions significantly benefited our ancestors in this region.

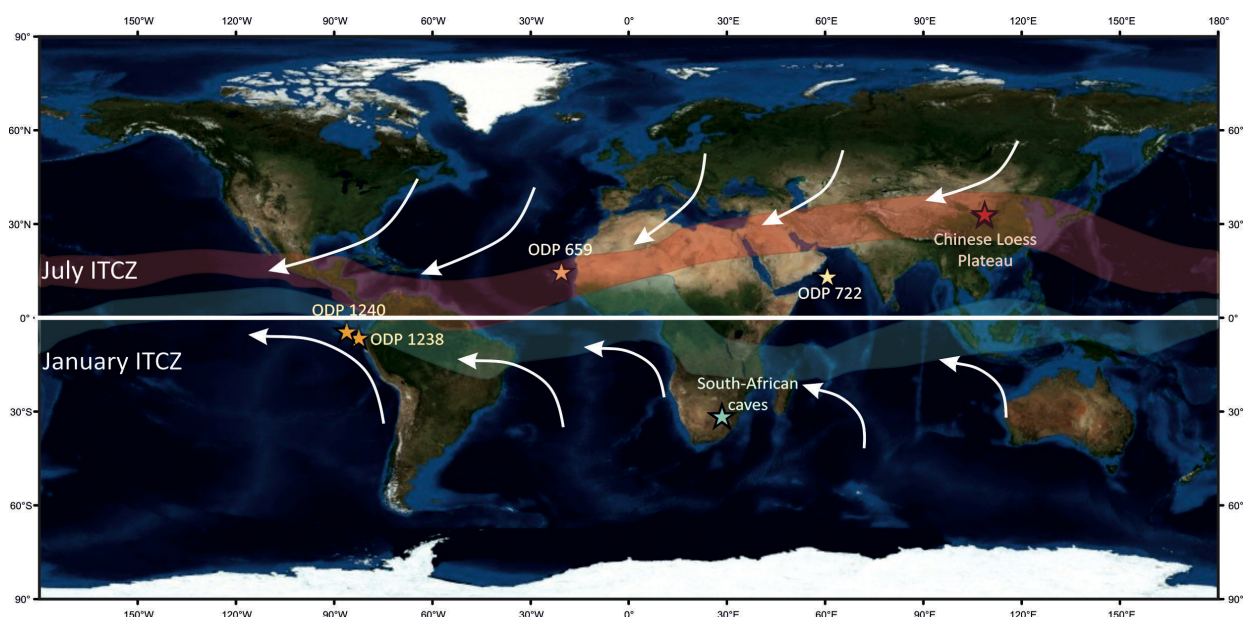
### 2.3.2. Introduction

Changes in Earth's climate oscillations have been tentatively related to pulses of hominin specification, proposing a cause-effect link between climate and human evolution. In particular, changes in the intensity and length of the glacial-interglacial cycles have been related to a shift towards more arid conditions in the African continent supported by a change in the vegetation dominance from C3 to C4 plants [deMenocal, 2004; Feakins et al., 2005; Hopley et al., 2007; Lee-Thorp and Sponheimer, 2012]. Evidences of climate aridification started in the late Miocene after 4 Ma presenting some fluctuations during the Pliocene [Feakins et al., 2005], then a major change to more open habitats occurs at 2.5 Ma [Reed, 1997], broadly at the time of the onset of the major north hemisphere glaciations [Raymo, 1994]. But C4 became a really dominant part of the flora biomass ecosystems after 1.8 Ma, when an environmental shift to grassier conditions occurred in both east and south Africa, and in concordance with the emergency of a more technologically advanced hominin (*homo erectus sensu lato*) [Lee-Thorp and Sponheimer, 2012] and the usage patterns of stone tools [Rogers et al., 1994]. Such climate shifts were not exclusive of Africa, evidence from the South American continent also support a marked change in the faunal diet, ranging from C3 to C4 plants [MacFadden et al., 1994].

According to the global paleoclimatic record, represented by the benthic  $\delta^{18}\text{O}$  stack, which serves as a indicator of the global ice volume/sea level changes, this 1.8 Ma transition occurred within the so-called "41-kyr world" when climate conditions progressively evolved towards a colder glacial cycles paced by the obliquity (41-kyr) frequency [Lisiecki and Raymo, 2005]. No major change in cyclicity nor in intensity can be observed for this time period. Nevertheless, records along the tropical belt show some major changes supporting the occurrence of a significant atmospheric reorganization from 2 to 1.5 Ma. These changes have been ascribed from an intensification of the Walker circulation in the Pacific Ocean [Ravelo et al., 2004; Etourneau et al., 2010] but without a clear teleconnection with the African climate has been described. The scarcity of available paleoclimate data comparing marine and terrestrial records, and the very low resolution of most of them, make it difficult to complete characterizations of these key climatic changes in the tropical and subtropical belt.

Here we review some new high resolution records from the EEP sediment core ODP Site 1240 retrieved from the Panama Basin ( $0^{\circ}1.311' \text{ N}$ ,  $86^{\circ}27.758' \text{ W}$ ), which revealed high instability in the atmospheric system from 2 to 1.5 Ma that we argued to reflect changes in the location of the Intertropical Convergence Zone (ITCZ) [Povea et al., 2016]. The global extent of some of these changes is evaluated by comparing, in a common age frame, ODP Site 1240 record with previous published results from Atlantic Ocean (ODP Site 659;  $18^{\circ}04.63' \text{ N}$ ,  $21^{\circ}01.57' \text{ W}$ ) [Tiedemann et al., 1994], Western Arabian Sea (ODP Site 722;

16°37.312'N, 59°47.755'E) [deMenocal, 1995, 2004a; Clemens et al., 1996, 2008], and loess record from China [Clemens et al., 1996, 2008] (Fig. 2.13). This demonstrates the global impact of some of these ITCZ migrations. We finally compare and discuss new cave carbonate or speleothem age data from South African caves [Pickering et al., 2011 and in prep], where unprecedentedly high precision ages allow to locate and examine the occurrence of some major wet events in the global evolution of the tropical belt. These new paleoclimatic frameworks allow us to discuss the interplay between environmental conditions and human evolution.



**Fig. 2.13.** Map of the marine ODP Sites [ODP 1240 (0°1.311' N, 86°27.758' W), ODP 659 (18°04.63'N, 21°01.57'W) and 722 (16°37.312'N, 59°47.755'E); yellow stars] and continental sites from Chinese Loess (red star) and flowstones from the Cradle of Humankind caves (located between 25° 50'S – 26° 02' S), South Africa (blue star). Seasonal ITCZ locations are marked with blue (January) and red (July) bands, and the trade winds convergence along the equator are labelled with white arrows.

### 2.3.3. Results and discussion

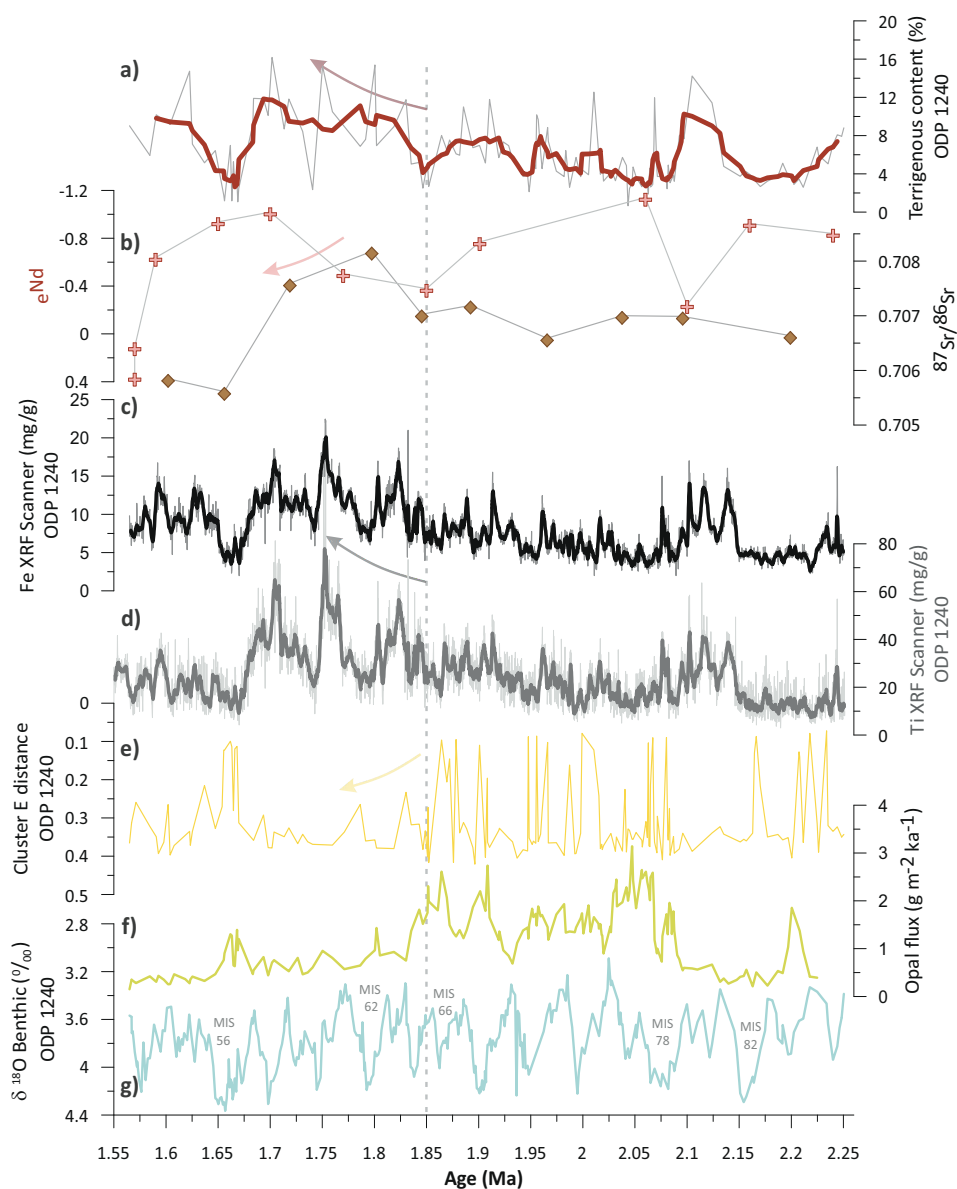
#### 2.3.3.1. Eastern Equatorial Pacific dust provenance

A multi proxy approach has been used to study both the terrigenous and the biogenic components of ODP 1240 sediments from 2.25 to 1.55 Ma [Povea et al., 2016]. In this way, changes in the wind dynamics, revealed by the terrigenous components, can be directly linked to the upwelling response (biogenic components) to better assess changes in this coupled tropical system. The chronology of the records is based on benthic  $\delta^{18}\text{O}$  stratigraphy by tuning to the LR04 stack [Lisiecki and Raymo, 2005]. Glacial periods are mostly highlighted by enhanced fluxes of biogenic components (i.e opal fluxes in Fig. 2.14) but a clear boundary in most of the analyzed proxies can be set at 1.85 Ma. Detail-

led analysis of the grain-size distribution (Fig. 2.14) reveal a change at that moment from poorly sorted fine and coarse modes to samples with a well sorted intermediate mode (Fig. 2.14; see supplementary material for more explanations). Lithic, Fe and Ti content show an upward trend along the studied period with a marked increase at 1.85 Ma (Fig. 2.14 and 2.15). These proxies are interpreted to reflect an intensification of the eolian transport through the strengthening of the trade winds. Prior to 1.85 Ma, terrigenous components are dominated by wet deposition due to the more proximal position of the ITCZ and later, a more northern ITCZ position enhances wind strength and coastal upwelling conditions. Biogenic components also support this hypothesis, since the high Si fluxes recorded prior to 1.85 Ma reflect the dominance of heavy silicified diatoms with large frustules (*Thalassiothrix spp.*), characteristic of stratified surface waters in the vicinity of the Equatorial Front [Kemp et al., 2000, 2006; Pike and Stickley, 2007] and thus supporting this closer position of the ITCZ to ODP 1240. After 1.85 Ma, productivity and nutrient proxies reflect the dominance of typically upwelling conditions [Povea et al., 2016].

Here we go deeper into the interpretation of these ODP 1240 proxies through the study of radiogenic isotopes,  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios, measured in the lithic fraction in order to assess the potential source of these dust particles and test its consistency with the discussed changes in the ITCZ position (see supplementary material for technical information on samples preparation and analytical methods). Strontium and Nd isotope analyses allow us to characterize accurately the region of dust provenance in many parts of the world [Biscaye et al., 1997; Grousset and Biscaye, 2005] (Nd isotopes are typically expressed in the epsilon notation ( $\epsilon_{\text{Nd}}$ ) which denotes the deviation of a measured  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio from a bulk earth value in part per 10,000). Our new results  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios from ODP 1240 show more radiogenic values after 1.85 Ma (Fig. 2.14), paralleling the trend to increased values observed in other dust proxies (Fe and terrigenous content). Note that all these proxy records show a significant drop associated with the glacial period at 1.65 Ma (MIS 56), where  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios show the lowest values (Fig. 2.14). This exceptional glacial period has already been interpreted to reflect a return to conditions comparable to those of glacial pre-1.85 Ma [Povea et al., 2016]. This increase in the radiogenic composition of the dust particles, particularly after 1.85 Ma, seems to suggest a significant shift of the source region. Maximum values in  $^{87}\text{Sr}/^{86}\text{Sr}$  concentrate on the south Andean Arc with very distinctive values to those of Central America (Fig. S2.11), while  $\epsilon_{\text{Nd}}$  have a more scatter distribution and therefore, these results are less conclusive on the dust source. According to the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\epsilon_{\text{Nd}}$  data, the ITCZ could have acted as a dust barrier from Northern or Southern hemisphere, depending on its migration. Thus, before 1.85 Ma and also at MIS 56, the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  is consistent

with a material source region from Central America (Fig. 2.14 and Fig. S2.11 supplementary material). Therefore, this reduced radiogenic signal along with a minor terrigenous arrival to the EEP, endorses a strong weakening of the trade winds associated with a dominant southern position of the ITCZ. In contrast, this trend breaks from 1.85 Ma when the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\epsilon_{\text{Nd}}$  values become more radiogenic (Fig. 2.14), suggesting a dust input from South America, from the Andean arc (Fig. S2.11). The parallel increase in the terrigenous input supports the dominance of stronger trade winds linked to a northern ITCZ position. This atmospheric reorganization is in line with a major intensification of Walker Circulation reported previously in base to enhanced of a thermal gradient across the Pacific tropical region [Ravelo et al., 2004; Wara et al., 2005].



**Fig. 2.14.** EEP dust provenance through the detailed analysis of biogenic and lithogenic fraction from ODP 1240. (a) Terrigenous content (%) [Povea et al., 2016]; (b)  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\epsilon_{\text{Nd}}$ ; (c) (d) Iron (Fe) and Titanium (Ti) content (mg/g) from XRF Core Scanner; (e) Cluster E distance [Povea et al., 2016]; (f) Opal flux ( $\text{g m}^{-2} \text{ka}^{-1}$ ) and (g)  $\delta^{18}\text{O}$ -Benthic ( $\text{‰}$ ) [Povea et al., 2016]. Marine Isotope Stages (MIS) 56, 62, 66, 78 and 82 are located according to Pillans and Gibbard (2012).

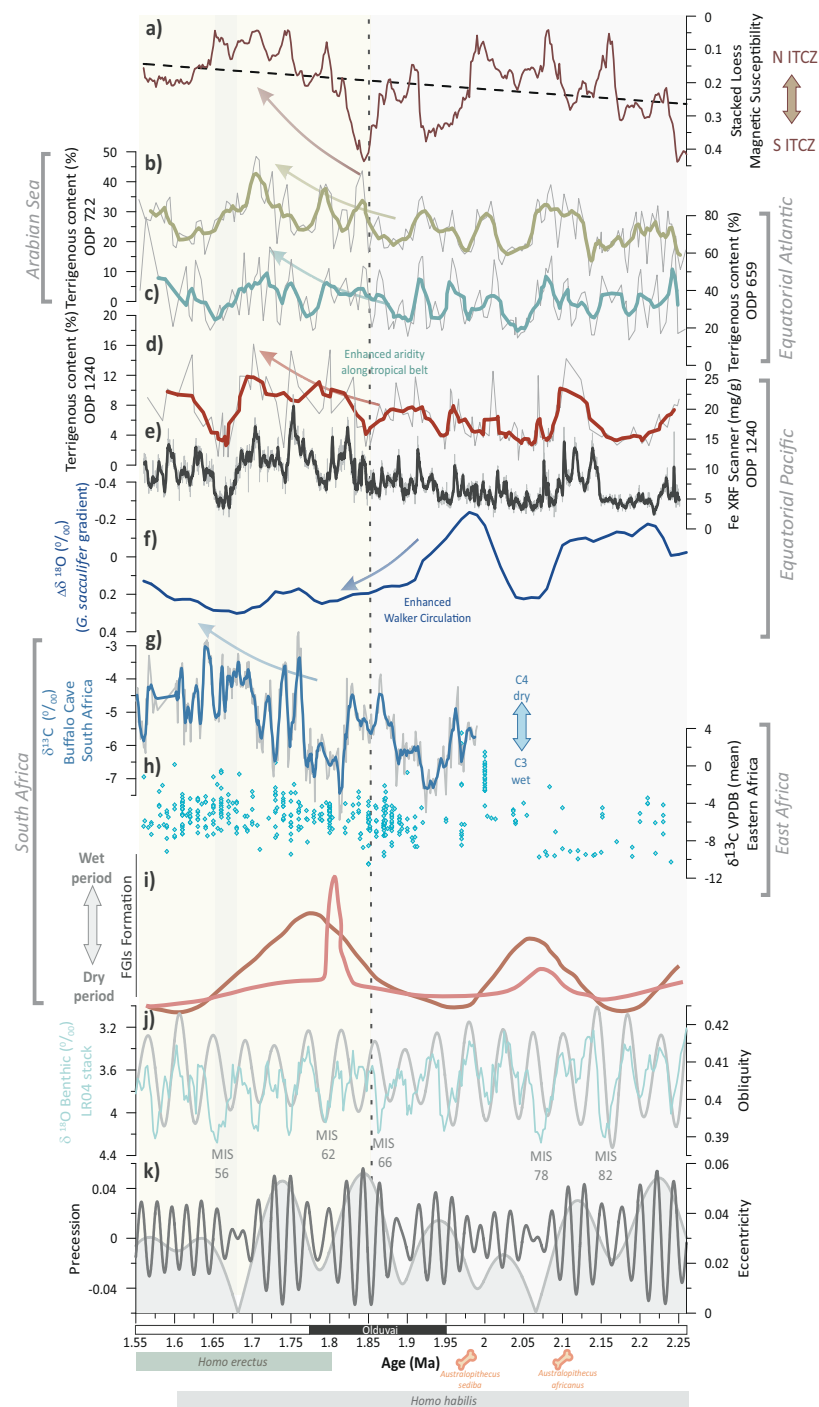


### 2.3.3.2. Teleconnections along the tropical band

In order to evaluate the global implications of the described atmospheric changes in the EEP, a set of records under the influence of the ITCZ, with comparable resolution and solid chronological control, have been selected (Fig. 2.13, 2.15 and S2.10): the terrigenous content of ODP 659 from the eastern tropical Atlantic Ocean [Tiedemann et al., 1994] and of ODP 722 from the Arabian Sea [deMenocal, 1995, 2004a; Clemens et al., 1996, 2008], and the magnetic susceptibility stack record from Chinese Loess [Clemens et al., 1996, 2008]. Chronology from ODP 659 has been readjusted to those from ODP 1240 (see supplementary material) and the comparison of the  $\delta^{18}\text{O}$  benthic records from the three marine sites show very consistent chronologies, allowing robust comparison between the sites (Fig S2.10). The terrigenous content for the three marine records show a strong parallelism (Fig. 2.15), confirming in all cases the enhanced arrival of terrigenous components between 1.85 and 1.65 Ma (MIS 56). This is consistent with an overall intensification of the trade winds and/or tropical land aridification after 1.85 Ma. Indeed, Chinese Loess also registers an important shift at 1.85 Ma with the onset of a major decrease of the magnetic susceptibility values [Clemens et al., 2008]. This is consistent with the proposed northwards migration of the ITCZ in the Pacific sector (ODP 1240) after 1.85 Ma which would have led to stronger summer monsoon over the Chinese Plateau.

In fact, this 1.85 Ma turning point is also recorded in African paleosol carbonates [Cerling and Hay, 1986; Cerling, 1992; Wynn, 2000, 2004; Feakins et al., 2005, 2013; Levin, N., 2013]. This shift has been related to an enhanced global aridity episode which generated an environmental change in African low latitudes, from woodland C3-pathway to C4 arid-adapted grassland vegetation (Fig. 2.15) [Cerling and Hay, 1986; Cerling, 1992; Wynn, 2000, 2004; Feakins et al., 2005, 2013; deMenocal, 2004]. In addition, this aridification trend has been also registered in large mammals from Turkana Basin, eastern Africa [Hernández Fernández and Vrba, 2006]. This arid shift is also detected along the South American continent with a forest declination and its replacement with extensive grasslands [Pascual, 2006].

Furthermore, we analyzed our terrigenous results using frequency analysis methods to determine significant periodicities of variability. The terrigenous content spectrum shows the highest power in the precession band, but also has considerable power at 100-kyr (Fig. S2.12). Thus, frequency analysis demonstrates the strong orbital control in the aridity conditions of the tropical zones, which is dominated by the precession band.



**Fig. 2.15.** Comparison of early Pleistocene's climate evolution along the tropical region. (a) Stacked loess magnetic susceptibility [Clemens et al., 2008]; (b) Terrigenous content ODP 722 (wt%) [deMenocal, 1995, 2004a; Clemens et al., 1996, 2008]; (c) Terrigenous content ODP 659 (wt%) [Tiedemann et al., 1994]; (d) Terrigenous content ODP 1240 (wt%) [Povea et al., 2016]; (e) XRF core scanner Fe ODP 1240 (mg/g) [Povea et al., 2016]; (f) Oxygen isotope difference ( $G. sacculifer$ ) between ODP 851 (eastern Pacific) [Cannariato and Ravelo, 1997] and ODP 806 (western Pacific) [Berger et al., 1993; Jansen et al., 1993]; (g)  $\delta^{13}C$  (‰) Buffalo Cave (24° 08'S, 29° 11'E), South Africa [Hopley et al., 2007a]; (h) Compilation of  $\delta^{13}C$  VPDB (mean) from pedogenic carbonates of the eastern Africa [Levin, N., 2013]; (i) Wet events from Cradle of Humankind flowstones, South Africa [Pickering, et al., in prep; 2011]; (j)  $\delta^{18}O$  Benthic LR04 stack (‰) [Lisiecki and Raymo, 2005] and obliquity [Laskar et al., 2004]; (k) Precession and eccentricity of the astronomical solution [Laskar et al., 2004]. Marine Isotope Stages (MIS) 56, 62, 66, 78 and 82 are located according to Pillans and Gibbard (2012), along with the paleomagnetic record. Disappearance of *Australopithecus africanus* (2 Ma) and the appearance of *Australopithecus sediba* (1.95 Ma) have been marked. Note also the periods with the existence of *Homo habilis* and *Homo erectus* in African continent.



### 2.3.3.3. Climate imprints on South African Caves

South Africa's climate, although further south of the tropical band, is today governed by the seasonal migration of the ITCZ, whose southern position contributes to enhanced rainfalls over this region [Indeje et al., 2000]. A speleothem record from Buffalo Cave (flowstone  $\delta^{13}\text{C}$ ) offers a unique continuous paleoclimatic signal from the region with an exceptional resolution for the discussed period [Hopley et al., 2007a]. Among the obliquity-paced oscillations, the  $\delta^{13}\text{C}$  curve presents a migration phase toward less negative values centered between 1.80-1.70 Ma, and interpreted as an change towards more dominant C4 plants due to an increase in aridity [Hopley et al., 2007a, 2007b], a situation consistent with the discussed more dominant northward position of the ITCZ after 1.85 Ma, albeit with an apparent 50 ka delay in onset.

Further south, the area known as the Cradle of Humankind (CoH) (located between 25° 50'S – 26° 02' S) hosts a series caves and provides evidences of a series of wet events, represented by calcium carbonate flowstones inter-bedded between fossiliferous sediments, which form the richest collection of early hominin site in the world [Dart, 1925; Broom, 1938; Clarke et al., 1970; Berger et al., 2010, 2015]. Recent improvements in the Uranium-Lead (U-Pb) dating method [Pickering et al., 2010] has provided a new set of accurate absolute ages for the cave carbonates (speleothems, specifically flowstones) preserved in these caves [de Ruiter et al., 2009; Dirks et al., 2010; Pickering and Kramers, 2010a; Pickering et al., 2011a, 2011b]. These new ages improve substantially the accuracy of the previous published ages these sites [Pickering et al., 2011a, 2011b] and allow us to precisely compare them within the other discussed paleoclimatic records (Fig. 2.15). During the studied period two major flowstone growth intervals (FGIs) occurred concretely at 2.06 and 1.8 Ma, although other older wet events occurred at 2.26 and 2.7 Ma. In contrast, after 1.8 Ma only two very weak events were recorded by minor FGIs dated at 1.4 and 1.5 Ma [Pickering et al., in prep]. Flowstones formation implies extreme climatic conditions, characterized by enhanced rainfalls and effective precipitation. The most intense of these FGIs was that centered at 1.8 Ma and it is coincident with the Buffalo Cave flowstone  $\delta^{13}\text{C}$  record with an intense and persistent wet event right before the described transition towards more arid conditions [Hopley et al., 2007a]. Therefore, both South African records points toward the occurrence of an extreme wet event right after the 1.85 Ma transition, when the whole tropical system is in a transient period towards stronger trade winds and more arid conditions on the tropical belt. Interestingly, a humid phase superimposed on a long term aridification trend has also been described in the lake record from East Africa and also centered at 1.8 Ma [Trauth et al., 2005].

The origin of these intense South African wet events is puzzling as there appears to be no single forcing factor. Both the 2.06 and 1.8 Ma FGIs were formed during glacial periods (MIS 78 and MIS 64 respectively), as is the case of the other previous and later FGIs. All the FGIs until 1.8 Ma occurred during eccentricity minima, an orbital configuration that would lead to minimum hemispheric contrast in insolation, a situation that favors the anchorage of the ITCZ in fixed latitude. But the two weak events after 1.8 Ma occurred during maximum in eccentricity. Apparently, something changed in the climate system after 1.8 Ma that was not so favorable to the occurrence of these extreme wet conditions in South Africa, probably related to the tropical transition towards a more northward ITCZ location. Nowadays, the wettest events in this South Africa region occur during years of strong “la Niña” conditions (Fig. S2.13) [Pohl et al., 2010], this effect is significantly boosted when it is combined with a positive phase of the Antarctic Oscillation (AAO) [Kidson, 1988; Thompson and Wallace, 2000] and enhanced westerly storm tracks [Stuut et al., 2002; Green et al., 2015]. Thereby, these extreme wet intervals during the early Pleistocene could result from a combination of factors, such as the external orbital forcing, the glacial climate state and a tropical atmospheric configuration more prone to ITCZ southern locations. Overall they could have led to an increase in frequency and/or strength of “la Niña-like” events and/or positive AAO phase which drove extreme wet events in the region.

#### 2.3.3.4. Climate and human evolution linkages

These new U-Pb dates from the CoH and the identification of FGIs allows for the hominin fossil record from this region to be accurately placed in a global paleoclimatic context. The last appearance of *Australopithecus africanus* occurred right before the wet episode at 2.06 Ma [Pickering and Kramers, 2010; Herries and Shaw., 2011] and after this episode, at about 1.95 Ma, the *Australopithecus sediba* appeared [Berger et al., 2010]. After the most dramatic wet episode (the one at 1.8 Ma), when the aridification trend accelerated in South Africa, the Australopithecines (both *Au. Africanus* and *Au. Sediba*) have disappeared from Sterkfontein and Malapa, with *Paranthropus robustus* and early *Homo* appearing at Swartkrans, Drimolen and Kromdraai [Broom and Robinson, 1950; Clarke, 1977; Brain, 1981; Grine et al., 1996; Keyser et al., 2000; de Ruiter et al., 2009; Moggi-Cecchi et al., 2010; Pickering et al., 2011a]. It is difficult to establish a direct causal effect between these climatic and human changes [Behrensmeyer, 2006], but the temporal link supports the existence of strong environmental pressures associated with major changes in hominin distribution in South Africa. The interest of these new data relies in the fact that the environmental pressure was not only due to the general aridification trend described in Africa

for the last few millions of years [Cerling and Hay, 1986; Cerling, 1992; Wynn, 2000, 2004; Feakins et al., 2005, 2013; deMenocal, 2004; Hernández and Vrba, 2006]. The discussed high resolution paleoclimatic records demonstrate the occurrence of some more rapid transitions, with some reversals to much wetter conditions which added extra-pressure on the environment [Trauth et al., 2005; Hopley et al., 2007a]. In particular, the occurrence of the dramatic wet episodes discussed above should have acted as a setback to the existing hominin species, which were already in the process of adapting to a dryer ecosystems. The overall picture shows a very unstable environment that could have contributed to the appearance and disappearance of the different South Africa genera.

This time period also sees the first appearance of the genus *Homo*, at 2.4 Ma in East Africa [Hill et al., 1992] and possibly as early as 2.8 Ma [Villmoare et al., 2015]. The described climate shift at 1.8 Ma, which marks the onset of an intensification phase in the longer trend African aridification process, appears to be related to the *Homo habilis* extinction in favor of the appearance of *Homo erectus*. This shift would have exposed *Homo habilis* to a new habitat rules and, as a consequence, to a change of food resources. This induces a dietary change and a progressive weakening of *Homo habilis* species, which together a process of natural selection and a phyletic transformation could lead to new species, *Homo erectus*. This new species is well-adapted to the emergent habitat and improves the hunting technique thanks to the further development of the stone tools. This hunt progress would have increased meat consumption and a rise of protein ingestion, consequently enhancing dopamine uptake [DeLouize et al., 2016]. In fact, the emergence and spreading of *Homo erectus* coincides with the highest extinction rates of carnivorous species in eastern Africa at 1.8 Ma [Lewis and Werdelin, 2007]. This dietary change promotes the development of new capabilities such as enhanced visuospatial memory, social abilities and the ability to run long distances. These emergent competences would have allowed the migration of *Homo erectus* specimens out of Africa at 1.8 Ma.

#### 2.3.4. Conclusions

Tropical paleoclimatic records reveal the 2.2 to 1.5 Ma as a particular unstable period attributed to global reorganization phases in the main position of the ITCZ, which ultimately contributed to the aridification of some regions of the African continent. A major change occurred after 1.85 Ma with a northward displacement of the ITCZ in the Pacific sector associated to an enhancement of the Walker circulation. This was associated to an aridification phase in the African continent. Well dated flowstone records from South Africa show the occurrence of extraordinary wet intervals over imposed this general aridification trend.

The most remarkable wet event was centered at 1.8 Ma (corresponding to the glacial MIS 62) a key moment in hominin speciation. These anomalous wet conditions are discussed to reflect a climatic situation that allowed the recurrent development of intense “la Niña” like events. These overall variable climatic conditions, with intense abrupt climate reversals toward humid conditions, appear to have produced a strong environmental pressure and can be related to the appearances and/or disappearances of some *Homo* and *pre-Homo* species.

### 2.3.5. Supplementary material

#### 2.3.5.1. Study area

ODP 1240 (0°01.31 N 86° 27.76 W; 2921 meters depth) was retrieved from the northern flank of Carnegie Ridge in the Panama Basin, in the Eastern Equatorial Pacific (EEP) [Weltje, 1997; Mix et al., 2003] (Fig. 2.13). Its location under the equatorial upwelling influence driven by the southeasterly trade winds and at the northern edge of the Atacama dust plume [Molina-Cruz, 1977] that provides a key record to assess the variability the terrigenous input processes.

The eastern equatorial Atlantic dust record [Tiedemann et al., 1994] is based on ODP 659 (18°04.63' N 21° 01.57' W; 3070 meters depth) (Fig. 2.13), located under the African easterly jet stream [Tetzlaff and Peters, 1986]. This location is perfect for recording the Saharan dust plume that arrives to the Atlantic Ocean.

The lithogenic record from the western Arabian Sea [deMenocal, 1995, 2004a] is based on ODP 722 (16°37.312'N, 59°47.755'E; 2028 meters depth) (Fig. 2.13), located near the crest of the Owen Ridge [Prell, W. L. et al., 1989]. This site is located in a strategic place to study the dust variability to the deep ocean associated to the ITCZ and monsoonal transport.

#### 2.3.5.2. Atmospheric and oceanographic features

This tropical region is extremely susceptible to atmospheric changes, displaying the interaction of the trade winds systems and the fluctuation of the Intertropical Convergence Zone (ITCZ) position (Fig. 2.13). The equatorial atmospheric circulation marks deeply the EEP oceanographic pattern circulation. The surface ocean circulation pattern is characterized by the asymmetry of surface currents, north and south of the equator, reflecting the location of the ITCZ and the convergence of the northeast and southeast winds [Wyrtki, 1974]. The atmospheric circulation is weakest beneath this zone and strengthens towards the north and south [Hovan, 1995].

At present, ITCZ is placed north of Equator and it migrates southward during February to April when southeasterly trades are weaker (Fig. 2.13). Instead, during Southern Hemisphere winter, the southeasterly trades are stronger, the ITCZ is positioned at about 10° N and both maximum upwelling and eolian transport from the mainland is produced.

### 2.3.5.3. Methods

The retrieved sedimentary sequence of ODP 1240 is mainly constituted by high fossil mud with variable composition along the sequence [Mix et al., 2003]. Lithogenic content was isolated after the biogenic fraction removal by applying the procedure outlined in [Povea et al., 2015], and is expressed in percent by weight.

We measured radiogenic isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\epsilon_{\text{Nd}}$  values) on the isolated lithogenic fraction in two different laboratories following the leaching procedures summarized in Hemming et al. (2007) at Lamont-Doherty Earth Observatory of Columbia University (LDEO) and Povea et al., (2015). Strontium samples were further prepared at Lamont-Doherty Earth Observatory (LDEO) and Nd samples were prepared at Imperial College London.

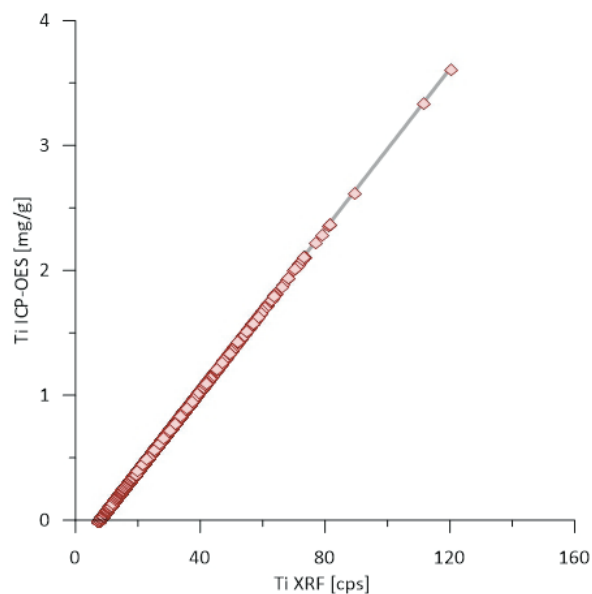
At LDEO, a representative ~50 mg subsample was taken for hotplate digestion. To break down silicates samples were treated with a mixture of  $\text{HNO}_3$ :HF of 4:1. Dissolved samples were dried down, taken up in 3 N  $\text{HNO}_3$  and loaded on cleaned and equilibrated 0.03 ml columns of Eichrom's strontium specific resin. Approximately 750 microliters of 3 N  $\text{HNO}_3$  was passed through the columns. Strontium was eluted with approximately 750 microliters of quartz-distilled water, and dried for analysis. Strontium was subsequently loaded onto tungsten filaments using a  $\text{TaCl}_5$  solution [Birck, 1986]. Isotope measurements were made on a VG Sector 54 multiple collector thermal ionization mass spectrometer (TIMS), using a multidynamic collection routine and an exponential fractionation correction based on  $^{86}\text{Sr}/^{88}\text{Sr}$  of 0.1194. Measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were corrected to the recommended value for NBS987 of 0.710245 using the standards measured during the same session as the samples.

At Imperial, a representative ~50 mg subsample was taken for hotplate digestion. To break down silicates and organic within the sample, 1ml of nitric acid, 0.8 ml of perchloric acid and 2ml of hydrofluoric acid were added to each samples. Samples were left on a hotplate at 120°C in for at least four days with intermittent short periods of ultrasonification to aid digestion. Samples were dried down at 230°C and converted to nitrate form using concentrated nitric acid. Dissolved samples were subjected to two stages of ion chromatography to separate Nd from the sample matrix using cation exchange resin (Biorad AG50W-X8, and Eichrom Ln Spec (see Struve et al. (2016) for details on the first column and Cook et al. (2013) for details on the second column). Neodymium isotope measurements were conducted on a Nu Instruments multiple collector inductively coupled plasma mass spectrometer (MC-ICP-MS) in static mode. To correct for instrumental mass bias  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios were corrected to  $^{146}\text{Nd}/^{144}\text{Nd}$  ratios of 0.7219 using an exponential law. Samples were monitored for interferences from  $^{144}\text{Sm}$ , which were well below the

correctable level of 0.1% of the  $^{144}\text{Nd}$  signal in all samples. Repeated analysis of Nd standard JNdi were used to correct measured  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios relative to the recommended ratio of 0.512115 [Tanaka et al., 2000] over the course of four measurement sessions, which yielded a precision of 20 to 26 ppm. Repeat processing of reference material BCR-2 gave a  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  $0.512640 \pm 0.000019$  ( $n=5$ ), in excellent agreement with the published value by Weis et al. (2006).

Iron (Fe) and Titanium (Ti) XRF composition of ODP1240 was determined by means of X-ray fluorescence from the University of Bremen at the surface sediment over an 1 cm<sup>2</sup> area, using 30 seconds count time, 20 kV X-ray voltage and an X-ray current of 0.087 mA. The resulting data are element intensities in counts per second (cps), with all the intensities located above the detection limits [Richter, 2006]. Concentrations have been obtained through the conversion from the intensity values and the calibration with absolute elemental concentrations obtained from 30 sediment samples selected along this section. Thus, sediment samples were analyzed by ICP-OES at the CCiT-UB after total digestion of 50 mg of dried bulk sediment material in a pressure digestion system with a mixture of 3 ml  $\text{HNO}_3$  65%, 2 ml HF 40%, and 2 ml HCl 32%. After decomposition, the samples were heated to dryness, re-dissolved in 5 ml of 6.5 %  $\text{HNO}_3$  and homogenized in the microwave. Ti element was analyzed by ICP-OES in a Perkin Elmer Optima 3300 RL with a precision better than 2%. The accuracy of element determinations was checked using standard reference materials. The ICP-OES obtained values were used to transform the XRF data into concentration values (mg/g). Correlation equations with  $r^2= 0.99$ , indicate a high correlation between both methods, thus allowing the data conversion (Fig. S2.9 supplementary material).

Subsequently, we performed a spectral analysis of the tropical terrigenous records (ODP 1240, 659 and 722) using REDFIT software [Schulz and Mudelsee, 2002], with a rectangular window. Evolutionary wavelet spectra were obtained by the Matlab script provided by [Torrence and Compo, 1998].



**Fig. S2.9.** Correlation analysis between Ti values obtained with XRF Core Scanner method (x) and with ICP-OES (y) method, with a correlation coefficient of 0.99.

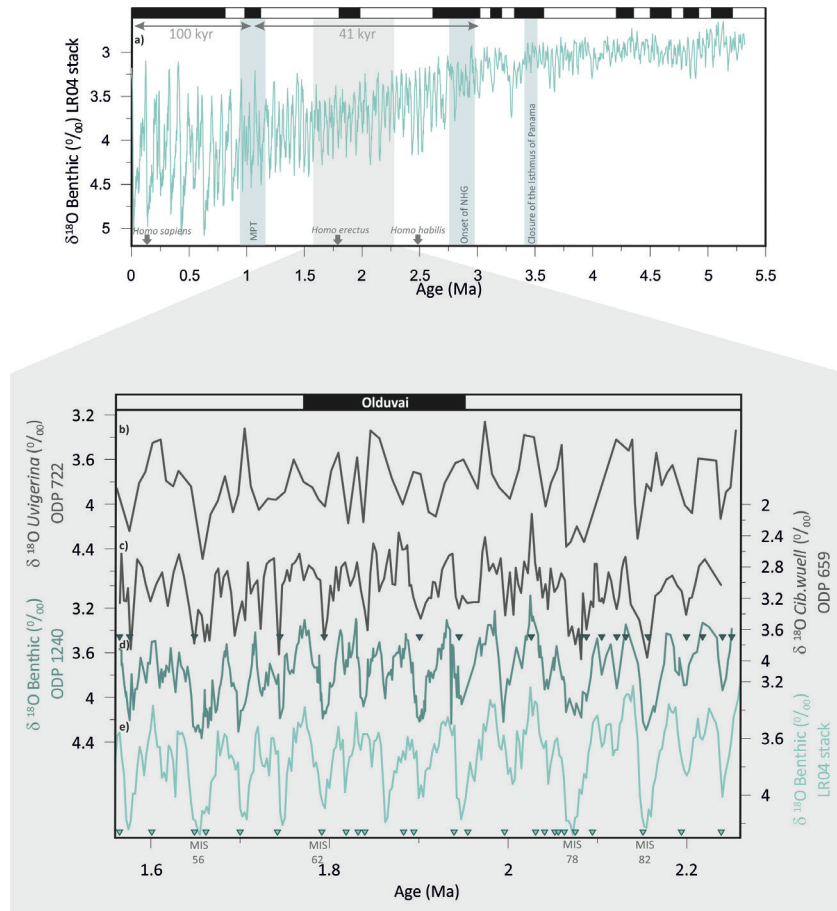
#### 2.3.5.4. Chronological framework

The age model is based on the comparison of high resolution stratigraphy of benthic isotopic oxygen record from ODP 1240 with LR04 stack [Lisiecki and Raymo, 2005] (Fig. S2.10). The studied period corresponds to the Early Pleistocene (1.6 to 2.2 Ma), and during this period occurred the greatest changes in the sedimentary composition of ODP 1240 sediments likely related a major reorganization of the Equatorial atmospheric system.

Furthermore, the age model of ODP 659 has been modified by correlation with ODP 1240 and LR04 stack (Fig. S2.10).

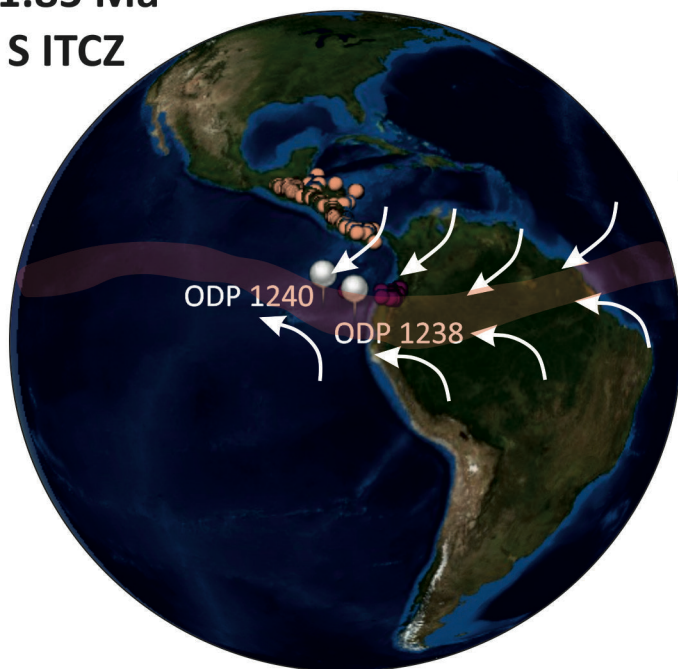


### 2.3. Major atmospheric reorganization in the tropical band



**Fig. S2.10.** Chronological framework for ODP Sites 1240, 659 and 722. (a)  $\delta^{18}\text{O}$  Benthic LR04 stack ( $^{\circ}/_{\text{oo}}$ ) [Lisiecki and Raymo, 2005]; (b)  $\delta^{18}\text{O}$  *Uvigerina* ODP 722 ( $^{\circ}/_{\text{oo}}$ ) [deMenocal, 1995, 2004b; Clemens et al., 1996, 2008]; (c)  $\delta^{18}\text{O}$  *Cibicides wuellerstorfi* ODP 659 ( $^{\circ}/_{\text{oo}}$ ) [Tiedemann et al., 1994]; (d)  $\delta^{18}\text{O}$  Benthic ODP 1240 ( $^{\circ}/_{\text{oo}}$ ) [Povea et al., 2016]; (e)  $\delta^{18}\text{O}$  Benthic LR04 stack ( $^{\circ}/_{\text{oo}}$ ) [Lisiecki and Raymo, 2005]. Chronology from ODP 1240 was developed by comparison of high-resolution ODP 1240  $\delta^{18}\text{O}$  Benthic and global  $\delta^{18}\text{O}$  LR04 stack, and tie points are shown as a light green triangles. Chronology from ODP 659 has been readjusted to ODP 1240, and tie points are marked as dark green triangles. Marine Isotope Stages (MIS) 56, 62, 66, 78 and 82 are located according to Pillans and Gibbard (2012), along with the paleomagnetic record.

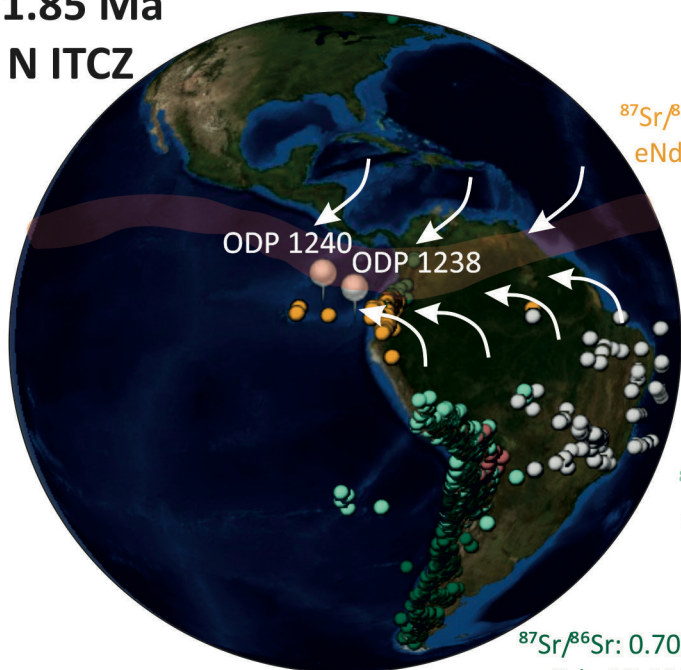
**>1.85 Ma**  
**S ITCZ**



**Central American Arc**  
 $^{87}\text{Sr}/^{86}\text{Sr}$ : 0.70273-0.70433, Av: 0.704626  
 eNd: -10.6898-11.25551, Av:5.945049

**Colombia**  
 $^{87}\text{Sr}/^{86}\text{Sr}$ : 0.703765-0.704804, Av: 0.704177  
 eNd: -0.40965-10.20213, Av:4.595118

**<1.85 Ma**  
**N ITCZ**



**Ecuador**  
 $^{87}\text{Sr}/^{86}\text{Sr}$ : 0.70281-0.72675, Av: 0.704255  
 eNd: -24.7348-17.59526, Av:4.201555

**Brasil**  
 eNd: -36.9071-11.15797, Av:-3.03508

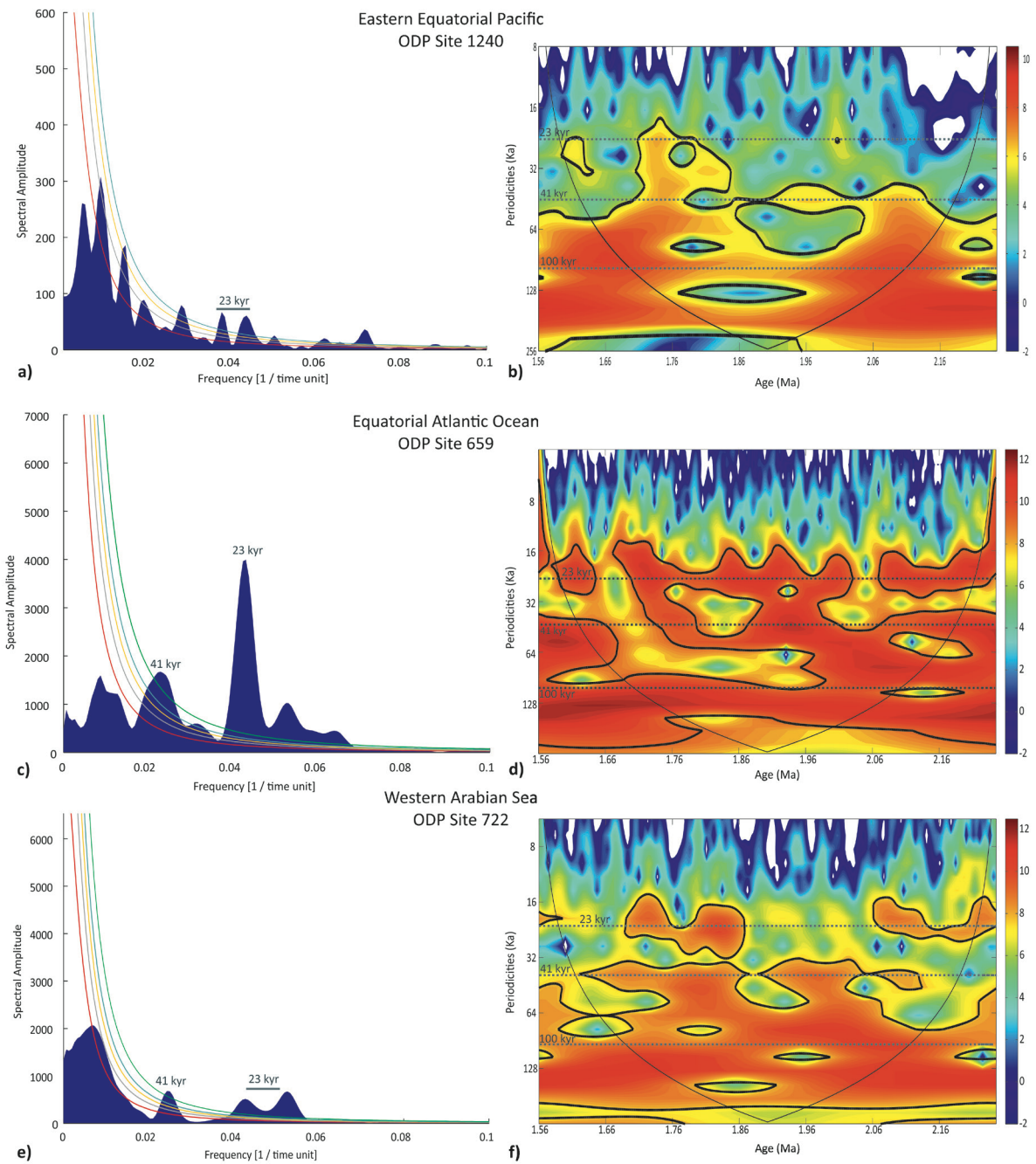
**Atacama desert**  
 eNd: -12.46494-3.784347, Av:-5.316565

**Andean Arc\_extended**  
 $^{87}\text{Sr}/^{86}\text{Sr}$ : 0.7027-1.2748, Av: 0.709996  
 eNd: -26.1198-9.519388, Av:-3.84123

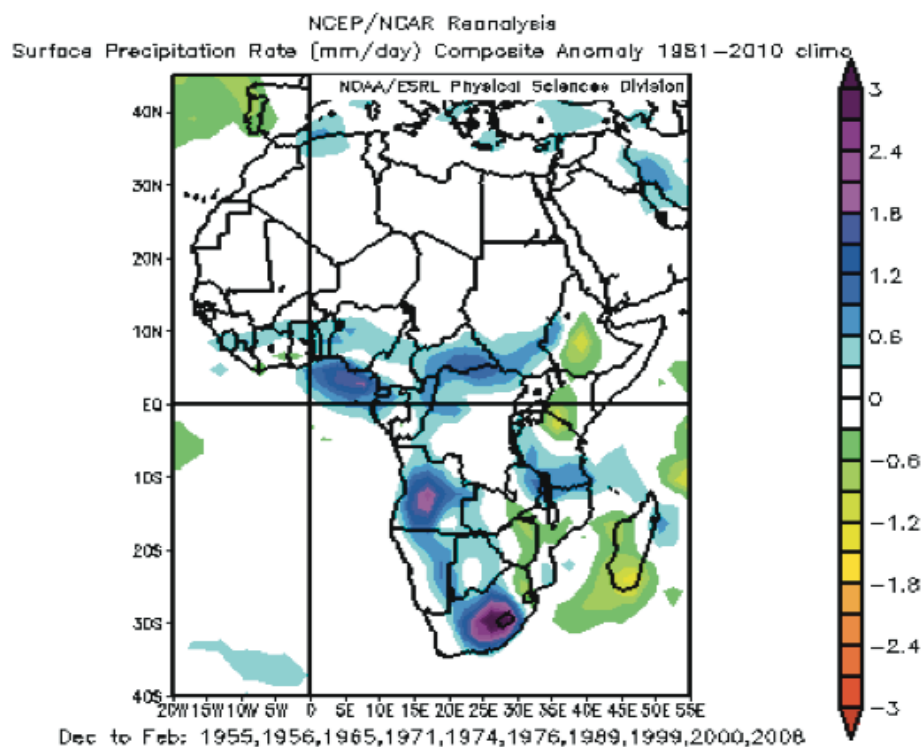
**Andean Arc**  
 $^{87}\text{Sr}/^{86}\text{Sr}$ : 0.7028-0.736315, Av: 0.705664  
 eNd: -12.4649-16.52238, Av:-0.31679

**Fig. S2.11.** Dust provenance to ODP 1240 from South American continent. Note that the Andean arc presents higher values in  $^{87}\text{Sr}/^{86}\text{Sr}$  than Central America. According to the  $^{87}\text{Sr}/^{86}\text{Sr}$  data, the ITCZ could have acted as a dust barrier from Northern or Southern hemisphere, depending from its migration. Thus, minimum values in  $^{87}\text{Sr}/^{86}\text{Sr}$  reflect a southwards ITCZ migration that would have allowed a greater input material from Central America. Instead, maximum values in  $^{87}\text{Sr}/^{86}\text{Sr}$  demonstrate a northern position of the ITCZ with a major dust supply from South America.

### 2.3. Major atmospheric reorganization in the tropical band



**Fig. S2.12.** Spectral analysis and evolutionary wavelet analysis of the terrigenous records from ODP 1240, 659 and 722. Note that the spectral analysis the dominance of the 23-kyr and 41-kyr cycles, while the wavelet analysis are not so clear and also show the dominance of the 100-kyr.



**Fig. S2.13.** Change of the rainfall pattern in Africa during “La Niña” events, based in a precipitation rate composite (mm/day) from 10 events between December and February. The anomaly is relative to the time period from 1981-2010. Note that South Africa receives a greater amount of rainfall during La Niña events. The CoH caves are marked with a red star and eastern African lakes with a black line. Precipitation rate data was downloaded from NOAA ([www.esrl.noaa.gov](http://www.esrl.noaa.gov)).

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## 2.4. RESUM DE RESULTATS

L'estudi detallat de la fracció lítica i biogènica ens aporta informació sobre canvis en el sistema acoblat atmosfera-oceà al Pacífic equatorial. L'anàlisi d'aquesta interconnexió atmosfera-oceà s'ha dut a terme durant el Plistocè inferior com revela la cronostratigrafia acomplerta en aquesta Tesi gràcies a l'anàlisi del registre de isòtops de l'oxigen ( $\delta^{18}\text{O}$ ) d'alta resolució realitzat en foraminífers bentònics del ODP 1240. Així, el model d'edat ha estat realitzat a partir de la comparació del registre bentònic de  $\delta^{18}\text{O}$  del ODP 1240 amb la corba patró LR04 de foraminífers bentònics [Lisiecki and Raymo, 2005], que inclou punts d'ancoratge cada 27.000 anys amb un coeficient de correlació de 0,76. La seqüència estudiada correspon al Plistocè inferior, que comprèn el període de temps entre 2,25 i 1,56 Ma, des de l'etapa isotòpica marina (MIS, de l'anglès Marine Isotope Stage) 82 fins a la 52. Aquest registre bentònic de  $\delta^{18}\text{O}$  del ODP 1240 presenta valors entre 3,2 i 4,5 ‰, amb oscil·lacions periòdiques corresponents a cicles glacials/interglacials i transicions molt marcades. Durant aquest interval temporal hi ha tres períodes glacials que són especialment destacables per la seva llarga durada temporal i per presentar els valors més pesats de  $\delta^{18}\text{O}$ , MIS 58 (1,67-1,65 Ma), MIS 78 (2,09-2,07 Ma) i MIS 82 (2,15-2,17 Ma).

### 2.4.1. Caracterització i procedència de la fracció lítica al Pacífic equatorial

Per a l'estudi de les condicions atmosfèriques, és de gran importància el correcte aïllament de la fracció lítica a través de l'eliminació de l'elevat contingut de components biogènics que es produeixen en aquesta zona com a conseqüència de l'aflorament equatorial i l'elevada productivitat primària associada (cf. secció 2.1. i Annex I). Després de l'aplicació de diferents protocols estàndards, que funcionen en aquesta i en altres regions geogràfiques, es va procedir a la comprovació del bon funcionament d'aquests mitjançant una anàlisi granulomètrica i microscòpica del sediment processat. Aquesta comprovació va demostrar que els protocols estàndards no funcionen satisfactòriament per a l'eliminació total d'aquestes restes biogèniques. Els principals problemes detectats van ser en la eliminació de la matèria orgànica, amb una elevada presència de pèl·lets fecals, i particularment en l'eliminació de components silícics, amb abundants radiolaris i diatomees. Conseqüentment, es van realitzar una sèrie de modificacions dels protocols estàndards utilitzats anteriorment [Chester and Hughes, 1967; Rea and Janecek, 1981; Mortlock and Froelich, 1989; DeMaster et al., 1991; Muller and Schneider, 1993; Hovan, 1995; McCave et al., 1995; Fabres et al., 2002; Lyle and Lyle, 2002], per tal d'adaptar-los a les característiques dels sediments de zones d'alta productivitat com el Pacífic equatorial (cf. secció 2.1. i Annex I). Aquest nou protocol

està constituït de quatre passos per a l'eliminació de matèria orgànica, carbonats biogènics, òxids de ferro i manganés i sílice biogènica.

Un cop eliminada satisfactòriament la fracció biogènica es va procedir a realitzar la caracterització de la fracció lítica del ODP 1240. Aquesta caracterització ha revelat una composició mineralògica dominada per sis fases minerals principals que romanen constants al llarg de l'interval estudiat (1,56-2,26 Ma). Així doncs, les fases minerals més abundants són els feldspats (42,15%), minerals opacs (25,45%), quars (19,43%), i les minoritàries són l'epidota (6,50%), vidre volcànic (4,52%) i els amfíbols (1,95%).

A més, l'anàlisi granulomètrica d'aquesta fracció lítica mostra una distribució modal predominantment trimodal, amb una moda principal localitzada a 4-5  $\mu\text{m}$ , una moda inicial entorn a 0,5  $\mu\text{m}$  i un ampli rang granulomètric de modes terminals. Posteriorment, l'aplicació d'una anàlisi estadística de tipus clúster ha permès diferenciar sis grups ("clústers"), basats en la seva distribució modal característica. Aquests clústers presenten característiques distintives i han estat anomenats com clústers, A, B, C, D, E i F. El clúster A mostra el patró dominant, amb un 36 % de freqüència, i presenta una moda principal situada a 4  $\mu\text{m}$ . Els clústers B i C, amb un 19,51 % i 13,41% de freqüència respectivament, presenten característiques similars al clúster A, però el clúster B mostra un percentatge més alt de partícules en la moda dominant mentre que el clúster C té una moda principal menys abundant i una major presència de la moda terminal. En canvi, el clúster D (16,46%) presenta un patró diferent amb una moda principal més grollera. Els clústers E i F són els menys freqüents (9,76% i 4,88 %, respectivament) però mostren un patró totalment diferent de la resta de clústers, amb un major contingut de materials grollers. La moda principal del clúster E es troba situada al voltant dels 250  $\mu\text{m}$ , mentre que al clúster F es localitza a 400  $\mu\text{m}$ .

Per altra banda, la comparació del percentatge de lítics amb el contingut de ferro i titani, mesurat amb el XRF-Core scanner, revela una tendència ascendent gairebé idèntica per a tot l'interval estudiat que també es produeix en els fluxos de lítics i ferro. Però, aquests registres no mostren grans diferències entre les tres subunitats descrites a l'apartat 1.4.2.1. No obstant, si que presenten valors més alts durant els períodes glacials entre 1,68 i 1,85 Ma, curiosament quan el clúster E i el paràmetre Llim+Sorra/Total (de l'anglès Silt+Sand/total) no coincideixen. En canvi, els valors més baixos succeeixen durant els períodes glacials anteriors a 1,85 Ma quan el clúster E està millor representat. A més, la baixada pronunciada fins arribar als valors mínims de tot l'interval es produeix durant el MIS 56, corresponent a l'última i més intensa laminació (L1). L'alta correlació entre aquests registres demostra el seu origen comú, i juntament amb l'absència d'aports fluvials recolça l'aport eòlic de la fracció lítica i del ferro i titani. L'anàlisi dels isòtops radiogènics,  $^{87}\text{Sr}/^{86}\text{Sr}$  i  $\epsilon_{\text{Nd}}$ , pot ajudar a desxifrar la procedència d'aquest material terrigen [Biscaye et al., 1997; Grousset and

Biscaye, 2005]. Així doncs, els resultats obtinguts de  $^{87}\text{Sr}/^{86}\text{Sr}$  i  $\epsilon_{\text{Nd}}$  del ODP 1240 mostren un patró similar, al del contingut en lítics i en ferro i titani, amb un senyal diferenciat entre 1,85 i 1,65 Ma. Així, els valors baixos durant aquest període responen a un senyal provinent de Centre-Amèrica, on es donen valors més lleugers. En canvi, a partir de 1,85 Ma aquesta tendència es trenca observant una fracció lítica amb un senyal radiogènic més pesat, típic de la regió de Sud-Amèrica, concretament característic de l'arc Andí.

#### 2.4.2. Paleoproductivitat al Pacífic equatorial

L'estudi de la fracció biogènica ens aporta informació sobre les condicions oceanogràfiques (cf. secció 2.2), i ha estat focalitzat principalment en l'anàlisi de carboni orgànic, nitrogen total, òpal i abundància de foraminífers bentònics. Tant el carboni orgànic (TOC, de l'anglès Total Organic Carbon) com el nitrogen total (TN, de l'anglès Total Nitrogen) presenten una variabilitat molt marcada al llarg del període estudiat, amb els valors més alts durant els períodes glacials coincidint amb la presència de les laminacions de diatomees de l'espècie *Thalassiothrix spp.* (LDO, de l'anglès Laminated Diatom Oozes). Aquests registres mostren tres intervals ben marcats, que van en línia amb els intervals marcats prèviament per Mix et al. (2003), on els continguts més alts es produeixen a la unitat 1B amb uns límits molt marcats entre les diferents unitats. La unitat superior (1,65-1,56 Ma) mostra els valors més baixos de tot l'interval estudiat, mentre que l'interval mig (2,09-1,65 Ma) presenta els valors màxims de TOC, TN i Òpal. Per altra banda, els fluxos de carboni orgànic i d'òpal també presenten els valors màxims en la unitat 1B, sobretot quan es produeixen les LDO. En canvi, la unitat 1C (2,25-2,09 Ma) presenta valors més baixos que la unitat 1B.

Per altra banda, l'anàlisi de la fauna bentònica ha revelat l'elevada variabilitat en termes d'abundància que presenta la espècie *Uvigerina spp.*, oscil·lant des de 0 a 80% de la població bentònica total. Principalment, l'elevada abundància de *Uvigerina spp.* succeeix en intervals amb elevats percentatges de carboni orgànic però s'observen algunes excepcions. Aquests períodes excepcionals es produeixen principalment durant la presència de les LDO, on es donen continguts elevats en carboni orgànic, i alhora una abundància baixa en *Uvigerina spp.*







# **CAPÍTOL III**

## **DISCUSSIÓ**

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En aquest capítol es realitza una breu discussió sobre els resultats obtinguts en els tres articles presentats en el capítol II.

Aquesta Tesi ha estat centrada en dos registres propers situats al Pacífic equatorial oriental amb la finalitat de detectar canvis en el sistema acoblat atmosfera-oceà durant el Plistocè inferior, com ara importants migracions de la ITCZ, i la seva implicació en el mecanisme de fertilització de l'oceà superficial. A més, s'ha realitzat la comparació amb altres registres marins i continentals ja publicats al llarg de la regió tropical i subtropical per tal de detectar aquests canvis a una escala global.

Tal i com s'ha descrit a l'apartat 1.1.1.2. i 1.2.2., un tret determinant que controla la connexió atmosfera-oceà a la regió equatorial és la ITCZ i la seva migració estacional. Per tant, l'estudi integrat de la fracció lítica i biogènica a alta resolució pot aportar llum sobre grans canvis en aquesta connexió durant el Plistocè inferior, així com de variacions del sistema climàtic a baixes latituds.

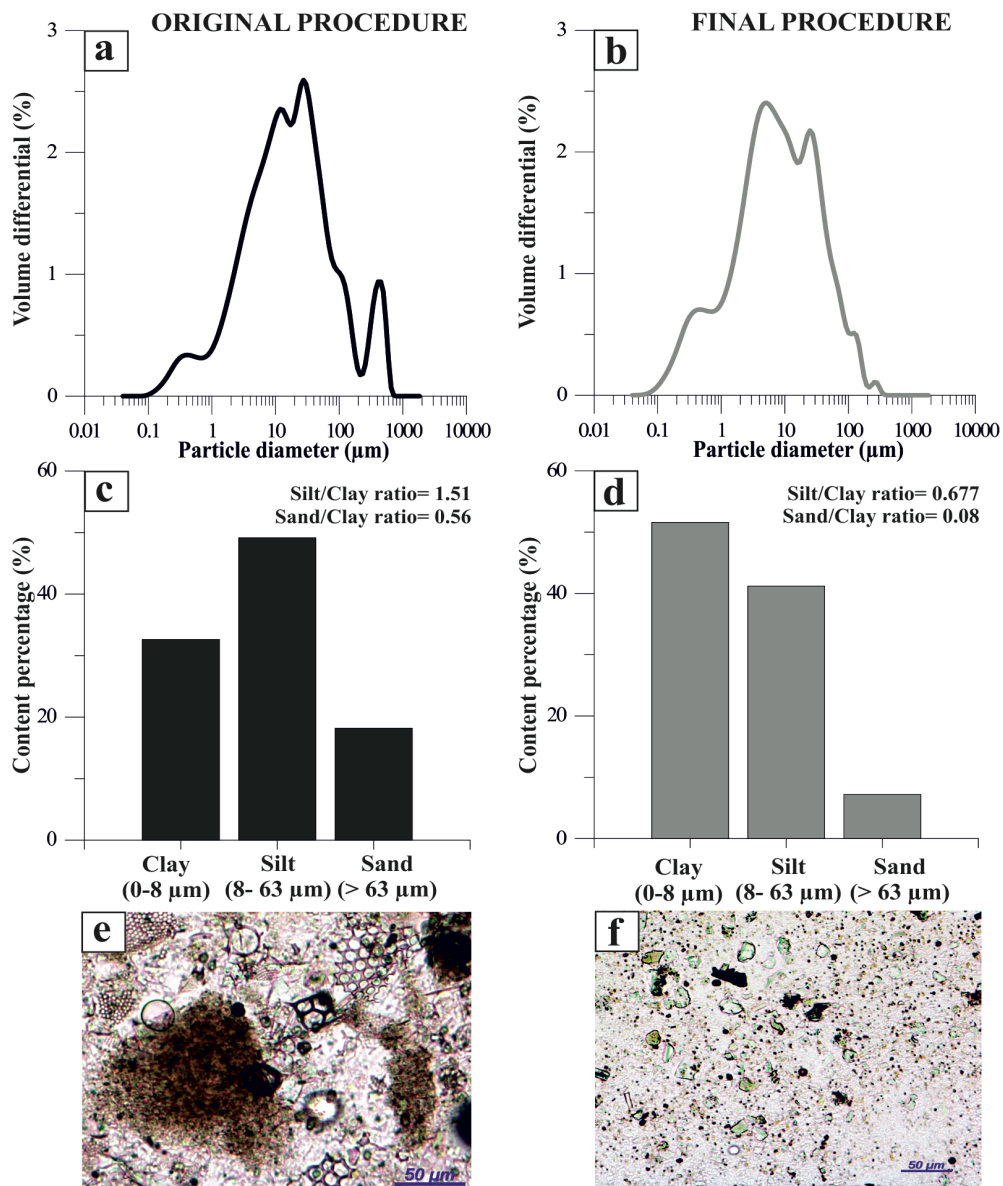
#### 3.1. Optimització d'un nou protocol per a l'aïllament de la fracció lítica

Un dels grans reptes a la hora d'interpretar dades corresponents a la fracció lítica és l'aplicació del protocol adient per a la correcta eliminació de la fracció biogènica. Això és d'especial rellevància en regions d'alta productivitat primària on les restes biogèniques arriben a representar un percentatge molt significatiu de la fracció total. Donat que el Pacífic equatorial oriental és una de les regions del planeta amb major productivitat primària, l'aplicació de protocols d'eliminació de la fracció biogènica ja utilitzats anteriorment [Chester and Hughes, 1967; Rea and Janecek, 1981; Mortlock and Froelich, 1989; DeMaster et al., 1991; Muller and Schneider, 1993; Hovan, 1995; McCave et al., 1995; Fabres et al., 2002; Lyle and Lyle, 2002] ha demostrat la seva ineficàcia en aquesta regió equatorial. Per tant, aquesta zona requereix d'un protocol més agressiu especialment focalitzat en l'eliminació de la matèria orgànica i la sílice biogènica. Aquest protocol s'ha posat a prova després de una sèrie de modificacions a partir dels protocols estàndards i a partir de la monitorització de cada pas modificat, fins a aconseguir eliminar la fracció biogènica sense cap pertorbació de la fracció lítica.

Els sediments d'aquesta regió equatorial presenten un elevat contingut en matèria orgànica, entorn al 3% en carboni orgànic (cf. secció 2.2.6). Per tant, aquest pas del protocol és decisiu per tal d'assegurar un correcte aïllament de la fracció lítica. De fet, després de l'aplicació d'un protocol estàndard aplicat en aquesta i en altres regions geogràfiques s'ha observat un elevat contingut en partícules marrons de mida gran. L'identificació de l'origen d'aquestes partícules s'ha realitzat a través de l'observació al microscopi i del tamisatge

de la mostra un cop processada. Això ha permès l'identificació d'aquestes partícules com a pèl·lets fecals, demostrant l'incorrecte funcionament d'aquest protocol estàndard en aquesta regió. Per tant, s'ha procedit al disseny d'un nou protocol a partir de la modificació dels protocols estàndards, on s'ha incrementat la concentració del reactiu, utilitzat normalment en aquest tipus de procediments com el peròxid d'hidrogen ( $H_2O_2$ ), passant del 5% al 10% (cf. secció 2.1.4.1). Després de l'aplicació d'aquest nou protocol, es va procedir a la comprovació de la seva eficàcia a través de l'observació de la fracció total al microscopi i de la fracció superior a  $63\ \mu m$  a la lupa binocular. Aquesta va demostrar l'eficàcia d'aquesta modificació del protocol, corroborada a l'hora pels resultats granulomètrics que mostren que les mostres no tractades presenten pèl·lets fecals en un rang de mides entre 300 i 500  $\mu m$ , mentre que desapareixen en les mostres processades amb aquest nou protocol. A més, anàlisis del contingut en matèria orgànica realitzats posteriorment mostren que l'aplicació d'aquest protocol elimina més del 80% de la matèria orgànica.

Per altra banda, els components de sílice biogènica representen una fracció significativa de la fracció total del sediment, concretament entre un 5% i un 15% (cf. secció 2.2.6.4), constituïts principalment per diatomees i radiolaris. Després de l'aplicació dels protocols habituals utilitzats en aquesta regió l'observació de les mostres al microscopi va revelar un abundant contingut en restes de sílice biogènica. En conseqüència, es van dissenyar una sèrie de protocols més agressius amb l'objectiu d'eliminar eficaçment aquestes restes silíciques sense pertorbar la fracció lítica. Aquests han estat dissenyats variant dues variables, el reactiu i la seva concentració, i per altra banda el temps i el nombre d'extraccions. Cal remarcar que aquestes dues variables s'han anat incrementant progressivament per tal de minimitzar al màxim l'impacte en la fracció lítica silicatada. L'efectivitat i el control de cada procediment s'ha avaluat gràcies a l'observació al microscopi de les mostres processades. Aquest control ha permès detectar restes silíciques en gran part dels protocols aplicats, excepte en el protocol 6 (cf. secció 2.1.4). Per tant, s'ha demostrat que el reactiu més adient per eliminar les restes silíciques d'aquesta regió equatorial i d'altres zones d'alta productivitat és l'hidròxid sòdic (NaOH). A més, les distribucions de la mida de gra del sediment tractat amb aquest protocol mostren una reducció de mida de la moda principal, passant de mides superiors a  $10\ \mu m$  amb els anteriors protocols, a una moda centrada entorn a  $3-4\ \mu m$ . A més, les partícules superiors a  $20\ \mu m$  també han estat reduïdes dràsticament en aquest protocol 6 respecte als protocols utilitzats anteriorment (Fig. 3.1). Aquestes diferències en la caracterització granulomètrica del sediment poden tenir un gran impacte en paràmetres estàndards utilitzats amb freqüència en Paleoceanografia, tals com els ratios Llim/Argiles (de l'anglès Silt/Clay), el de Sorres/Argiles (de l'anglès Sand/Clay), o l'índex UP10 (sediments  $>10\ \mu m$ ).



**Fig. 3.1.** Comparació dels resultats obtinguts en una mostra tractada amb el procediment estandard original i amb el nou procediment. (a, b) Distribució de la mida de gra; (c, d) percentatge d'argiles, llims i sorres; (e, f) Imatges dels frotis realitzats amb el protocol original i el procediment modificat respectivament.

Per tant, en la present tesi ha quedat demostrat que és necessari un estudi previ de les característiques de les mostres a analitzar per tal d'utilitzar el protocol adient per a una correcta interpretació dels processos sedimentaris associats a la fracció lítica. A més, una inadequada eliminació de la fracció biogènica pot produir artefactes en els paràmetres granulomètrics utilitzats sovint en estudis paleoceanogràfics tal i com es presenta a la figura 3.1.

### 3.2. Evolució del sistema atmosfera-oceà al Pacífic equatorial

Aquesta regió tropical es troba sota la influència de les migracions de la ITCZ que venen controlades en gran part per la intensitat dels sistemes de vents alisis que convergeixen a l'equador (cf. secció 1.1.1.2.). Donat que la fracció lítica arriba principalment per via atmosfèrica, l'anàlisi de la seva distribució granulomètrica ens aporta informació sobre les condicions atmosfèriques que l'han transportat i dipositat, així com de la distància a l'àrea font i dels canvis en l'aridesa d'aquesta. I per tant, són un reflex de la posició de la ITCZ i de les seves migracions al llarg del temps. De fet, estudis previs han trobat que l'aport eòlic que arriba al Pacífic equatorial prové de zones àrides de l'oest de Sud-Amèrica [Nakai et al., 1993], sobretot del desert d'Atacama [Molina-Cruz, 1977] o de la regió andina [Janecek and Rea, 1985; Chuey et al., 1987; Rea, 1990].

La deposició del material terrigen, inclòs el ferro i titani, va ser relativament baixa durant el període de temps anterior a 1,85 Ma (cf. secció 2.2.6). Durant aquest interval de temps, la distribució granulomètrica del ODP 1240 mostra la presència dominant de partícules gegants ( $>60 \mu\text{m}$ ) i una fracció grollera poc seleccionada. Fins i tot, en alguns casos extrems, dins d'aquest període, la moda fina dominant entre 4 i 6  $\mu\text{m}$  es redueix o desapareix completament. Aquestes mostres són representades per una distància baixa al clúster E, el que significa una elevada similitud a aquest clúster. Tanmateix, aquestes succeeixen particularment durant períodes glacials que coincideixen amb la presència de les LDO, així com durant l'intens esdeveniment del MIS 56. Per contra, després de 1,85 Ma, les mostres mostren una distribució trimodal amb una característica moda principal entre 6 i 7  $\mu\text{m}$ , indicant la presència dominant de partícules fines millor seleccionades, particularment durant períodes glacials (MIS 58, 60 i 62). Aquests períodes glacials també enregistren una major arribada de partícules lítiques, ferro i titani.

La mida de les partícules de pols transportades durant centenars de quilòmetres és normalment inferior a 10  $\mu\text{m}$  [Tegen et al., 1996]. No obstant, la presència de partícules eòliques gegants ( $>10 \mu\text{m}$ ) ha estat ja documentada en estudis previs [Glaccum and Prospero, 1980; Betzer et al., 1988; Moreno et al., 2001; Jeong et al., 2013]. Aquestes partícules poden ser transportades al llarg de grans distàncies si es produeix una corrent d'advecció ascendent de masses d'aire que porta a aquestes partícules cap a altituds més elevades [Windom, 1985; Pye, 1995] o un cinturó de vents troposfèric que pot induir a un transport ràpid de la pols [Jeong et al., 2013]. Un factor addicional que controla la distribució de la mida de gra és la contribució relativa de la deposició humida i seca [Guerzoni et al., 1997]. El rang de mides de gra de la pols dipositada a través d'un esdeveniment humit s'ha estudiat a través de l'anàlisi d'una sèrie de mostres de pols provinents del desert del Sàhara,

que van ser recollides a Barcelona durant esdeveniments de pluges. Aquest ha demostrat que un ampli rang de mides de partícules pot ser transportat i dipositat, però amb una presència dominant de partícules grolleres.

Aquestes observacions suggereixen que la majoria de les mostres són el resultat d'una barreja de processos, tant de deposició humida com seca. No obstant això, quan les mostres s'apropen més al clúster E, la deposició dominant és la humida, d'acord amb la proximitat a la distribució de la mida de partícula de la pols del Sàhara (deposició humida) (Fig. S2.7). Aquests canvis en la distribució de la mida de gra reflecteixen la posició de la ITCZ. Al sud de la ITCZ es produeixen vents intensos del sud-est, mentre que dins de la ITCZ els vents alisis es debiliten i domina la deposició humida [Hovan, 1995]. Conseqüentment, durant els períodes glacials amb la presència de les LDO, predominantment abans de 1,85 Ma, la ITCZ es va situar en la posició més al sud, just a sobre del ODP 1240. La presència de partícules grolleres, i fins i tot partícules gegants ( $>200 \mu\text{m}$ ), així com el baix contingut en lítics, ferro i titani, indiquen un debilitament dels vents del sud-est i un increment de les precipitacions, i per tant de la deposició humida. La fracció lítica presenta una tendència coherent amb l'excentricitat [Laskar et al., 2004], amb valors mínims en els mínims d'excentricitat. La baixa excentricitat en els períodes glacials anteriors a 1,85 Ma hauria reduït el contrast estacional entre els dos hemisferis, i per tant de la migració estacional de la ITCZ, ancorant-la en una posició més al sud. Això és particularment evident en les fases glacials MIS 78 i MIS 56 on s'observen unes condicions glacials llargues i intenses, i on destaca la rellevància del cicle d'excentricitat de 400-kyr proposat anteriorment en el Pacífic equatorial per a aquest interval de temps [Herbert et al., 2010]. A més, els valors més lleugers que presenten els isòtops radiogènics,  $^{87}\text{Sr}/^{86}\text{Sr}$  i  $\epsilon_{\text{Nd}}$ , i el menor contingut en lítics durant l'interval anterior a 1,85 Ma reflecteixen una entrada de lítics provinent de Centre Amèrica, el que confirmaria aquest ancoratge de la ITCZ al sud i el conseqüent debilitament del sistema de vents. D'acord amb les dades de  $^{87}\text{Sr}/^{86}\text{Sr}$  i  $\epsilon_{\text{Nd}}$ , aquesta posició de la ITCZ al sud hauria actuat com una barrera per al pols provinent de sud Amèrica durant aquest interval. Per contra, quan l'excentricitat va ser més alta en l'interval posterior a 1,85 Ma, l'estacionalitat terrestre s'hauria incrementat provocant una major migració latitudinal de la ITCZ. És a dir, la ITCZ podria haver estat localitzada més al nord, propera a la seva posició actual, amb una intensificació dels vents locals i una disminució de les precipitacions. Aquesta situació hauria permès una major entrada de lítics, incloent el ferro i el titani, ben classificats entorn a una moda de gra fi. Aquest material provindria de Sud Amèrica i concretament de l'arc Andí en base al senyal radiogènic ( $^{87}\text{Sr}/^{86}\text{Sr}$  i  $\epsilon_{\text{Nd}}$ ) més pesat que presenten. Altrament, l'augment general de les aportacions de lítics al llarg del període estudiat, amb un major increment a partir de 1,85 Ma, també indica condicions més àrides d'aquesta àrea font.



El Pacífic equatorial oriental és una de les regions del planeta amb les taxes més elevades de productivitat primària, on aquesta és controlada per la disponibilitat de nutrients en el sistema que al seu torn està influïda pel sistema acoblat atmosfera-oceà. Per tant, també és sensible a les migracions de la ITCZ o del Front Equatorial (EF, de l'anglès Equatorial Front), i al sistema d'aflorament equatorial associat. La productivitat més elevada es va produir durant aquests períodes glacials entre 1,85 i 2,1 Ma i l'interval glacial a 1,65 Ma (MIS 56), i particularment durant la formació de les LDO. El registre de la fracció lítica suggereix que durant aquests períodes glacials, la ITCZ s'hauria localitzat sobre l'equador, en la localització del ODP 1240, probablement en la seva posició més meridional de tot l'interval. El domini del clúster E durant els períodes en què els continguts en òpal i TOC van ser alts, suggereix que uns vents alisis dèbils no podrien haver estimulat aquest sistema d'alta productivitat. A més, aquesta elevada productivitat tampoc pot ser explicada a través d'un procés de fertilització per entrada de ferro al sistema, el que seria esperable en una regió oceànica limitada per ferro [Martin, 1990; Jickells et al., 2005], donat que els valors de ferro són relativament baixos en el període anterior a 1,85 Ma. Així mateix, la comparació amb el registre sedimentari de l'isòtop  $\delta^{15}\text{N}$  realitzat al mateix testimoni [Etourneau et al., 2013] revela també valors baixos  $\delta^{15}\text{N}$ , especialment durant aquest interval anterior a la transició de 1,85 Ma. En aquest cas, aquest treball interpreta aquest senyal com un reflex d'una major disponibilitat de nitrats en el sistema del Pacífic equatorial oriental, el que suggereix que el consum de nutrients va ser inferior en relació a la seva entrada. Així mateix, els valors baixos de  $\delta^{15}\text{N}$  quan la productivitat primària era elevada, indica un aport significatiu de nutrients, d'àcid silícic i nitrats [Billups et al., 2013], al Pacífic equatorial entre 1,85 i 2,1 Ma. Donat que aquesta regió es colimitada en sílice i ferro [Brzezinski et al., 2008, 2011], les diatomees tendeixen a esgotar l'àcid silícic de les aigües superficials en preferència als nitrats, reduint el rati  $\text{Si}(\text{OH})_4:\text{NO}_3$  de la superfície oceànica [Hutchins and Bruland, 1998]. Aquest major consum d'àcid silícic va promoure la presència de diatomees més silicificades, amb frústules més grans i pesades [Franck et al., 2000; Beucher et al., 2007], cosa que hauria permès un ràpid enfonsament i la formació de les LDO durant el període anterior a 1,85 Ma. Les diatomees de l'espècie *Thalassiothrix* spp., típiques d'aquestes laminacions, han estat associades a aigües superficials estratificades en la proximitat del EF [Kemp et al., 2000, 2006; Pike and Stickley, 2007]. A més, la presència d'aquestes laminacions ha estat també associada a esdeveniments intensos de refredament en aquesta regió [Kemp et al., 1995]. Això es confirma per les SST més fredes durant la deposició d'aquestes LDO, com s'evidencia en el registre d'alquenones [Liu and Herbert, 2004; Herbert et al., 2010]. Per contra, això no s'evidencia en dues de les laminacions, concretament la L3 i L8, les quals les SST són més elevades. Aquest fet es pot explicar per la estacionalitat de la població de

coccolitoforis. Així, les condicions d'estratificació inferides van en consonància amb la localització interpretada de la ITCZ sobre l'equador. No obstant això, l'estimulació en la productivitat de diatomees també requereix d'una major entrada d'àcid silícic al Pacífic equatorial oriental, probablement a través de l'advecció d'aigües intermèdies riques en nutrients que alimenten el corrent equatorial subsuperficial (EUC, de l'anglès Equatorial Undercurrent). Estudis previs han identificat una forta connexió entre latituds altes i baixes, principalment a través de l'advecció d'aigua intermèdia de l'oceà Antàrtic (SOIW de l'anglès Southern Ocean Intermediate Water) fins a la EUC [Kessler, 2006; Pena et al., 2013]. Aquest component antàrtic hauria proporcionat aigües riques en silici a la termoclina tropical [Calvo et al., 2011], estimulando la producció de diatomees amb el conseqüent augment de la disponibilitat de nitrats [Sarmiento et al., 2004]. A més, el fort senyal d'obliquïtat que modula el registre d'òpal durant l'interval anterior a 1,85 Ma confirmaria a forçament d'altres latituds. Així doncs, durant l'interval previ a 1,85 Ma, la fertilització del EEP s'hauria produït gràcies a un major subministrament de nutrients a través de la EUC, potencialment d'origen Antàrtic, com també s'ha publicat a Etourneau et al., (2013).

Després de 1,85 Ma, i d'acord amb la interpretació de la fracció lítica, la ITCZ va canviar la seva posició mitjana cap a un lloc més septentrional, particularment durant els períodes glacials. Aquesta situació hauria provocat un major aflorament equatorial, amb unes aigües superficials menys estratificades, una termoclina poc profunda i un major gradient E-W al Pacífic equatorial, consistent amb una intensificació de la circulació de Walker com proposen estudis anteriors [Ravelo et al., 2004, 2014; Wara et al., 2005; Ford et al., 2012]. Així mateix, els registres de productivitat mostren una disminució, però tot i així presenten encara valors relativament alts amb un canvi clar en la comunitat de fitoplàncton, recolzat per una disminució en el rati  $Si_{bio}:TOC$  i la desaparició de les diatomees silicificades més pesades que conformen les LDO. Aquesta evidència i el paral·lel augment en el consum de nitrats suggereixen un canvi en el rati de  $Si(OH)_4:NO_3$ , consistent amb una reducció en la disponibilitat d'àcid silícic i/o una major fertilització per ferro. L'intensificació del sistema d'aflorament pels vents alisis del sud-est hauria produït unes SST lleugerament inferiors després de 1,85 Ma, i hauria augmentat el transport de pols atmosfèrica com es dedueix dels fluxos alts de lítics i ferro. L'excepció a aquesta situació es va produir durant el glacial MIS 56 (1,65 Ma), quan les condicions van tornar a les prèvies a 1,85 Ma, però amb una expressió més extrema. Aquest desplaçament cap al sud de la ITCZ podria haver estat una conseqüència de la glaciació extrema desencadenada per un mínim d'excentricitat de 400-ka a 1,65 Ma, com ja s'ha vist en els models numèrics [Masunaga and L'Ecuyer, 2011]. Aquest desplaçament de la ITCZ hauria arribat més al sud, concretament a la localització del ODP 1238, el que confirmaria la severitat del període glacial MIS 56. D'altra banda, encara que els canvis més

notables i importants es produeixen durant els períodes glacials anteriors i posteriors a 1,85 Ma, els períodes interglacials també mostren un patró de comportament diferent entre aquests dos períodes marcats, com ara en els fluxos de TOC i d'òpal.

Per tal de caracteritzar millor l'impacte geogràfic dels desplaçaments de la ITCZ, s'ha examinat el ODP 1238, situat més al sud-est ( $1^{\circ} 52.310'S$ ,  $82^{\circ} 46.934'W$ ) en el Pacífic equatorial oriental, durant el període on es produeix la LDO més intensa de tot el període estudiat (L1; 1,6-1,79 Ma), que es va produir durant el glacial MIS 56. Si aquests esdeveniments van tenir lloc durant un debilitament dels vents del sud-est també s'hauria d'haver reflectit en el ODP 1238. Per tant, el senyal registrat en aquest site amb alts fluxos d'òpal, partícules grolleres amb una distribució similar al clúster E, fins i tot amb un senyal més amplificat degut a una distància més curta de transport de les partícules lítiques, dóna suport a aquest desplaçament cap al sud de la ITCZ i il·lustra l'àmplia extensió geogràfica de la L1.

Per altra banda, la població bentònica també mostra respostes desiguals en base a aquests diferents escenaris de productivitat. En general, l'abundància d'*Uvigerina spp.* segueix en paral·lel la variabilitat mostrada pel TOC, amb els percentatges més elevats d'*Uvigerina spp.* durant els màxims de TOC. *Uvigerina spp.* és un foraminífer bentònic infaunal i detritívor, típic d'ambients amb alts fluxos de carboni orgànic i baixos contingut d'oxigen [Seiglie, 1968; Murray, 1991; Rathburn and Corliss, 1994]. No obstant, aquesta relació entre l'abundància d'*Uvigerina spp.* i TOC no es compleix durant la major part de les LDO. Aquests intervals de fluxos màxims de TOC cap a l'oceà profund no van estimular la proliferació de *Uvigerina spp.*, teòricament propensa a fluxos alts de carboni. Aquesta diferent resposta suggereix diferents mecanismes d'enfonsament del carboni orgànic cap a l'oceà profund. Aquestes laminacions formades per diatomees pennades, tals com *Thalassiothrix spp.* [Mix et al., 2003] (cf. secció 1.5.2.), que tendeixen a formar grans xarxes, i que podrien arrossegar grans quantitats de carboni orgànic i altres partícules cap el fons de l'oceà. Aquests alts fluxos de TOC s'haurien produït en esdeveniments ràpids, probablement durant cicles estacionals (especialment durant la tardor o principis d'hivern) [Kemp et al., 2000], en lloc de com una pluja contínua i homogènia i, pel que sembla, haurien impedit el desenvolupament de *Uvigerina spp.* a causa dels continguts extremadament elevats de TOC. Aquests resultats posen en relleu el paper del transport vertical de partícules en el control de la població bentònica i també documenten l'alta eficiència de les laminacions en la transferència i emmagatzematge de carboni al fons i el seu potencial per augmentar l'emmagatzematge de  $CO_2$  atmosfèric a l'oceà profund [Kemp et al., 2000, 2006; Dugdale and Wilkerson, 2001].

Així, aquestes evidències donen suport a una estreta connexió entre els canvis atmosfèrics i oceànics, que modulen alhora els diferents mecanismes de fertilització en aquest sistema equatorial durant el període estudiat.

### 3.3. Teleconnexions al llarg del cinturó tropical i subtropical durant el Plistocè inferior

Per tal d'avaluar les implicacions globals dels canvis atmosfèrics que es descriuen al EEP, s'han seleccionat un conjunt de registres sota la influència de la ITCZ amb una resolució comparable i un marc cronològic sòlid per a la seva comparació. Entre aquests, el registre de terrígens de ODP 659 de l'oceà Atlàntic equatorial oriental [Tiedemann et al., 1994] i l'ODP 722 del Mar Aràbic [deMenocal, 1995, 2004, Clemens et al., 1996, 2008], i el registre de susceptibilitat magnètica del loess xinès [Clemens et al., 1996, 2008]. La cronologia del ODP 659 s'ha reajustat a la del ODP 1240 (cf. Secció 2.3.5.4), i la comparació dels registres bentònics de  $\delta^{18}\text{O}$  dels tres testimonis marins mostren cronologies molt consistents per permetre la seva comparació. El contingut en terrígens dels tres registres marins mostra un extraordinari paral·lelisme, el que confirma en tots els casos una major arribada de components terrígens entre 1,85 i 1,65 Ma (MIS 56). Això és consistent amb una intensificació general dels vents alisis i/o aridesa de la regió tropical després de 1,85 Ma. De fet, el loess xinès també registra aquest canvi a partir de 1,85 Ma amb una important disminució dels valors de susceptibilitat magnètica [Clemens et al., 2008]. Aquest fet és coherent amb la migració de la ITCZ cap al nord en la regió del Pacífic (ODP 1240) després de 1,85 Ma el que hauria donat lloc també a una intensificació del monso d'estiu sobre l'altiplà xinès.

De fet, aquest punt d'inflexió situat a 1,85 Ma també s'enregistra en carbonats de paleosòls de l'Àfrica [Cerling and Hay, 1986; Cerling, 1992; Wynn, 2000, 2004, Feakins et al., 2005, 2013; Levin, N., 2013]. Aquesta alteració ha estat relacionada amb un episodi de major aridesa global que va generar un canvi ambiental a baixes latituds d'Àfrica, des de vegetació de tipus bosc (C3) fins a vegetació de tipus herbaci (C4), adaptada a un ambient àrid [Cerling and Hay, 1986; Cerling, 1992; Wynn, 2000, 2004; deMenocal, 2004; Feakins et al., 2005, 2013]. A més, aquesta tendència àrida s'ha enregistrat també en els grans mamífers de la conca Turkana a l'Àfrica oriental [Hernández Fernández and Vrba, 2006]. Aquest canvi també es detecta al llarg del continent sud-americà amb una disminució dels boscos i la seva substitució per extenses praderes [Pascual, 2006].

A més, s'han avaluat els registres de terrígens dels tres testimonis localitzats al llarg de la regió tropical realitzant una anàlisi de freqüència per determinar periodicitats significatives de variabilitat. Així, l'espectre de freqüència dels continguts de terrígens mostra la potència més alta en la banda de la precessió, però també mostra un pic destacable a 100-ka. Per tant, l'anàlisi de freqüència demostra un fort control orbital de les condicions d'aridesa en les zones tropicals, que està dominat per la banda de la precessió.

#### *Empremtes climàtiques a coves de Sud-àfrica*

El clima de Sud-àfrica, encara que més al sud de la franja tropical, es regeix avui en dia també per la migració estacional de la ITCZ, on la posició sud contribueix a un increment de les precipitacions sobre aquesta regió [Indeje et al., 2000]. El registre  $\delta^{13}\text{C}$ , extret de colades de la cova de Buffalo, ofereix un senyal paleoclimàtic continu i únic en la regió amb una resolució excepcional per al període discutit [Hopley et al., 2007a]. A part de les oscil·lacions controlades per l'obliquïtat, la corba de  $\delta^{13}\text{C}$  presenta una fase de migració cap a valors menys negatius centrada entre 1,80-1,70 Ma, que s'interpreta com un canvi cap a una major dominància de plantes C4 a causa d'un augment de l'aridesa [Hopley et al., 2007a, 2007b]. Aquest fet és coherent amb la discutida posició dominant de la ITCZ més cap al nord després de 1,85 milions d'anys, però amb un aparent retard de 50 milers d'anys en el seu inici.

Més al sud, les coves de Sterkfontein (situades entre els 25° 50'S - 26° 02 'S) proporcionen evidències d'una sèrie d'esdeveniments humits, representats pel carbonat de calci de la formació de colades (FGIs, de l'anglès Flowstones Growth Interval), que conformen la localització més singular i rica en restes d'homínids del món [Berger et al., 2010; Pickering et al., 2011a]. Les millores recents en el mètode de datació radiogènica d'urani-plom (U-Pb) han permès obtenir edats absoluts més precises dels dipòsits de carbonat d'aquesta edat [Pickering et al., en preparació]. Aquestes noves edats han millorat substancialment la precisió de les datacions per als FGIs de Sterkfontein publicades anteriorment [Pickering et al., 2011b] i ens permeten comparar detalladament amb altres registres paleoclimàtics analitzats.

Durant el període estudiat s'han descrit dos grans intervals de creixement de FGIs, concretament a 2,06 i a 1,8 milions d'anys, encara que també s'han produït altres esdeveniments humits més antics, a 2,26 i 2,7 Ma. Però, per contra, després de 1,8 Ma només s'han enregistrat dos esdeveniments molt dèbils de FGIs, datats a 1,4 i 1,5 Ma [Pickering et al., en preparació]. La formació d'aquestes colades implica unes condicions climàtiques extremes amb més precipitacions, sent aquestes més efectives. L'episodi més intens d'aquests FGIs és el que està centrat a 1,8 Ma, i que és coincident amb el registre de  $\delta^{13}\text{C}$  de la colada de la cova Buffalo amb un intens i persistent esdeveniment humit just abans de la transició descrita cap a condicions més àrides [Hopley et al., 2007a]. Per tant, ambdós registres del sud d'Àfrica apunten cap a l'ocurrència d'un esdeveniment de pluja extrema just després de la transició de 1,85 Ma, quan tot el sistema tropical es trobava en un període transitori cap a condicions més àrides i vents més forts a la zona tropical. Curiosament, una fase humida

superposada a una tendència d'aridesa a llarg termini també s'ha descrit en el registre lacustre de l'est d'Àfrica, també centrada a 1,8 Ma [Trauth et al., 2005].

L'origen d'aquests intensos esdeveniments humits a Sud-àfrica és sorprenent ja que no es van produir per un únic forçament. Els FGIs formats a 2,06 i 1,8 Ma es van formar durant períodes glacials (MIS 78 i 64, respectivament), que és també el cas dels FGIs més antics i dels més moderns. Tots els FGIs fins a 1,8 Ma es van produir durant mínims d'excentricitat, una configuració orbital que condueix a un contrast estacional mínim entre els dos hemisferis en la insolació, una situació que afavoreix l'ancoratge de la ITCZ en una latitud fixa. Però, els dos esdeveniments més febles després de 1,8 Ma van ocórrer durant màxims d'excentricitat. Pel que sembla, alguna cosa va canviar en el sistema climàtic a partir de 1,8 Ma, que no era tan favorable a l'aparició d'aquestes condicions de pluja extrema al sud d'Àfrica, probablement relacionat amb la transició cap a una ubicació tropical de la ITCZ més cap al nord. Avui en dia, els esdeveniments més humits en aquesta regió del sud d'Àfrica es produeixen durant els anys de condicions extremes de "La Niña" [Pohl et al., 2010], i aquest patró de precipitació s'incrementa significativament quan es combina amb una fase positiva de l'oscil·lació antàrtica (AO, de l'anglès Antarctic Oscillation) [Kidson, 1988; Thompson and Wallace, 2000] i amb majors tempestes de l'oest [Stuut et al., 2002]. D'aquesta manera, aquests intervals de pluja extrema durant el Plistocè inferior podrien ser el resultat d'una combinació de factors com ara el forçament orbital, l'estat del clima glacial i una configuració atmosfèrica tropical més propensa a una localització de la ITCZ més al sud. En general, això hauria permès un augment de la freqüència i/o la força dels esdeveniments de "La Niña" i/o de la fase positiva de la AAO, que podrien haver impulsat aquests esdeveniments de pluja extrema a la regió.

### *Clima i evolució humana*

Les noves datacions de Urani-Plom (U-Pb) dels FGIs de Sterkfontein també han permès col·locar amb precisió algunes restes d'homínids en el context paleoclimàtic global [Pickering et al., 2011]. L'última aparició de l'*Australopithecus africanus* es va produir just abans de l'episodi humit situat a 2,06 Ma [Pickering and Kramers, 2010a] i després d'aquest episodi, al voltant de 1,95 milions d'anys, va aparèixer l'*Australopithecus sediba* [Berger et al., 2010]. Després de l'episodi humit més intens (localitzat a 1,8 Ma), quan la tendència cap a l'aridesa es va accelerar a Sud-àfrica, van desaparèixer les restes d'homínids a la localització de Sterkfontein. És difícil establir la causa-efecte directa entre aquests canvis climàtics i humans, però el vincle temporal és compatible amb l'existència de fortes pressions ambientals

associades a alguns canvis importants en la distribució d'homínids. L'interès en aquestes noves dades radica en les evidències que la pressió ambiental no es va deure només a una tendència àrida general descrita a l'Àfrica durant els últims milions d'anys [Cerling and Hay, 1986; Cerling, 1992; Wynn, 2000, 2004; deMenocal, 2004; Feakins et al., 2005, 2013; Hernández Fernández and Vrba, 2006]. Els registres paleoclimàtics d'alta resolució discutits demostren l'ocurrència d'unes transicions més ràpides amb alguns episodis humits extrems que van produir una pressió ambiental afegida [Trauth et al., 2005; Hopley et al., 2007a]. En particular, l'aparició dels episodis dramàtics humits discutits anteriorment, hauria empitjorat les condicions de l'habitat de les espècies existents d'homínids, que ja estaven en un procés d'adaptació a un ecosistema més sec. Així, el panorama general mostra un entorn molt inestable que podria haver contribuït a l'aparició i desaparició de diferents espècies. Va ser també durant aquest període quan es va produir la primera aparició del gènere *Homo*, concretament de l'*Homo habilis* (2,5 Ma). El canvi climàtic descrit a 1,8 Ma, i que marca l'inici d'una fase d'intensificació de la llarga tendència d'aridificació africana, sembla estar relacionat amb l'extinció de *Homo habilis* en favor de l'aparició de *Homo erectus*. Aquest canvi hauria exposat a *Homo habilis* a un nou hàbitat i, com a conseqüència, a un canvi dels recursos alimentaris. Això hauria induït a un canvi en la dieta i a un debilitament progressiu de l'espècie *Homo habilis* que junt amb un procés de selecció natural i una transformació filogenètica podrien haver conduït a una nova espècie, *Homo erectus*. Aquesta nova espècie estaria millor adaptada a aquest hàbitat emergent deguda a una millora de les tècniques de caça i a un major desenvolupament de les eines de pedra. Aquesta millora hauria provocat l'augment del consum de carn i un augment de la ingesta de proteïnes, millorant en conseqüència la captació de dopamina [DeLouize et al., 2016]. De fet, l'aparició i propagació d'*Homo erectus* coincideix amb les taxes més altes d'extinció d'espècies carnívores a l'est d'Àfrica a 1,8 Ma [Lewis and Werdelin, 2007]. Aquest canvi en la dieta hauria promogut el desenvolupament de noves capacitats, com la memòria visuoespacial millorada, habilitats socials i la capacitat de córrer llargues distàncies. Així, aquestes competències emergents haurien permès la migració fora d'Àfrica dels primers espècimens d'*Homo erectus* a 1,8 Ma.









# **CAPÍTOL IV**

# **CONCLUSIONS**

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Aquesta tesi ha estudiat canvis del sistema acoblat atmosfera-oceà al Pacífic equatorial oriental (ODP 1240 i 1238) durant el Plistocè inferior, valorant també l'impacte dels canvis atmosfèrics identificats al llarg del cinturó tropical, i establint una correlació directa amb alguns esdeveniments claus de l'evolució humana.

L'estudi de les condicions atmosfèriques a través de l'anàlisi de la fracció lítica del Pacífic equatorial, ha posat de manifest la necessitat de desenvolupar un protocol adequat per a la correcta eliminació de la fracció biogènica en zones d'elevada productivitat primària. Amb aquest objectiu, es va dissenyar un experiment que ha demostrat la ineficàcia dels procediments estàndard per a la completa eliminació de components biogènics, com és el cas dels pèl·lets fecals, i sobretot de les restes biogèniques silíciques de diatomees i radiolaris. Per aquest treball s'ha dissenyat un procediment específic, més agressiu que els que normalment s'apliquen en aquesta i en altres àrees estudiades. A més, el monitoratge continu de la distribució de la mida de gra després de cada etapa del protocol, ha revelat que els procediments inadequats per a l'eliminació de la fracció biogènica poden induir a grans biaixos en els resultats d'anàlisis granulomètrics utilitzats habitualment en estudis paleoceanogràfics.

L'anàlisi combinat de la fracció lítica amb la biogènica al ODP 1240 ha permès detectar canvis significatius que s'han associat a desplaçaments latitudinals de la ITCZ al llarg del Plistocè inferior, posant de manifest una important reorganització atmosfèrica i oceànica, i descrivint l'alternança entre dos mecanismes diferents de fertilització a la regió del Pacífic equatorial.

Els resultats han permès interpretar que prèviament a 1,85 Ma, particularment durant els períodes glacials, la ITCZ es va situar en una posició més meridional que l'actual, localitzant-se just a sobre de l'equador (ODP 1240). Això hauria donat lloc a un debilitament dels vents alisis sobre aquesta regió i a una menor arribada de pols, però aquest es va dipositar per via humida degut a les pluges freqüents que es produeixen sota la ITCZ. Aquesta situació és consistent amb un domini de diatomees més silicificades i pesades que van formar uns nivells laminats rics en macro-diatomees del tipus *Thalassiothrix*, típiques d'aigües superficials estratificades a les proximitats dels fronts oceànics. L'augment de la disponibilitat de nitrats i dels elevats fluxos d'òpal enregistrats entre 2,1 i 1,85 Ma, donen suport a un canvi en la disponibilitat de nutrients que s'ha interpretat com un possible augment en l'arribada d'aigües riques en àcid silícic d'origen antàrtic. L'absència d'*Uvigerina spp.* durant aquest període, una espècie bentònica que generalment s'aprofita de fluxos elevats de TOC, indicaria que l'elevat flux de carboni cap al fons oceànic es va produir en polsos ràpids, induïts per l'arrossegament de les xarxes formades per les frústules de diatomees, i asfixiant l'ecosistema bentònic mentre es formaven els nivells laminats. Aquestes observacions evidencien l'eficiència d'aquest procés sedimentari en l'emmagatzematge de carboni al fons oceànic.

Els períodes glacials posteriors a 1,85 Ma presenten un augment en el contingut de lítics, sent aquestes més fins i seleccionats, coincidint amb fluxos més elevats de ferro. Aquestes condicions s'han interpretat com el domini d'una deposició eòlica seca del material lític, gràcies a una intensificació dels vents alisis associada a una migració cap al nord de la ITCZ. Altrament, el sistema oceànic va respondre sincrònicament, on l'elevada productivitat primària i el major consum de nitrats enregistrat indicarien un aflorament més intens i una major fertilització per l'arribada atmosfèrica de ferro a l'oceà superficial, fruit de la intensificació dels vents. Aquest fet hauria augmentat el gradient tèrmic E-W al Pacífic equatorial d'acord amb l'enfortiment, prèviament descrit, de la circulació de Walker després de 1,85 Ma. Durant aquest interval, el flux de carboni cap a l'oceà profund també va ser elevat però s'hauria produït a un ritme més homogeni, afavorint el desenvolupament de *Uvigerina spp.*. Un període glacial particularment excepcional va succeir a 1,65Ma (MIS 56), amb un senyal típic dels glacials anteriors a 1,85 Ma, fins i tot amplificat, indicant un últim període de desplaçament de la ITCZ cap al sud. Tant aquest MIS 56 com el 78 destaquen dins del registre per la presència de laminacions de diatomees més desenvolupades i unes condicions més fredes. A més, aquests dos glacials coincideixen amb mínims d'excentricitat de 400 ka, ressaltant la rellevància de la configuració astronòmica, juntament amb les dimensions del casquet de gel de l'Hemisferi Nord en el control de les migracions de la ITCZ. Aquests desplaçaments de la ITCZ han estat recolzats també per dades d'isòtops radiogènics, Nd i Sr, que confirmen un major domini de l'arribada de partícules de Centre-Amèrica abans de 1,85 Ma, quan la ITCZ es situa sobre l'equador, i un increment de l'arribada de partícules de Sud-Amèrica durant el període post 1,85 Ma, quan la ITCZ es desplaça cap al nord, amb l'excepció del MIS 56.

La comparació dels registres obtinguts al Pacífic equatorial oriental amb dades similars d'altres localitzacions, sota la influència de la ITCZ, indiquen que els canvis descrits en la ITCZ en el Pacífic van tenir efectes a escala global. El desplaçament cap al nord de la ITCZ després de 1,8 Ma hauria afavorit l'aridificació de zones tropicals africanes i sud-americanes, donant lloc al canvi enregistrat en el tipus de vegetació. La disponibilitat de noves i precises datacions de colades carbonatades de coves de Sud-Àfrica, riques en restes d'homínids, ha permès establir correlacions precises entre els diferents registres paleoclimàtics, marins i terrestres, i situar alguns esdeveniments en l'evolució dels nostres antecessors. Les colades sud-africanes mostren una sèrie d'esdeveniments humits extrems que van interrompre de forma abrupte el patró general descrit cap a l'aridificació. L'esdeveniment humit més marcat es localitza a 1,8 Ma, curiosament coincident amb un dels moments claus en l'evolució i especiació humana. Aquesta intensificació de les precipitacions a Sud-Àfrica, vindria donada per una combinació de factors, primerament modulada per una configuració orbital

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específica (mínim d'excentricitat) que afavoriria un ancoratge de la ITCZ en una posició meridional i que hauria permès l'ocurrència d'unes condicions més extremes de "La Niña" durant fases positives de l'oscil·lació antàrtica. Situació que afavoreix les pluges intenses a Sud-Àfrica. Aquestes condicions climàtiques extremes i canviants haurien afegit una forta pressió ambiental en l'habitat dels homínids, tal i com suggereix l'aparició durant aquest període, de *Homo erectus* i la desaparició de la primera espècie del gènere *Homo*, *Homo habilis*, així com altres espècies d'hominins, com l'*Australopithecus africanus* i l'*Australopithecus sediba*.

Així, l'alta resolució dels nous registres analitzats al ODP 1240 i 1238, i la seva comparació amb altres registres tropicals, han permès caracteritzar l'alta inestabilitat del clima tropical durant el Plistocè inferior, atribuïda a una reorganització global de la posició principal de la ITCZ. Aquesta situació, hauria causat l'aridificació continental a baixes latituds, i hauria provocat un gran impacte en l'habitat i l'alimentació de les diferents espècies d'homínids africans.





# **CAPÍTOL V**

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# ANNEXOS

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## ANNEX I. PROTOCOL DETALLAT PER A L'ÀLLAMENT DE LA FRACCIÓ LÍTICA





*Selecció de la mostra*

- Agafar 1,5 grams de mostra seca i introduir-la en un vas de precipitats de 400 ml.

*Atac de la matèria orgànica*

- Afegir 80 ml de  $H_2O_2$  al 10% a cada vas de precipitats.
- Agitar.
- Ficar a l'estufa a 60°C durant tota la nit.
- Al dia següent afegir 80 ml de  $H_2O_2$ , ja que gran part s'evapora a l'estufa.
- Agitar.
- Ficar a l'estufa a 60°C durant tota la nit.
- Traspassar el contingut restant del vas de precipitats a un vial de 50 ml.
- Centrifugar.
- Decantar líquid.

*Atac del carbonat*

- Afegir 35 ml de solució d'àcid acètic ( $CH_3COOH$ )-acetat sòdic ( $CH_3COONa$ ).
- Agitar.
- Col·locar a la placa agitadora (4-6 h).
- Agitar.
- Centrifugar 30 minuts a 5000 rpm.
- Decantar líquid.
- Afegir 35 ml més de solució.
- Agitar.
- Col·locar a la placa agitadora (6-12 h).
- Agitar.
- Centrifugar 30 min a 5000 rpm.
- Decantar.
- Afegir 35 ml de solució.
- Agitar.
- Col·locar a la placa agitadora (6-12 h).
- Agitar.
- Centrifugar 30 min a 5000 rpm.
- Afegir 30 ml d'aigua miliQ.
- Agitar.
- Centrifugar 30 min a 5000 rpm.
- Decantar líquid.

*Atac dels òxids Fe-Mn*

- Afegir 45 ml de solució HH ( $(NH_3OH)Cl$ ).
- Agitar.

- Posar a la taula agitadora durant dues hores.
- Centrifugar 30 min. a 5000 rpm.
- Decantar líquid.
- Afegir 35 ml més de solució HH.
- Agitar.
- Deixar tota la nit a la taula agitadora.
- Centrifugar 30 min. a 5000 rpm.
- Decantar líquid.
- Afegir 30 ml d'aigua miliQ.
- Agitar.
- Centrifugar 20 min a 5000 rpm.
- Decantar líquid.
- Repetir de nou el rentat amb aigua miliQ.

#### Atac de la sílice

- Afegir 35 ml de solució de NaOH 1,5 M.
- Agitar.
- Sonificar 10 minuts.
- Posar a l'estufa a 60 °C durant tota la nit.
- Bany a 85°C durant dues hores. Mentre s'escalfa el bany sonifiquem els vials 10 minuts més.
- Centrifugar 30 min. a 5000 rpm.
- Decantar líquid.
- Afegir 35 ml de solució de NaOH 1,5 M.
- Agitar.
- Sonificar 10 minuts.
- Bany a 85°C durant dues hores.
- Posar a l'estufa a 60 °C durant tota la nit.
- Centrifugar 30 min. a 5000 rpm.
- Decantar líquid.
- Afegir 35 ml de solució de NaOH 1,5 M.
- Agitar.
- Sonificar 10 minuts.
- Bany a 85°C durant dues hores.

- Posar a l'estufa a 60 °C durant tota la nit.
- Afegir 35 ml d'aigua miliQ
- Agitar
- Centrifugar 30 min. a 5000 rpm.
- Repetir el procés de rentat amb aigua miliQ un cop més.

#### Disgregació de la mostra per al Coulter

- Afegir 35 ml de solució disgregant de polifosfat sòdic.
- Sonificar 15 minuts.
- Agitar durant tota una nit.

#### Preparació de reactius

- Preparació d'aigua oxigenada ( $H_2O_2$ ) al 10%  
En un matràs d'un litre de capacitat es fiquen 100 ml d'aigua oxigenada ( $H_2O_2$ ) i 900 ml d'aigua miliQ.
- Solució d'àcid acètic( $CH_3COOH$ )- acetat sòdic ( $CH_3COONa$ )  
En un matràs de 1 litre es posen 500 ml d'aigua miliQ. Posteriorment, en un vas de precipitats es pesen 28 grams de NaAc, i en una proveta es posen 27 ml d'àcid acètic. Llavors, es barregen els 28 grams d'acetat sòdic amb els 27 ml d'àcid acètic, i es neteja el vas de precipitats 2 ó 3 vegades amb aigua MiliQ. Aquesta barreja es fica al matràs i s'enrasa a 1 litre amb aigua miliQ. En aquesta preparació és important que el pH sigui 4, si aquest no és de 4 s'ha d'anar variant la proporció d'àcid acètic- acetat sòdic fins que ho sigui.
- Solució de Hydroxilamine Hydrochloride (HH)  
Per dur a terme aquesta solució es fiquen 500 ml d'aigua miliQ i 250 ml d'àcid acètic en un matràs de 1 litre. Per altra banda, es pesen 1,3893 grams de HH ( $(NH_3OH)Cl$ ) i s'agreguen al matràs. Aquesta preparació s'ha de deixar reposar un mínim de vuit hores abans d'enrasar a 1 litre. Passades aquestes vuit hores, s'enrasa a 1 litre.
- Solució d'Hidròxid de sodi 1,5M (NaOH)  
Per realitzar aquesta solució es posen 60 grams de NaOH en un matràs d'un litre de capacitat i s'enrasa amb aigua MiliQ fins a un litre.
- Solució disgregant de polifosfat de sòdic al 25%  
Aquesta solució es fa disgregant 25 grams de polifosfat sòdic amb l'agitador magnètic en un litre d'aigua destil·lada. Llavors d'aquesta solució s'agafen 40 ml i s'enrasa fins a un litre amb aigua destil·lada.



## ANNEX II. ABREVIATURES







## LLISTAT D'ABREVIATURES

AAIW: Antarctic Intermediate Waters  
AAO: Antarctic Oscillation  
CC: California Current  
CCiTUB: Centres Científics i Tecnològics de la Universitat de Barcelona  
CORTEX: Corescanner Texel  
CPS: Contes Per Segon  
ECC: Equatorial Counter Current  
EIC: Equatorial Intermediate Current  
ENSO: El Niño- Southern Oscillation  
EUC: Equatorial Under Current  
FGI: Flowstone Growth Intervals  
ICP-MS: Inductively Coupled Plasma Mass Spectrometer  
ICP-OES: Inductively Coupled Plasma Optic Spectrometer  
IPCC: Intergovernmental Panel on Climate Change  
ITCZ: Intertropical Convergence Zone  
LDO: Laminated Diatom Ooze  
LGM: Last Glacial Maximum  
LIA: Little Ice Age  
MCD: Meters Composite Depth  
MIS: Marine Isotope Stage  
NEC: North Equatorial Current  
NECC: North Equatorial Counter Current  
NHG: Northern Hemisphere Glaciation  
NPIW: North Pacific Intermediate Water  
ODP: Ocean Drilling Program  
OMZ: Oxygen Minimum Zone  
PCC: Peru-Chile Current  
PDW: Pacific Deep Water  
PIDS: Polarization Intensity Differential Scattering  
SEC: South Equatorial Current  
SEM: Scanning Electron Microscope  
SST: Sea Surface Temperature  
SV: Sverdrups  
TN: Total Nitrogen  
TOC: Total Organic Carbon  
XRF: X-Ray Fluorescence



## ANNEX III. PUBLICACIONES



## A new procedure for the lithic fraction characterization in marine sediments from high productivity areas: Optimization of analytical and statistical procedures

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### Abstract

The lithogenic fraction in marine sediments can be a key proxy to reconstruct past changes in atmospheric circulation, river runoff among other sedimentary processes. But, accurate isolation of the lithic component within biogenic-rich sediments can be particularly challenging in areas of high marine productivity. We present an experiment to isolate and characterize this lithogenic fraction that ensures the full elimination of biogenic and authigenic components. This experiment demonstrates that standard procedures used in most of the studies of terrigenous fraction in marine sediments, are inadequate to remove efficiently most of the biogenic components in sediments from high productivity regions such as the Eastern Equatorial Pacific. The experiment reviews each of the procedure steps designed for the removal of organic matter, carbonate, Fe-Mn oxides, and biogenic silica. The most critical steps were the removal of organic matter incorporated in fecal pellets, and the elimination of the biogenic silica. The continuous monitoring of the grain-size distribution of the samples along the experiment steps allows evaluating the impact that an inadequate procedure can induce on the grain size. Finally, lithic grain-size distributions were characterized using *k-means* statistical technique providing objective information for climate interpretation. The proposed approach ensures the quality of the results and allows magnifying the information provided by the lithic fraction in marine sediments.

Marine sediments contain lithic particles whose study can provide very useful information about different sedimentary processes which ultimately may reflect climate dynamics. This sediment fraction is mostly from terrestrial source and the particles can be transported to the marine environment through the atmosphere or by river runoff. The grain-size distribution and composition of the terrigenous fraction has proved to be a proxy for paleocontinental aridity and wind strength in areas such as the Atlantic and Pacific basins (Stuut and Lamy 2004; Holz et al. 2007) and Mediterranean Sea (Hamman et al. 2008). Dust fluxes have also been used to estimate the paleoposition of the Intertropical Convergence Zone (ITCZ) in northwest Africa (Tiedemann et al. 1994) and the spatial variability of the Asian monsoon (Nagashima et al. 2007). Mineralogical and geochemical data can be used as indicator of the source for eolian dust and the transport mechanisms (Hyeong et al. 2005; Hamman et al. 2009). According to the sediment core location, the lithic fraction can also be a good proxy for river runoff

(Lantsch et al. 2010; Frigola et al. 2012) or an indicator of changes in the intensity of deep water currents (Bianchi et al. 1999; Hall and McCave 2000; Frigola et al. 2007).

This study is focused on the analysis of the lithic fraction and its size distribution in Equatorial Pacific sediments. The samples were collected from ODP Leg 202 Site 1240 in the Eastern Equatorial Pacific, Panama Basin (0°01.31 N 86°27.76 W; 2921-m depth). This region acts as a sediment trap that collects biogenic particles formed under equatorial upwelling (Mix et al. 2003). This tropical region is characterized by the convergence of the trade winds at the ITCZ (Pisias et al. 1995). The ITCZ position has a seasonal fluctuation, being shifted south toward the equator during the Southern Hemisphere summer when the southeasterly trade winds are weaker. During the Southern Hemisphere winter when the southeasterly trades are stronger, the ITCZ it is located further north at about 8° N, resulting in maximum equatorial upwelling and eolian transport of the lithic fraction. The sediment at the studied site is dominated by diatom ooze and nannofossil ooze containing diatoms (Mix et al. 2003), this sediment composition is representative of the deep marine

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sediments that can be found along the Pacific cold tongue, a broad oceanographic region that includes the eastern Pacific coastal and equatorial upwelling systems. Marine sediments rich in siliceous oozes can also be abundant in other upwelling regions of the North Pacific and Indian Oceans and along most of the Southern Ocean (Kennett 1982).

In this study, we show that most of the standard procedures applied to analyze grain-size distribution in marine sediments were not aggressive enough to totally remove the biogenic particles. Due to high content of biogenic particles in the sediments, the standard procedures must be modified to ensure the effective removal of organic (fecal pellets) and siliceous remains (diatoms, radiolaria, and sponge spicules). We propose a number of changes to standard procedures for their use under high-productivity areas. Finally, we applied a clustering technique (*k-means*) to the analysis of a large data base of grain-size distributions. This allowed us to group the samples using an objective and statistically significant procedure.

**Materials and procedures**

**Standard procedure**

The standard procedure described below and modified from Chester and Hughes (1967), Rea and Janecek (1981), Mortlock and Froelich (1989), Demaster (1991), Muller and Schneider (1993), Hovan (1995), McCave et al. (1995), Fabr s et al. (2002), and Lyle and Lyle (2002), is commonly used in the treatment of marine sediments for grain-size analysis. This procedure consists of four steps designed to remove the biogenic and authigenic fraction, specifically the organic matter, carbonate, Fe-Mn oxides, and biogenic silica fractions.

**First step: Removal of organic matter**

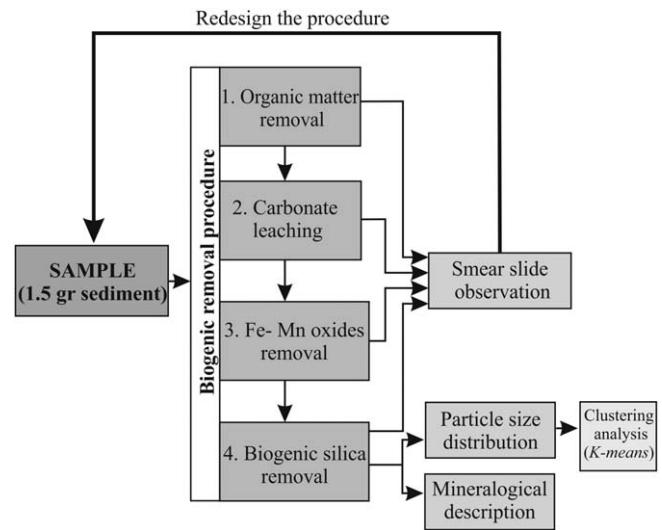
1.5 g of dry sediment sample were treated with 35 mL of 5% hydrogen peroxide to oxidize the organic matter. Samples were then agitated and remained for 30 min at the oven (60°C) to allow the reaction. The remaining solution was removed after sample centrifugation at 5000 rpm for 10 min.

**Second step: Removal of carbonate bioclasts**

The carbonate was leached by the addition of 35 mL of 2.7% acetic acid—0.34 M sodium acetate solution (pH = 4) based in Biscaye (1965) method (Table 2) and placed in the shaker for five hours. After this time, the vials were centrifuged during 15 min (5000 rpm) and the solution removed. This attack is repeated twice during the second time the samples were left stirring overnight. At the end of treatment, the samples were washed one time with MilliQ water and centrifuged 15 min (5000 rpm) to remove the leaching solution.

**Third step: Removal of Fe-Mn oxides**

These oxides produced by authigenic processes, which have been proven to be abundant in this setting (Pena et al. 2005, 2008), were treated with a 0.02 M hydroxylamine hydrochloride and 25% acetic acid to eliminate the Fe-Mn oxides (modified after Chester and Hughes 1967). These oxides were removed by adding 45 mL of Hydroxylamine



**Fig. 1.** Diagram of the procedure used to isolate and analyze the lithogenic fraction, including the monitoring for each step of the protocol.

hydrochloride solution (Table 2) and placed in the shaker during two hours. The solution was then removed by centrifuge for 15 min (5000 rpm). The attack was repeated a second time leaving the samples on the shaker overnight. Then, the samples were centrifuged for 15 min (5000 rpm) and were washed two times with MilliQ water.

**Fourth step: Removal of biogenic silica**

Removed biogenic silica using a solution of Na<sub>2</sub>CO<sub>3</sub> 2 M, from the procedure described by Mortlock and Froelich (1989). This step consisted on the addition of 35 mL of 2 M Na<sub>2</sub>CO<sub>3</sub> solution. The samples were shaken and left five minutes of sonication, the samples stayed in a warm water bath (85°C) for two hours. The procedure was later repeated for two additional hours. The extracted solution was finally removed after sample centrifugation and the samples were further cleaned adding MilliQ water for two consecutive times.

**Smear slide preparation and microscope observation**

Smear slides were prepared systematically during the procedure setup after each chemical step to monitor the efficiency of the biogenic and authigenic fraction removal (Fig. 1). Smear slides were prepared using a UV curing adhesive and dried under ultraviolet light (Backman and Shackleton 1983; Rothwell 1989). Samples were then observed under the microscope, first to ensure the elimination of the biogenic and authigenic fraction and second to broadly characterize the lithic fraction.

**Grain-size distributions and clustering analysis**

Grain-size analysis were realized after each of the experimental tests to check the effect that the different procedures could have in the grain-size distribution and finally, samples treated with the optimized procedure were analyzed to characterize the grain-size distribution along time. Prior to the

grain size measurements, samples were disaggregated with sodium polyphosphate, sonicated for 15 min and shaken overnight. Grain-size distributions were characterized using a Coulter LS 230. The basic principle of this device is to analyze the particle size according to the angle of diffraction that occurs when sample grains pass through a light beam. This device measures the percentage volume of particles in 116 size classes, and its detection range is between 0.04  $\mu\text{m}$  and 2000  $\mu\text{m}$ .

A clustering statistical analysis of grain-size distributions was carried out to aid in the interpretation of the main types of grain-size distributions from the measured values. The clustering analysis applied is based in the nonhierarchical *k-means* technique (McQueen 1967), widely used for the analysis of different datasets (Serrano et al. 1999; Moreno et al. 2001; Metcalfe et al. 2010). This technique divides the  $N$  values of the dataset into  $n$  clusters assigned by the user. The number of clusters is decided after a series of tests with different options, and choosing the minimum that best represent the dataset. The input of the clustering analysis is composed by a matrix with measured samples of grain-size distributions (here,  $N = 164$  grain-size distributions for different core depths and 116 particle diameter percentage values for each measured grain-size laser class). Each cluster is defined by a prototype and includes the samples with a closer distribution to its prototype (Hastie et al. 2001; Davis 2002). The maximum-dissimilarity algorithm (MDA) is applied to initiate the prototypes, which guarantees a deterministic classification and the most representative initial subset. The MDA algorithm, which was first described by Kennard and Stone (1969), permits many variants. In this work, the initial data of the subset is considered to be the vector with the largest sum of dissimilarities relative to the others within the data sample. Once the number of clusters is established, the prototypes (centroids) are initialized, and on each iteration is identified the nearest data to each centroid. Then, the centroid is redefined as the mean of the corresponding data, minimizing the overall within-cluster distance until the iterative reinterpretation of data converges on a single solution, and the data assigned to each group remain constant. A matrix of similarities between the  $n$  clusters and  $N$  observations is calculated, and the closest observation is represented by the nearest cluster. So, *k-means* technique helps us to group the samples into clusters according to their grain-size distribution.

## Assessment and discussion

### Optimization of the organic matter removal procedure

Some of the samples analyzed contained up to 3% total organic content (TOC) (Mix et al. 2003) (Fig. 2c). The observation of the smear slides under the microscope after the treatment with the original procedure showed the presence of brownish particles whose origin was difficult to assert by

light microscope observation (Fig. 2d). The processed samples were sieved at 63  $\mu\text{m}$  to isolate the coarser fraction and observed under binocular microscope. This confirmed the presence of brown rounded aggregates that were identified as fecal pellets, indicating that the used protocol was not efficient enough to eliminate the organic matter associated to these biogenic aggregates.

Organic matter procedure was then modified increasing the concentration of the hydrogen peroxide solution to 10%. Then, samples were placed in an oven (60°C) for two days, after additional 50 mL of 10% hydrogen peroxide were added to replace the evaporated solution. This attack was repeated one more time or even twice, depending of organic matter content of the sample. Continuous monitoring of the samples through smear slides (Fig. 2e) and optical microscope (fraction coarser than 63  $\mu\text{m}$ ) during each step of the new procedure, confirmed a satisfactory removal of fecal pellets. The comparison of the grain-size distribution from untreated samples and samples processed by the two different protocols (Fig. 2a,b) reveals that the fecal pellets present a dominant mode between 300  $\mu\text{m}$  and 500  $\mu\text{m}$ . This mode is present in nontreated samples and in those treated with the standard protocol but it disappears in samples treated by our improved protocol. These observations further prove the efficiency of the new used protocol to remove the organic matter from the marine sediments. Furthermore, analyses of the organic matter content after the application of the new procedure have confirmed that its elimination is greater than 80%. The removal of this biogenic coarse fraction is essential in any grain-size study focused on the lithogenic fraction to properly interpret the results.

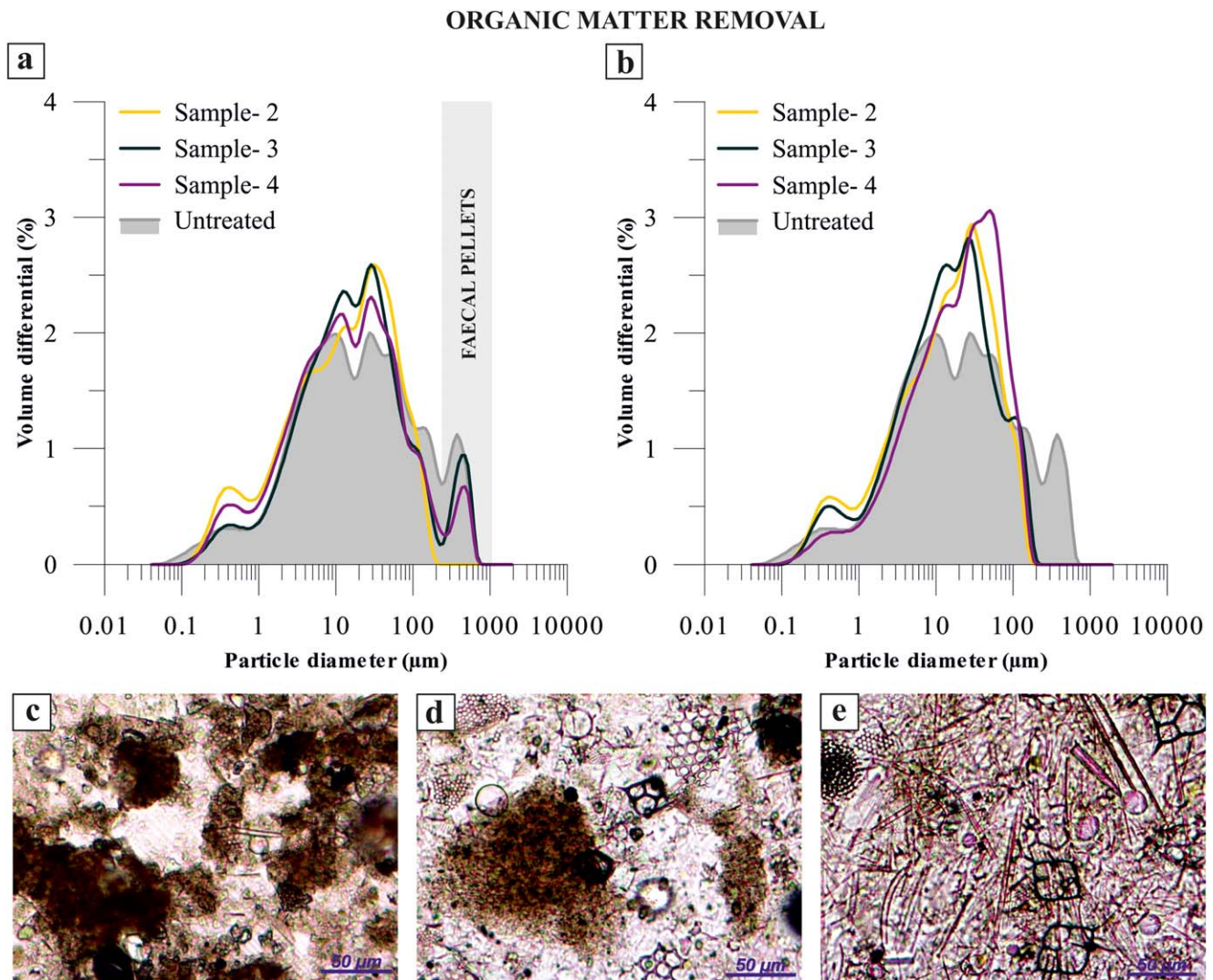
### Assessing the carbonate and Fe-Mn oxides removal procedure

The carbonate component and Fe-Mn oxides were removed adding an acetic acid-sodium acetate solution and hydroxylamine hydrochloride solution, following the standard procedure. After that, each removal step was evaluated by microscope observation of the smear slides, showing the good efficiency of the standard procedure.

### Optimization of the biogenic silica removal procedure

The biogenic silica component represents a significant fraction of the entire sample, concretely between 5% and 15% (unpubl. data), and it consists on diatoms and radiolarian remains (Fig. 3g). After using the standard protocol, microscope observation of the smear slides revealed the still abundant presence of radiolarian and diatoms remains (Fig. 3a). These observations were further confirmed by the visual binocular inspection of the fraction over 63  $\mu\text{m}$ . Consequently, a sequence of further steps was applied in order to increase the removal of biogenic silica without removing lithogenic silica. Six different protocols were tested changing two main variables: (1) the reagent and its concentration and (2) the time and number of extractions (Table 1). Both

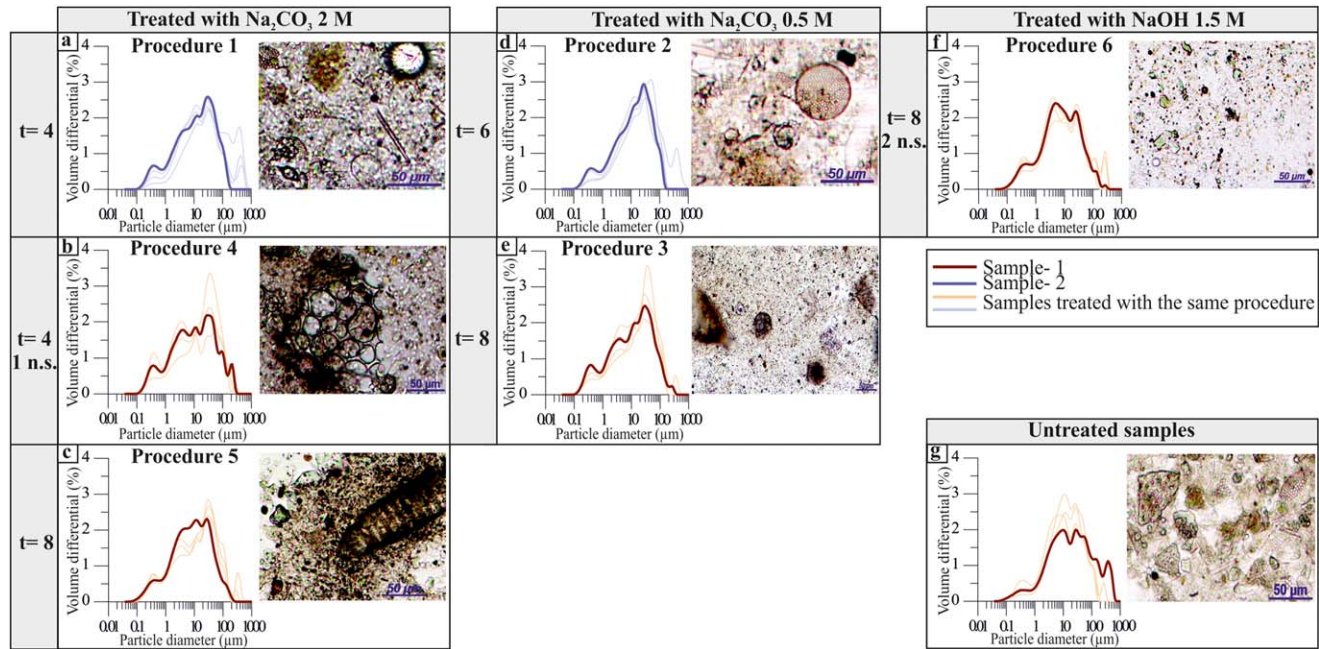




**Fig. 2.** Efficiency of organic matter removal step. (a) Granulometric distribution from four samples (colored lines) after removal of the organic matter with the standard protocol compared with untreated sample (shaded area). Vertical gray bar indicates the size distribution (300–800  $\mu\text{m}$ ) of fecal pellets. (b) Granulometric distribution of four different samples (colored lines) after removal of the organic matter with the improved procedure proposed that is here compared with untreated sample (shaded area). Note the disappearance of the terminal mode (300–800  $\mu\text{m}$ ). (c) Microscope picture of an untreated sample containing abundant brownish areas often associated to aggregates enriched in organic matter. (d) Microscope picture of a sample after the organic matter removal according to the standard protocol, note the persistence of some brownish areas. (e) Microscope picture of a sample after the organic matter removal according to the modified procedure, note the absence of brownish areas.

variables were increased progressively to ensure the biogenic silica removal but trying to minimize the impact on silicate leaching. The effectiveness and control of silicate leaching at each step was evaluated through the microscope observation of the processed samples (Fig. 3). These observations revealed that the silica microfossils persisted after most protocols with the single exception of protocol 6 (Table 1; Fig. 3f). These experiments show that the most efficient reagent for the elimination of the biogenic silica is the NaOH, without the lithic silica removal. Results of grain-size distribution (Fig. 3) show that the main mode in protocol 6 (Fig. 3) is centered on 3–4 microns, while in the other protocols it is

displaced toward larger particles (above 10 microns). These results also indicate that particles above 20 microns are severely reduced in the case of protocol 6 (Fig. 3). These different features in the grain-size distribution have a large impact in the standard parameters such as Silt/Clay or Sand/Clay, among others, that are often used for paleoceanographic studies (Fig. 4). Samples treated by protocol 1 (Fig. 4a,c,e) are dominated by the silt fraction while those treated with protocol 6 (Fig. 4b,d,f) are dominated by clay and the sand fraction is severely reduced. Therefore, the most appropriate protocol to remove the biogenic silica is using NaOH 1.5 M solution. The addition of NaOH instead of  $\text{Na}_2\text{CO}_3$



**Fig. 3.** Grain-size distribution and smear slides pictures after each of the procedures applied for biogenic silica removal. Reagent and concentration are indicated in the upper part of each column and, on the left, it is indicated the number of hours in solution (*t*) and the number of nights in the oven (*n.s.*). Note that from (a) to (e) pictures show the presence of biogenic silica remains (diatoms and radiolarian), and grain-size distributions show a dominant mode over 10 microns. (f) Correspond to the protocol chosen for the final procedure. The picture shows the only presence of lithic grains and the dominant mode is centered below 10 microns. (g) Grain distribution and picture of a nontreated sample as a reference. Detailed information for each procedures is indicated in Table 1.

**Table 1.** Different procedures tested in the biogenic silica removal step. Note that the Na<sub>2</sub>CO<sub>3</sub> was tested with different concentrations and timing. In contrast, when the reagent was changed there was a drastic elimination of biogenic silica as shown in Fig. 3f (procedure 6).

| Procedure | Reagent                         | Concentration (M) | Time in solution (h) | Nights in stove (60°C) | Nights in solution | N° extractions | Effectiveness of treatment |
|-----------|---------------------------------|-------------------|----------------------|------------------------|--------------------|----------------|----------------------------|
| 1         | Na <sub>2</sub> CO <sub>3</sub> | 2                 | 4                    | 0                      | 0                  | 2              | No                         |
| 2         | Na <sub>2</sub> CO <sub>3</sub> | 0.5               | 6                    | 0                      | 0                  | 3              | No                         |
| 3         | Na <sub>2</sub> CO <sub>3</sub> | 0.5               | 8                    | 0                      | 0                  | 4              | No                         |
| 4         | Na <sub>2</sub> CO <sub>3</sub> | 2                 | 4                    | 0                      | 1                  | 2              | No                         |
| 5         | Na <sub>2</sub> CO <sub>3</sub> | 2                 | 8                    | 0                      | 1                  | 4              | No                         |
| 6         | NaOH                            | 1.5               | 8                    | 2                      | 2                  | 4              | Yes                        |

has proven to produce a drastic reduction in the number of diatoms and radiolarian, being thus much more effective than previous standard protocol (Figs. 3 and 4).

**Final procedure**

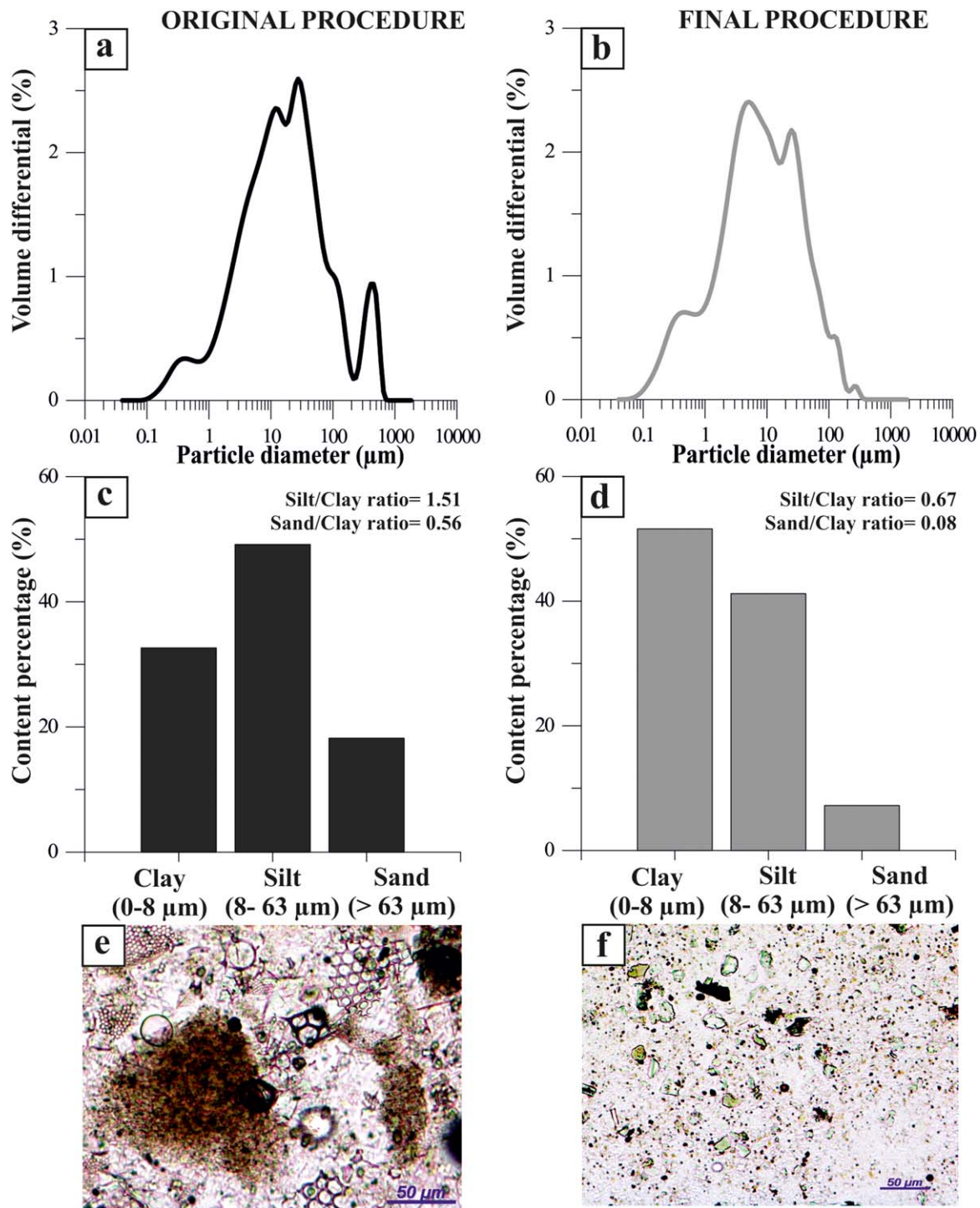
The improved procedure described below includes all modifications suggested to the standard procedure to be used in samples with a high biogenic content (Table 2). Figure 5 illustrates the effect of each step in the grain-size distribution. In general, the biogenic component removal takes out most of the coarse particles corresponding to

zooplankton remains, foraminifera and radiolarian as well as fecal pellets. Although the fine silt fraction is also removed corresponding to nannofossils and some small diatoms. This procedure consists of four removal steps, concretely of the organic matter, carbonate bioclasts, Fe-Mn oxides, and biogenic silica fractions, described in Table 2.

**Grain-size distributions and clustering analysis**

Grain-size distributions of the analyzed samples through ODP 1240 core depth are shown in Fig. 6a. The





**Fig. 4.** Comparison of the results obtained in Sample 1 after treatment with the standard procedure (a, c, e) and after treatment with the improved procedure (b, d, f). (a, b) Grain-size distribution; (c, d) percentages of clay (laser), silt, and sand, expressed in laser size classes; (e, f) smear slides pictures, where efficient removal of biogenic remains can be observed in (f). Note the disappearance of the coarser mode (300–800  $\mu\text{m}$ ), and the switch of the median toward finer grain sizes, around 3–4 microns, increasing the percentage of clay fraction.

grain-size distribution follows a clear pattern dominated by a mode around 4  $\mu\text{m}$ . Two marginal modes are also discernible: fine mode around 0.7  $\mu\text{m}$  and some random

modes on the coarser tail of the distribution. Nonetheless, the grain-size distributions present strong variability. Often, these grain size results are expressed as different

**Table 2.** Description of the improved procedure.

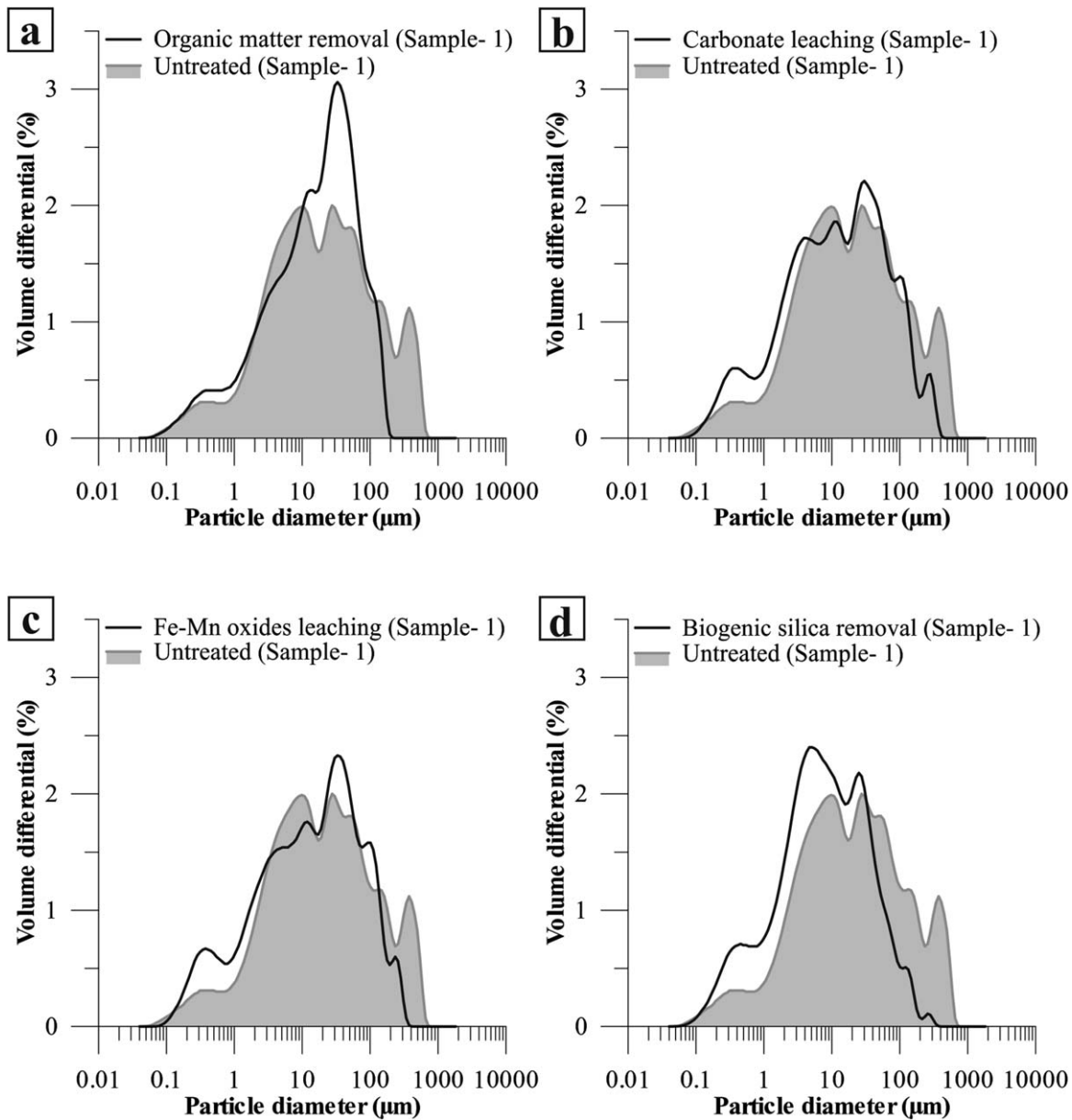
| Organic Matter                                 | Carbonate Component  | Fe-Mn Oxides   | Biogenic Silica   |
|--|--|--|---|
| 50 mL 10% H <sub>2</sub> O <sub>2</sub> pH = 3 | 35 mL Solution of 2.7% CH <sub>3</sub> COOH (27 mL) + 0.34 M CH <sub>3</sub> COONa (28 g) pH = 4 | 45 mL HH Solution of 25% CH <sub>3</sub> COOH (250 mL) + 0.02 M (NH <sub>3</sub> OH)Cl (1.3893 g) pH = 2 | 35 mL 1.5 M NaOH (60 g) pH = 13                               |
| ↓<br>Shake the samples                         | ↓<br>Shake the samples for five hours  | ↓<br>Shake the samples for two hours   | ↓<br>Shake and sonicate the samples for 10 min                |
| ↓<br>Left for two days                         | ↓<br>Centrifuge the samples for 15 min to remove the solution                                    | ↓<br>Centrifuge the samples for 15 min to remove the solution  | ↓<br>Remain the solution overnight in an oven (60°C)          |
| ↓<br>Dry in an oven (60°C)                     | ↓<br>Repeat the extraction, shaking the samples overnight.                                       | ↓<br>Repeat the extraction, shaking the samples overnight.   | ↓<br>Place the samples in a hot bath for two hours (85°C)     |
|  | ↓<br>Samples washing with MilliQ water   | ↓<br>Samples washing with MilliQ water two times   | ↓<br>Centrifuge the samples for 15 min to remove the solution |
|  | ↓<br>Centrifuge samples for 15 min to remove the solution  | ↓<br>Centrifuge samples for 15 min to remove the solution  | ↓<br>Repeat the extraction for two hours (85°C)               |
|  |  |  | ↓<br>Leave the sample rack in the oven overnight (60°C)       |
|  |  |  | ↓<br>Centrifuge the samples for 15 min to remove the solution |
|  |  |  | ↓<br>Repeat two extractions for two hours each one (85°C)     |
|  |  |  | ↓<br>Samples washing with MilliQ water two times              |

ratios such as Silt/Clay ratio (Hall and McCave 2000), Sortable Silt (McCave et al. 1995), or UP10 (Frigola et al. 2007). These basic representation of the data can reflect the coarser or finer character of the samples, but they do not reflect the modal distribution of the sample or the number of families presents in the samples and thus, very valuable information that is still present in the measurements may be missed. Some statistical approaches explored additional information in terms of compositional characterization (the so-called “end-member modeling”) (Weltje 1997). The approach used here divides the samples into a number of clusters according to their grain-size distribution similitude. Thus, this method gives us the more representative groups that characterize this high variability and helps to interpret the mechanisms responsible of their transport to the deep sea.

In this case, the grain-size dataset is composed by a matrix with 19,024 values (164 samples for several core depths, expressed in mcd, and 116 size laser classes of particle diameter, expressed in μm). After testing with several *n* clusters, it is concluded that the dataset is better characterized using *n* = 6 clusters, as shown in Fig. 6b. These clusters present distinctive features and have been

named as clusters A, B, C, D, E, and F. Cluster A is the dominant pattern (36% of the samples) and shows a clear mode around 4 μm. Clusters B (19.51%) and C (13.41%) show certain similarities with cluster A but cluster B has higher percentage of particles in the dominant mode, and cluster C shows a principal mode less abundant and a coarser terminal mode than Clusters A and B. Cluster D (16.46%) shows a distinctive pattern with a coarser principal mode, and higher percentages around 40 μm. Clusters E and F are less frequent but show a pattern totally different with respect to the rest of clusters as coarser sediments become more abundant. The main mode of cluster E (9.76%) is located around 250 μm, while cluster F (4.88%) presents a main mode well classified around 400 μm and the four-micrometer mode is more defined than in cluster E.

Cluster analysis brings the opportunity to objectively separate the samples in different families providing very useful information for the interpretation of the processes responsible for the lithic fraction arrival such as eolian and fluvial transport. In this way, this statistical approach offers a powerful tool to further understand past atmospheric changes in wind and/or rain dynamics.



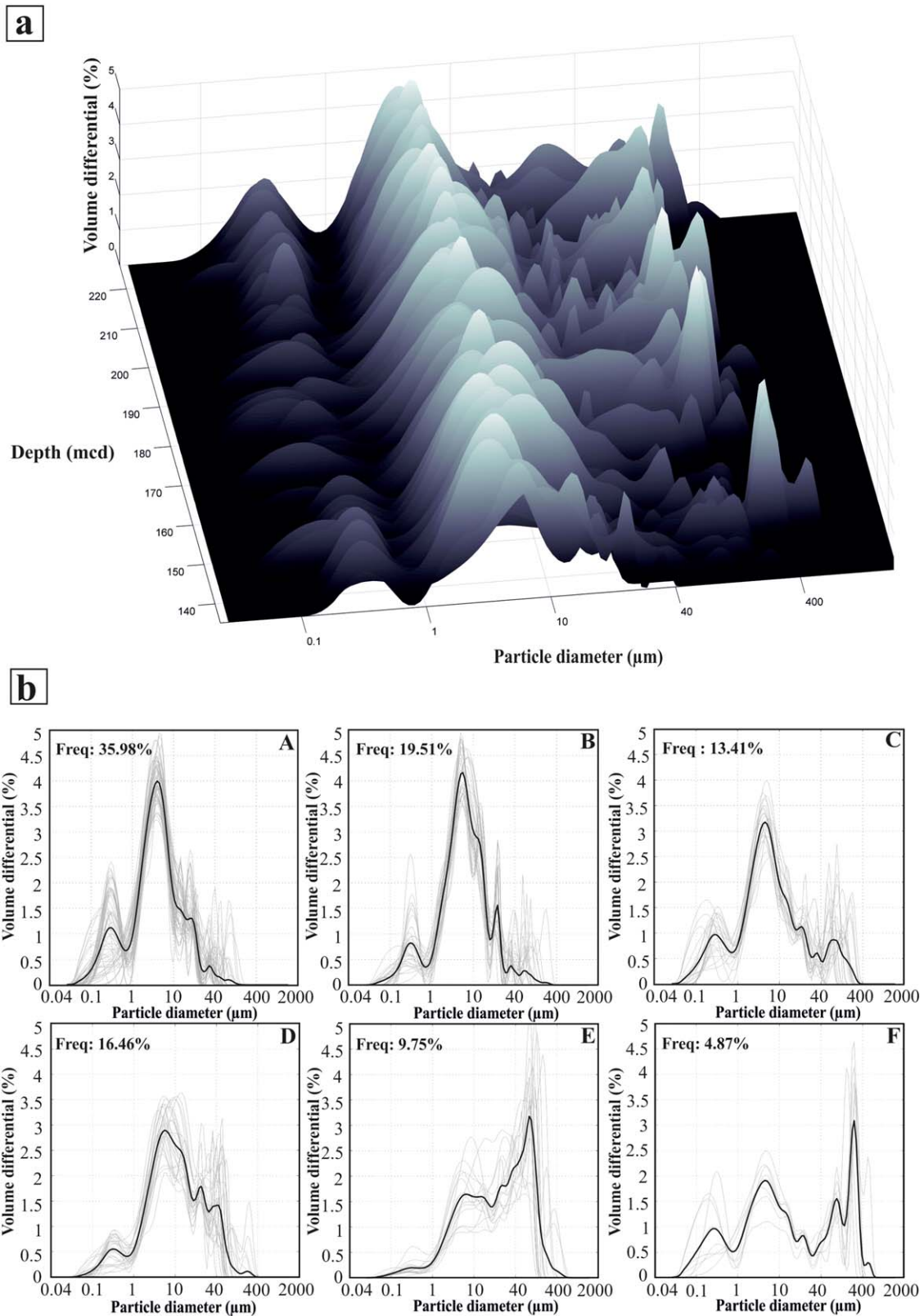
**Fig. 5.** Grain-size distribution of Sample 1 after each extraction step following the improved procedure (line) compared with a nontreated Sample 1 (shaded area). (a) Organic matter removal step; (b) carbonate leaching step; (c) Fe-Mn oxides leaching step; (d) biogenic silica removal step. Note the gradual reduction of the larger grain sizes, between 150  $\mu\text{m}$  and 800  $\mu\text{m}$ .

**Conclusions**

This experiment proves that the standard procedures applied to the biogenic removal are too weak in sediments of high productivity areas. These areas required the application of a more aggressive procedure than those normally applied in other studied areas. The final procedure has increased the time and the concentration of the reagents in different steps with respect to previous procedures. Particularly difficult was the biogenic silica removal due to the high

content of radiolarians and diatoms remains. In this case  $\text{Na}_2\text{CO}_3$  2 M, normally used in other works, was insufficient. NaOH digestions show, instead, a complete biogenic silica removal, without removing the lithogenic silica content.

The continuous monitoring of the grain-size distribution after each experimental step reveals that inappropriate procedures for the elimination of the biogenic fraction can induce large biases in the grain-size parameters broadly used in paleoceanographic studies.



**Fig. 6.** (a) 3-D plot of grain-size distributions of the studied period. The volume differential is expressed in percentage, particle diameter is expressed in  $\mu\text{m}$ , and depth is expressed as composite depth. (b) Clusters defined by *k-means* technique (A–F); particle diameter is expressed in  $\mu\text{m}$  and volume differential is expressed in percentage. Note that the frequency of each cluster is also expressed.



After obtaining the particle size distributions, *k-means* algorithm has been used to analyze the large grain-size dataset and characterize sample clusters with distinctive patterns.

### Comments and recommendations

Our new procedure points to the importance of an accurate protocol to obtain optimal results that allow a careful analysis of the lithogenic particle-size distribution in marine sediments from high-productive areas. This method avoids the overestimation of coarser lithic particles due to biogenic artifacts, which is crucial in paleoclimatic reconstructions, such as eolian and fluvial system inputs. This new method can also be useful to separate the lithic fraction and Fe-Mn oxide fraction in studies with radiogenic isotopes.

This procedure can be also used in areas with less productivity, such as the Mediterranean Sea, where, the biogenic silica content represents less than 4% (Rumín-Caparrós et al. 2013). In this case, it is recommended to do a few modifications mainly focused on biogenic silica step and in this case it would be enough to apply the method created by Mortlock and Froelick (1989).

The extraction timing control is crucial in the biogenic silica removal stage to avoid the siliciclastic fraction removal. The cleaning of the samples with MilliQ water in order to remove the remaining NaOH solution is recommended to avoid potential damages of grain-size analyzer instrumentation.

It is recommended to start the analysis of a specific area testing the effectiveness of each removal stage by monitoring the sample after each step through smear slide microscope observations.

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## RESEARCH ARTICLE

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## Key Points:

- Atmosphere-ocean coupled changes in the EEP region along the early Pleistocene
- Two phases are observed in the glacial reorganization of the ITCZ
- Distinct transport mechanisms of carbon toward the deep sea were characterized

## Supporting Information:

- Figures S1–S8
- Table S1

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## Atmosphere-ocean linkages in the eastern equatorial Pacific over the early Pleistocene

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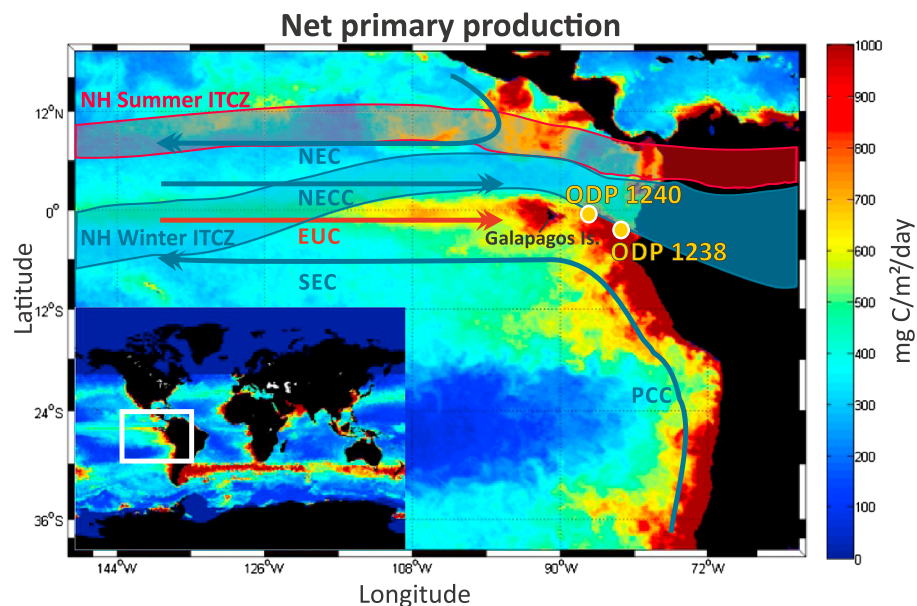
**Abstract** Here we present a new set of high-resolution early Pleistocene records from the eastern equatorial Pacific (EEP). Sediment composition from Ocean Drilling Program Sites 1240 and 1238 is used to reconstruct past changes in the atmosphere-ocean system. Particularly remarkable is the presence of laminated diatom oozes (LDOs) during glacial periods between 1.85 and 2.25 Ma coinciding with high fluxes of opal and total organic carbon. Relatively low lithic particles (coarse and poorly sorted) and iron fluxes during these glacial periods indicate that the increased diatom productivity did not result from dust-stimulated fertilization events. We argue that glacial fertilization occurred through the advection of nutrient-rich waters from the Southern Ocean. In contrast, glacial periods after 1.85 Ma are characterized by enhanced dust transport of finer lithic particles acting as a new source of nutrients in the EEP. The benthic ecosystem shows dissimilar responses to the high productivity recorded during glacial periods before and after 1.85 Ma, which suggests that the transport processes delivering organic matter to the deep sea also changed. Different depositional processes are interpreted to be the result of two distinct glacial positions of the Intertropical Convergence Zone (ITCZ). Before 1.85 Ma, the ITCZ was above the equator, with weak local winds and enhanced wet deposition of dust. After 1.85 Ma, the glacial ITCZ was displaced northward, thus bringing stronger winds and stimulating upwelling in the EEP. The glacial period at 1.65 Ma with the most intense LDOs supports a rapid southward migration of the ITCZ comparable to those glacial periods before 1.85 Ma.

### 1. Introduction

The Early Pleistocene climate evolution is marked by the progressive strengthening of the Northern Hemisphere glaciation (NHG), and it has been argued that this situation strengthened trade winds, inducing a cooling in tropical sea surface temperatures (SSTs) by enhanced upwelling activity [Marlow *et al.*, 2000]. Meanwhile, land records indicate an enhanced aridity along the tropical belt with consequences on African faunal evolution [deMenocal, 1995, 2004; Feakins *et al.*, 2005; Trauth *et al.*, 2007]. The obliquity imprint upon tropical proxy records further supports the high-latitude control over tropical regions during this period [Liu and Herbert, 2004; Herbert *et al.*, 2010].

The eastern equatorial Pacific (EEP) is known by its highly productive upwelling system, which has operated with varying intensity across glacial-interglacial cycles [Lyle *et al.*, 1988; Weber and Pisias, 1999; Murray *et al.*, 2000]. During the early Pleistocene, 400 kyr eccentricity cycles seem to have ultimately controlled major changes of SST in the EEP, with abrupt and intense cooling events at 1.7 and 2.1 Ma [Herbert *et al.*, 2010].

Nevertheless, several records from the EEP reveal a rather complex link between SST and primary productivity across the Pleistocene [Dekens *et al.*, 2007; Lawrence *et al.*, 2006; Ma *et al.*, 2015]. In particular, a remarkable period of enhanced EEP primary productivity between 1.6 and 2.9 Ma was reflected in unusually high-alkenone concentrations [Lawrence *et al.*, 2006] without any clear expression of colder SST. Such signal decoupling has been attributed to EEP fertilization due to an increase in nutrient availability finally driven by changes in nutrient utilization in the Southern Ocean [Lawrence *et al.*, 2006; Etourneau *et al.*, 2013]. Nitrogen isotopes support a sharp increase in EEP denitrification but starting later, after 2.1 Ma, which is attributed to an enhanced upwelling activity due to strengthened Walker circulation [Liu *et al.*, 2008]. This situation is consistent with a



**Figure 1.** Regional oceanography and net primary production (NPP) from the eastern equatorial Pacific (EEP). Surface and subsurface currents in the EEP, Equatorial Undercurrent (EUC), North Equatorial Current (NEC), North Equatorial Countercurrent (NECC), Peru-Chile Current (PCC), and South Equatorial Current (SEC). NPP in the surface waters of modern EEP is based on the standard VGPM algorithm [Behrenfeld and Falkowski, 1997]. Data were downloaded from the Ocean Productivity site. Northern Hemisphere summer and winter positions of the ITCZ have been marked with blue and red bands. ODP Sites 1240 and 1238 are labeled with yellow dots.

major atmospheric reorganization including an intensification of the Walker circulation and the onset of a strong equatorial west-east gradient at 1.5–2 Ma, as indicated by SST and isotopic records from both western equatorial Pacific (WEP) and EEP [Ravelo *et al.*, 2004; Wara *et al.*, 2005; Etourneau *et al.*, 2010; Ravelo *et al.*, 2014]. This time period also appears to be critical in Southern Atlantic Ocean where a reinforcement of trade winds and the strengthening of the associated upwelling have been noticed [Etourneau *et al.*, 2009].

Nevertheless, this atmospheric reorganization has been questioned by new long multiproxy records that suggest a relatively constant E-W equatorial Pacific SST gradient since the Pliocene and, consequently, an essentially rather constant and continuously active EEP upwelling system [e.g., Zhang *et al.*, 2014; O'Brien *et al.*, 2014]. The debate is far from being settled [Ravelo *et al.*, 2004; Wara *et al.*, 2005; Ravelo *et al.*, 2014].

Thus, several records support the occurrence of EEP productivity and atmospheric changes during the early Pleistocene, but their occurrence is not always apparently synchronous and their coupling is still puzzling. The lithic fraction of deep-sea sediments is a proxy that could shed light on atmospheric changes in the EEP. It has been used to track the location of the Intertropical Convergence Zone (ITCZ), which would have migrated southward from the late Miocene to present [Hovan, 1995; Hyeong *et al.*, 2006]. Unfortunately, these studies lack the temporal resolution to evaluate rapid changes that might have occurred during the early Pleistocene. Short-term reconstructions of changes in the average ITCZ location have concentrated on glacial-interglacial cycles of the late Pleistocene and Holocene and are mostly based on SST marine records, humidity terrestrial records, or model assimilations [Koutavas and Lynch-Stieglitz, 2004; Peterson and Haug, 2006; Broccoli *et al.*, 2006; McGee *et al.*, 2014; Schneider *et al.*, 2014].

Elucidating the link between any early Pleistocene atmospheric reorganization and productivity changes in the EEP upwelling requires using parallel records of proxies sensitive to both atmospheric and marine conditions. In this paper we present a novel very high resolution multiproxy study over the 1.56–2.26 Ma time interval in the EEP, resulting from the detailed analysis of biogenic and lithogenic components in deep-sea sediments. The study focuses on Ocean Drilling Program (ODP) Site 1240, located at the northern edge of the equatorial cold water tongue (Figure 1) and thus, made this site potentially sensitive to changes in the atmospheric-ocean coupled system [Hovan, 1995; Mix *et al.*, 2003]. Previous results for this ODP site have shown major changes in the sediment composition occurring along the early Pleistocene, which were linked to shifts in the regional



atmosphere-ocean system [Mix *et al.*, 2003]. Moreover, ODP Site 1240 contains sequences of laminated diatom oozes (LDOs), which become a valuable paleoproductivity indicator. In order to ground truth our results and achieve a broader evaluate the geographical extension, the data obtained from ODP Site 1240 have been compared with data from ODP Site 1238, located further south and closer to the South American coastline. Thus, this study offers an exceptional time resolution for the early Pleistocene and demonstrates that the observed changes occurred as rapid transitions related to glacial-interglacial cycles, rather than as progressive long-term change.

## 2. Oceanographic and Atmospheric Setting

The EEP is one of the most productive upwelling areas in the world controlled by the trade wind systems [Chelton *et al.*, 2001]. This atmospheric convergence near the equator and the ascending branch of the Hadley cell define the position of the ITCZ and control the surface ocean properties [Koutavas and Lynch-Stieglitz, 2004]. Surface ocean circulation in the EEP is characterized by the north-south asymmetry of the surface currents, as a consequence of the trade winds intensity [Wyrki, 1974]. ODP Sites 1240 and ODP 1238 locations are both influenced by the South Equatorial Current (SEC), which is the continuation of the Peru-Chile Current (PCC), centered at about 5°S under the southeast trade winds [Wyrki, 1967; Kessler, 2006]. During the Southern Hemisphere winter, when SE trade winds are strengthened, the SEC is more intense [Wyrki, 1967]. In the subsurface, the Equatorial Undercurrent (EUC) flows eastward along the equator, and replaces surface water driven westward by the trades [Kessler, 2006], providing nutrients to the EEP that are sourced in the polar regions, mainly from the Southern Ocean [Calvo *et al.*, 2011; Sarmiento *et al.*, 2004; Pena *et al.*, 2013] (Figure 1). Recent studies suggest that Galapagos Islands could influence the flow of EUC east of 95°W, acting as a topographic barrier, although its influence has not been fully characterized yet [Karnauskas *et al.*, 2007, 2010].

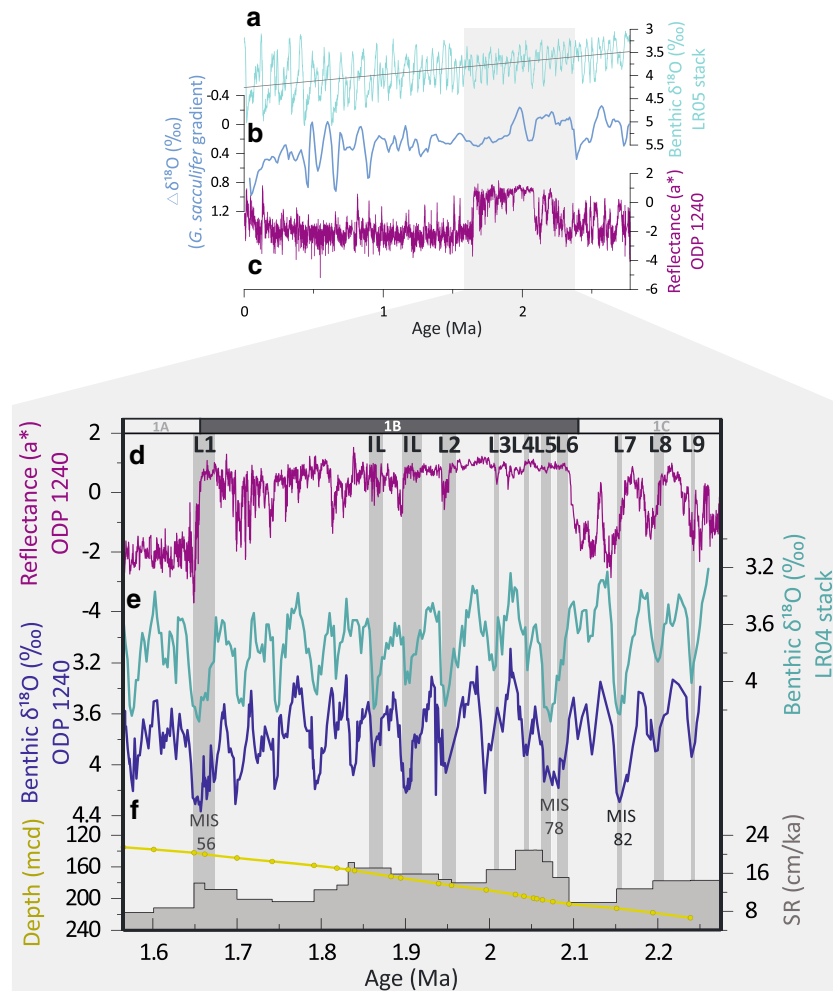
The strong southeasterly winds that cross the equator induce an Ekman divergence zone, which allows the upwelling of nutrient-rich and cold waters from the EUC, particularly during the Southern Hemisphere winter (Figure 1) [Wyrki, 1981]. The extent of the cold tongue created by the upwelling is limited by the equatorial front (EF), the position of which varies seasonally. The EF reaches its most northerly position during the Northern Hemisphere summer [Pak and Zaneveld, 1974; de Szoeke *et al.*, 2007]. In the modern EEP, biological activity does not consume all the macronutrients upwelled to the surface due to limitations in the supply of iron and silicic acid [Brzezinski *et al.*, 2008]. Iron is a micronutrient that limits macronutrient utilization, and thus, it can ultimately control the primary production of the upwelling system [Jickells *et al.*, 2005; Mahowald *et al.*, 2005]. Since the EUC is typically iron depleted by the time it reaches the EEP [Kaupp *et al.*, 2011], the main iron contribution occurs through eolian dust deposition. This induces a strong connection between dust fluxes, iron input, and primary productivity in the EEP [Martin, 1990; Jickells *et al.*, 2005].

At present, the mean ITCZ position is shifted toward the Northern Hemisphere as a consequence of a northward heat transport across the equator by ocean circulation [Marshall *et al.*, 2014]. ITCZ migrations can also be the result of changes in the interhemispheric temperature contrast [Broccoli *et al.*, 2006], responding to seasonal changes in insolation and atmosphere-ocean interactions [Xie and Philander, 1994]. During Northern Hemisphere summer, when the southeasterly trades are stronger [Chelton *et al.*, 2001; Koutavas and Lynch-Stieglitz, 2004], the ITCZ is positioned at about 10°N and both maximum upwelling and significant eolian deposition of dust from South America occur in the EEP [Molina-Cruz, 1977]. The ITCZ migrates southward when the southeasterly trades are weaker [Chelton *et al.*, 2001], between February and April, reducing the dust input and weakening upwelling. Paleoclimate records and numerical models suggest that the southward migration may have been greater during colder phases of the Northern Hemisphere on a variety of time scales, such as the Little Ice Age (LIA), shifting the ITCZ well south of its most southern present position [Koutavas and Lynch-Stieglitz, 2004; Chiang and Bitz, 2005; Broccoli *et al.*, 2006; Sachs *et al.*, 2009].

## 3. Materials and Methods

ODP Site 1240 (0°01.31'N, 86° 27.76'W; 2921 m water depth) and ODP Site 1238 (1°52.310'S, 82°46.934'W; 2203 m water depth) were retrieved in the EEP, from the northern and southern flank of the Carnegie Ridge, respectively, in the Panama Basin during the ODP Leg 202, by JOIDES Resolution in 2002 (Figure 1) [Mix *et al.*, 2003].

The recovered sedimentary sequence of ODP Site 1240 is a fossil-rich mud with variable composition [Mix *et al.*, 2003]. Three subunits (1A, 1B, and 1C) were defined according to their dominant sedimentological characteristics



**Figure 2.** Chronological framework for ODP Site 1240. (a) Global benthic  $\delta^{18}\text{O}$  stack (LR04 stack) [Lisiecki and Raymo, 2005]. (b) Oxygen isotope difference (*Globigerinoides sacculifer*) between ODP Site 851 (Eastern Pacific) [Cannariato and Ravelo, 1997] and ODP Site 806 (Western Pacific) [Berger et al., 1993; Jansen et al., 1993]. (c) ODP Site 1240 reflectance ( $a^*$ ) for the last 2.7 Ma [Blum et al., 2005] shows abrupt variations in sediment composition for the studied interval. (d) ODP Site 1240 reflectance ( $a^*$ ) for the studied period [Blum et al., 2005], showing three subunits clearly marked and represented as a white and gray bar (1A, 1B, and 1C). (e) Age model from ODP Site 1240, developed by comparison of high-resolution ODP Site 1240 benthic  $\delta^{18}\text{O}$  and global rates from ODP Site 1240 for the studied interval. (f) Tie points and linear sedimentation rates from ODP Site 1240 for the studied interval. The gray shaded vertical bars indicate the position of the observed and the interpreted LDOs, labeled as L1–L9 and IL, respectively. Marine isotopic stages (MISs) 56, 78, and 82 are also shown.

[Mix et al., 2003]. In this work we focus on subunit 1B, in the depth interval from 135.34 to 225.94 meters composite depth (mcd), between 1.65 and 2.1 Ma, which presents higher reflectance ( $a^*$ ) values (Figure 2). It was initially proposed to reflect an intensification of atmospheric circulation, based on the preliminary results of grain density, biogenic silica, total organic carbon (TOC) content, and the shipboard stratigraphic description presented in Mix et al. [2003]. Eleven LDOs were described mainly within subunit 1B (1.65–2.2 Ma) [Mix et al., 2003] (see section 5.1). They are composed largely of pennate diatoms, such as *Thalassiothrix* spp., that tend to form large grids of strongly intertwined cells.

The sedimentary sequence from ODP Site 1238 is mostly formed by diatom nannofossil ooze and bioturbated nannofossil oozes with a variable abundance of clay and foraminifera [Mix et al., 2003]. The analyzed sequence is centered from 79 to 99 mcd, in interval of 1.6–1.75 Ma.

### 3.1. Oxygen Isotope Record

In order to establish robust chronology, we measured benthic foraminifer  $\delta^{18}\text{O}$  from ODP Site 1240, which was based in the analysis of two different species of benthic foraminifera, *Uvigerina* spp. and *Cibicidoides wuellerstorfi*.

Each measurement of *Uvigerina* spp. was made on eight to ten individuals. Measurements of *C. wuellerstorfi* were performed on four to five individuals ( $>212\ \mu\text{m}$ ). Samples were crushed to open the foraminiferal chambers and then cleaned with reagent grade methanol in order to remove attached clay particles. All measurements were made with a Finnigan-MAT252 mass spectrometer fitted with a Kiel Carbonate Device I in the Scientific and Technological Center of the University of Barcelona (CCIT-UB). Values are reported as per mille with respect to the Vienna Pee Dee belemnite standard. For the duration of the analyses, external reproducibility was always better than  $0.06\text{‰}$  for  $\delta^{18}\text{O}$ . In order to produce the composite  $\delta^{18}\text{O}$  record, the *C. wuellerstorfi* results were corrected to the *Uvigerina* scale by adding  $0.64\text{‰}$  [Shackleton and Hall, 1984].

### 3.2. Biogenic Fraction: Total Organic Carbon, Nitrogen Content, Opal Content, and *Uvigerina* spp. Abundance

EEP biogenic fractions (TOC, total nitrogen (TN), opal, and *Uvigerina* spp. abundance) were analyzed to monitor past changes in the ocean productivity system. TOC and total nitrogen (TN) content were analyzed at the CCIT-UB using an elemental organic analyzer Thermo EA Flash 1112. TOC was measured in 25% HCl-treated sediment samples [Fabres et al., 2002].

Biogenic silica concentrations were measured in 200 mg samples of bulk sediment. The extraction method is modified from Povea et al. [2015] and includes a two-step leaching with a 1.5 M NaOH solution. Si concentration in both leachates was determined through inductively coupled plasma optic spectrometer (ICP-OES), using a PerkinElmer model Optima 3200 RL at the CCIT-UB. Biogenic opal concentrations were determined from Si concentrations multiplying the obtained values by 2.4 [Mortlock and Froelich, 1989].

The main benthic foraminifera genera present in the samples were counted to identify any major change in the assemblage, which could be indicative of changes in the deep ocean nutrient content and oxygen concentration. The principal benthic foraminiferal assemblage is formed by *Girovina* spp., *Uvigerina* spp., *Melonis* spp., *Cibicides wuellerstorfi*, and *Cibicides kullenbergi* in order of abundance. After a preliminary low-resolution counting (107 samples with a 6.5 kyr average time resolution) considering these five genera, *Uvigerina* spp. was selected to generate high-resolution counts over the whole sequence because it showed the greatest variability.

### 3.3. XRF Core Scanner Measurements

XRF core scanner was used in order to achieve at high resolution the elemental composition of the EEP sediments. Sampling for XRF core scanner analyses was done at the Gulf Coast ODP repository at Texas. U-channels were collected by pushing rigid u-shaped plastic liners ( $2 \times 2\ \text{cm}$  cross section, 1.5 m in length) into the core sections to collect narrow continuous samples of core. XRF core scanner analyses were done at the University of Bremen (Germany). The XRF analyzes the very top of the sediment surface over  $1\ \text{cm}^2$  area, using 30 s count time, 20 kV X-ray voltage, and an X-ray current of 0.087 mA to obtain statistically significant Fe counts. A detailed description of the applied X-ray fluorescence analysis and the system configuration of the XRF core scanner at the University of Bremen are given in Jansen et al. [1998] and Röhl and Abrams [2000]. The resulting data represent element intensities in counts per second, and all the intensities are above the detection limits [Richter et al., 2006]. Intensity values were converted to concentrations through calibration with absolute elemental concentrations obtained from 30 sediment samples selected along this section (see section 5.5). Sediment samples were analyzed by ICP-OES at the CCIT-UB after total digestion of 50 mg of dried bulk sediment material in a pressure digestion system with a mixture of 3 mL  $\text{HNO}_3$  65%, 2 mL HF 40%, and 2 mL HCl 32%. After decomposition, the samples were heated to dryness, redissolved in 5 mL of 6.5%  $\text{HNO}_3$ , and homogenized in the microwave. Fe element was analyzed by ICP-OES in a PerkinElmer Optima 3300 RL with a precision better than 2%. The accuracy of element determinations was checked using standard reference materials. The ICP-OES obtained values were used to transform the XRF data into concentration values (mg/g). Correlation equations with  $r^2 = 0.79$  indicate a high correlation between both methods, thus allowing the data conversion (Figure S1 in the supporting information).

### 3.4. Grain Size and Mineralogical Analyses

Grain size analysis and mineralogical description have been conducted to characterize the lithic fraction that reached the eastern equatorial Pacific. Prior to the grain size analysis, samples were processed with a protocol specifically designed to ensure the complete removal of all the biogenic (organic matter, carbonate, and biogenic silica) and authigenic components (diagenetic oxides), leaving only the lithogenic components [Povea et al., 2015]. After this procedure, smear slides were prepared for each sample using a UV curing adhesive

and dried under an ultraviolet light [Backman and Shackleton, 1983; Rothwell, 1989]. They were then observed with a microscope to ensure the quality of the procedure as well as to determine the percentages of the main mineralogical components of the lithic fraction [Povea et al., 2015]. Mineral abundance was estimated using the comparison chart for visual percentage estimation [Terry and Chillingar, 1955]. Grain size distributions were determined using a Coulter LS 230 on the lithic fraction. In addition, the lithic percentage was calculated for the studied interval (1.56–2.26 Ma). Bulk dry samples were weighed before the removal of the biogenic fraction. After the application of the biogenic removal procedure, the samples were lyophilized and weighed. The difference between these weights gives the biogenic fraction removed. Thus, the lithic percentage was obtained after subtracting the biogenic percentage from the total percentage (lithic percentage = 100% – % biogenic fraction). To aid in the interpretation of the large grain size data set, a statistical method using a k-means clustering algorithm was applied [Povea et al., 2015]. This method divides the data set into  $n$  clusters, which are represented by its centroid and formed by the data for which the centroid is the nearest [Hastie et al., 2001]. The degree of representation of each cluster in each sample is obtained by calculating the Euclidean distances between each cluster centroid and the  $N$  data.

#### 4. Chronological Framework

The age model is based on visual alignment of the high-resolution benthic  $\delta^{18}\text{O}$  isotopic record from ODP Site 1240 with the LR04 stack [Lisiecki and Raymo, 2005], including tie points every ~27 kyr on average ( $r^2 = 0.76$ ; Figure 2). Our sequence corresponds to the time interval between 1.56 and 2.26 Ma, comprising the early Pleistocene from marine isotopic stage (MIS) 52 to MIS 86. Sedimentation rates vary through this interval, with values oscillating between 7.7 and 20.9 cm/ka. These sedimentation rates are relatively high for this area and can be attributed both to the high particle flux from the equatorial upwelling system and to the basin morphology, an abyssal valley which acts as natural sediment trap [Mix et al., 2003]. The studied interval provides a time resolution of 4 kyr on average for the lithic and biogenic records and 170 years for the XRF scanner data.

Mass accumulation rates for the biogenic and lithic records were calculated based on linear sedimentation rates and dry bulk density (DBD). This density has been estimated from a linear correlation ( $r^2 = 0.92$ ) between gamma ray attenuation bulk density and the available DBD discrete measurements (Figure S2 in the supporting information) [Mix et al., 2003].

### 5. Results

#### 5.1. Laminated Diatom Oozes

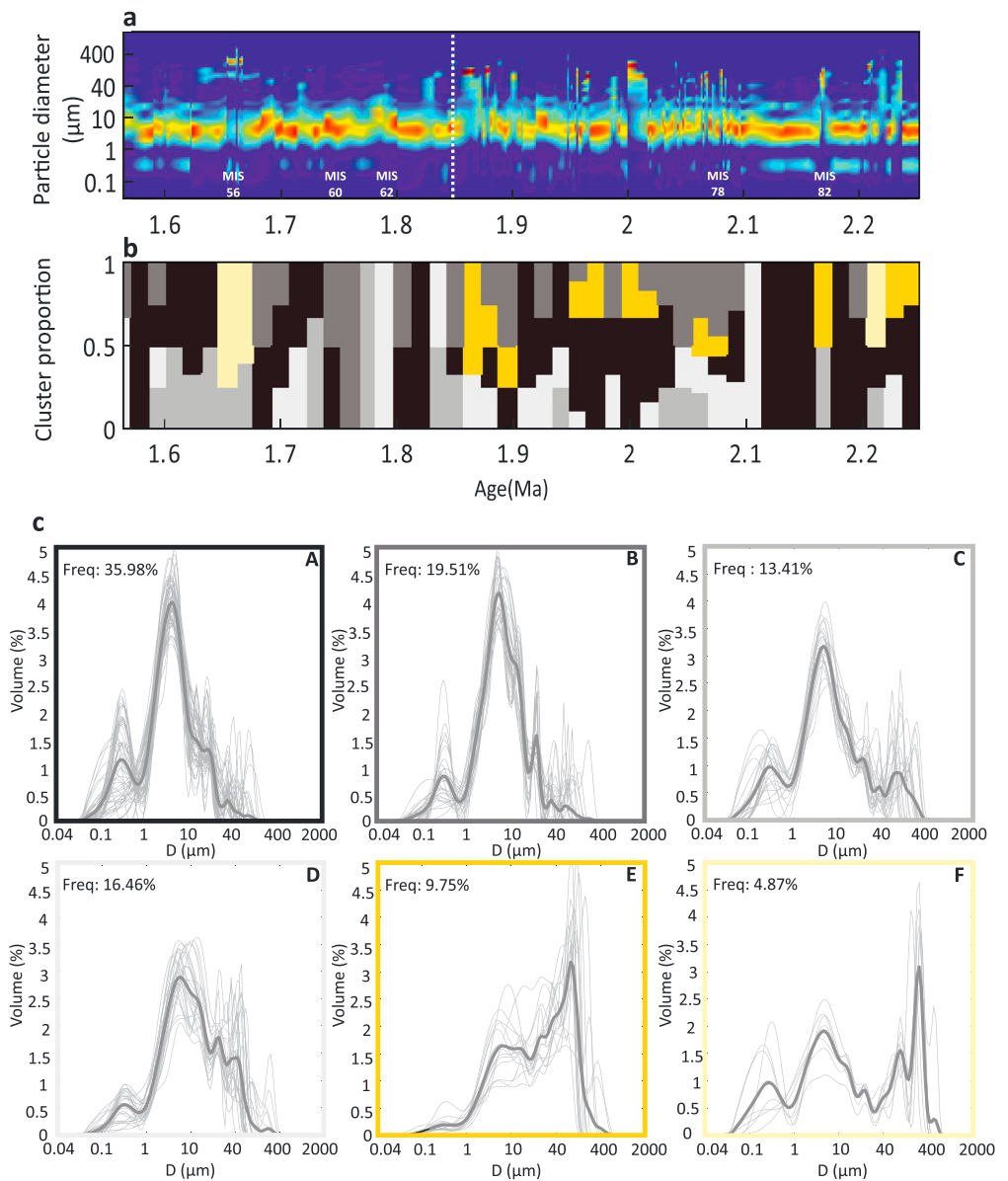
Lithology from ODP Site 1240 is mostly dominated by diatom-nannofossil ooze or diatom-bearing nannofossil ooze. The identification of the laminated diatom oozes is based on the visual identification of centimeter-thick color bands from dark olive to olive and dark olive brown. In contrast, the sediment color in the nonlaminated intervals alternates between pale olive and light olive gray and presents frequent bioturbation marks of *Zoophycos* burrowing [Mix et al., 2003]. Diatom assemblage during the laminated layers is dominated by *Thalassiothrix* spp. and *Thalassionema* spp., while the nonlaminated layers are dominated by *Azpeitia nodulifera* (Figure S3 in the supporting information). The observed LDOs (labeled as L1 to L9) have been defined based on the visual identification due the dark olive brown color. The interpreted LDOs (labeled as IL) have been determined since exhibiting the same pattern of the observed LDOs, based on the highest concentrations of biogenic silica and lithic contents, albeit its visual identification is not so clear.

#### 5.2. Oxygen Isotope Record

The benthic  $\delta^{18}\text{O}$  record has values that range from 3.2 to 4.5‰ with oscillations corresponding to glacial/interglacial cycles (Figure 2). The data reveal very sharp transitions between interglacial and glacial phases. Three remarkable glacial periods are recorded as presenting the highest  $\delta^{18}\text{O}$  values and the longest durations, MIS 56 (1.65–1.67 Ma), MIS 78 (2.07–2.09 Ma), and MIS 82 (2.15–2.17 Ma).

#### 5.3. Grain Size Distribution and Clustering Analysis

Particle size distributions reveal that most of samples are trimodal, with one initial mode around 0.5  $\mu\text{m}$ , followed by a principal mode centered at 6–7  $\mu\text{m}$ . After this principal mode, a high variability of grain size modes is observed between 100 and 400  $\mu\text{m}$  (Figure 3). However, in certain time intervals, mainly before 1.85 Ma, the main mode is displaced to coarser grains (>60  $\mu\text{m}$ ) and the samples are overall poorly sorted.

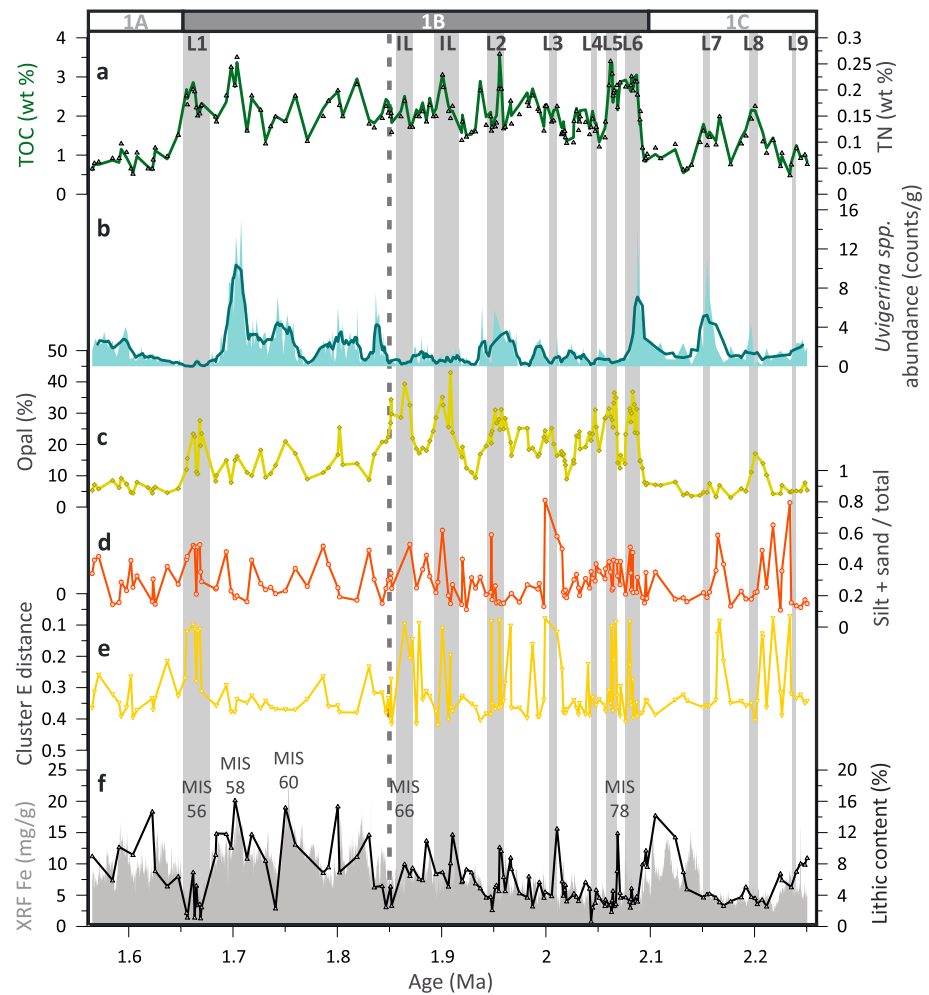


**Figure 3.** Clustering analysis of ODP Site 1240 particle size distribution. (a) Particle size distribution of the entire studied period. (b) Proportion and distribution of six clusters along the studied period; note that each color corresponds to each cluster of the next caption. (c) Cluster classification based on their particle size distribution [Povea et al., 2015]. Frequency distribution is noted for each cluster. Marine isotopic stages (MISs) 56, 60, 62, 78, and 82 are also shown.

According to the obtained modal distribution, *k-means* clustering analysis characterizes the grain size data set into six clusters (cluster A to cluster F), previously presented in Povea et al. [2015]. Clusters A, B, and C are the most dominant patterns, reaching almost 69% of the frequency (Figure 3c). These clusters show a well-defined main mode around 6–7 μm, a finer mode around 0.5 μm, and a more variable last mode. Clusters E and F are less abundant, with a combined frequency of 15%, and clearly different from the rest, presenting a main mode shifted to coarser sizes (Figure 3c). Cluster D seems to be the intermediate and transitional pattern between the well-sorted (clusters A, B, and C) and the poorly sorted and coarser (clusters E and F) clusters (Figure 3c), with the mode around 6–7 μm less defined and a terminal mode more abundant.

In order to better understand the time distribution of these distinct clusters, cluster E distance is estimated. This value reflects the degree of similarity between each sample and this cluster, where the lower value (close to 0) means the greater similarity to cluster E. Cluster E has been chosen for its most distinct modal distribution,





**Figure 4.** Biogenic and lithogenic fraction characterization from eastern equatorial Pacific (ODP Site 1240). (a) TOC (solid line) and TN (gray triangles) contents (%). (b) *Uvigerina* spp. abundance (counts/g); note that the green dark line shows the running average of five points. (c) Opal (%). (d) Grain size parameter shown as (silt + sand)/total. (e) Euclidean distance of cluster E to each sample. (f) XRF core scanner Fe (mg/g) and lithic content (%). The gray shaded vertical bars indicate the position of the observed and the interpreted LDOs, labeled as L1–L9 and IL, respectively. The white and gray bar on the top shows the three sedimentological units (1A, 1B, and 1C). The vertical dashed line marks the 1.85 Ma transition. Marine isotopic stages (MISs) 56, 58, 60, 66, and 78 are also presented.

displaying a coarser main mode, and its frequent presence during colder phases, especially during LDO deposition (Figure 4e). The comparison with the abundance of the coarse fraction represented by the silt + sand/total ratio (Figure 4d) shows a generally good agreement between these two parameters that both peak during glacial periods. However, cluster E practically disappears during glacial times without LDOs. While the silt-clay parameter does not differentiate between these two groups of glacial periods, the absence of cluster E indicates that the lithic fraction during the non-LDO glacial phases had a distribution closer to A, B, C, and D clusters (e.g., MIS 58 and MIS 60 in Figures 3 and 4).

#### 5.4. Paleoproductivity Proxies

TOC and TN records show substantial variability over the studied time interval, with generally higher values during the glacial intervals when LDOs occurred (Figure 4a). These records exhibit three distinct intervals, consistent with previously defined subunits [Mix et al., 2003], with higher TOC and TN mean values during subunit 1B (Table 1) and very sharp boundaries between subunits. The upper part (1.56–1.65 Ma) presents the minimum values of all the sequence, while the middle interval (1.65–2.09 Ma) shows the maximum values of TOC, TN, and opal (Table 1). The biogenic fluxes of TOC and opal also show the highest values during subunit 1B (Figures 5e and 5g), with maximum values during the LDO intervals.

**Table 1.** Biogenic Contents From Eastern Equatorial Pacific (TOC, TN, and Opal)<sup>a</sup>

| Record (wt %) | Unit 1A |         |         | Unit 1B |         |         | Unit 1C |         |         |
|---------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|               | Minimum | Maximum | Average | Minimum | Maximum | Average | Minimum | Maximum | Average |
| TOC           | 0.5     | 1.5     | 0.86    | 0.84    | 3.5     | 2.16    | 0.5     | 2.15    | 1.2     |
| TN            | 0.04    | 0.11    | 0.069   | 0.06    | 0.27    | 0.15    | 0.03    | 0.17    | 0.09    |
| Opal          | 4.41    | 9.19    | 6.24    | 7.81    | 43.03   | 21.12   | 3.02    | 17.10   | 6.51    |

<sup>a</sup>Divided in the three sedimentological subunits (1A, 1B, and 1C).

*Uvigerina* spp. abundance oscillates from 0 to 80% of the total benthic assemblage (Figure 4b). High *Uvigerina* spp. abundances typically occur in phases of relatively high TOC percentages with some exceptions, when peaks in TOC% correspond to low *Uvigerina* spp. abundance, and these events mostly correspond to the LDOs (Figures 4a and 4b).

### 5.5. Lithic Fraction and Iron

The record of lithic percentage mimics, at lower resolution, the iron content profile measured by the XRF scanner for the whole studied period (Figure 4f). This relationship ( $r^2 = 0.63$ ), together with the absence of fluvial runoff to the studied basin, supports their common origin and thus the eolian deposition of the measured iron. In contrast to the biogenic proxies, these terrigenous source proxies do not differentiate the three sediment subunits (Figure 4f) but show a general increasing trend toward the top of the studied period also shown in the lithic and iron fluxes (Figures 4f, 5j, and 5k and Figure S5 in the supporting information). Interestingly, the higher values occurred during the glacial periods between 1.68 and 1.85 Ma, when the cluster E and silt + sand/total parameter did not agree. On the contrary, the minimum values occurred during the glacial periods previous to 1.85 Ma when cluster E was better represented. The pronounced minimum in both iron and terrestrial content associated with MIS 56, corresponding to the last and very pronounced LDOs (L1).

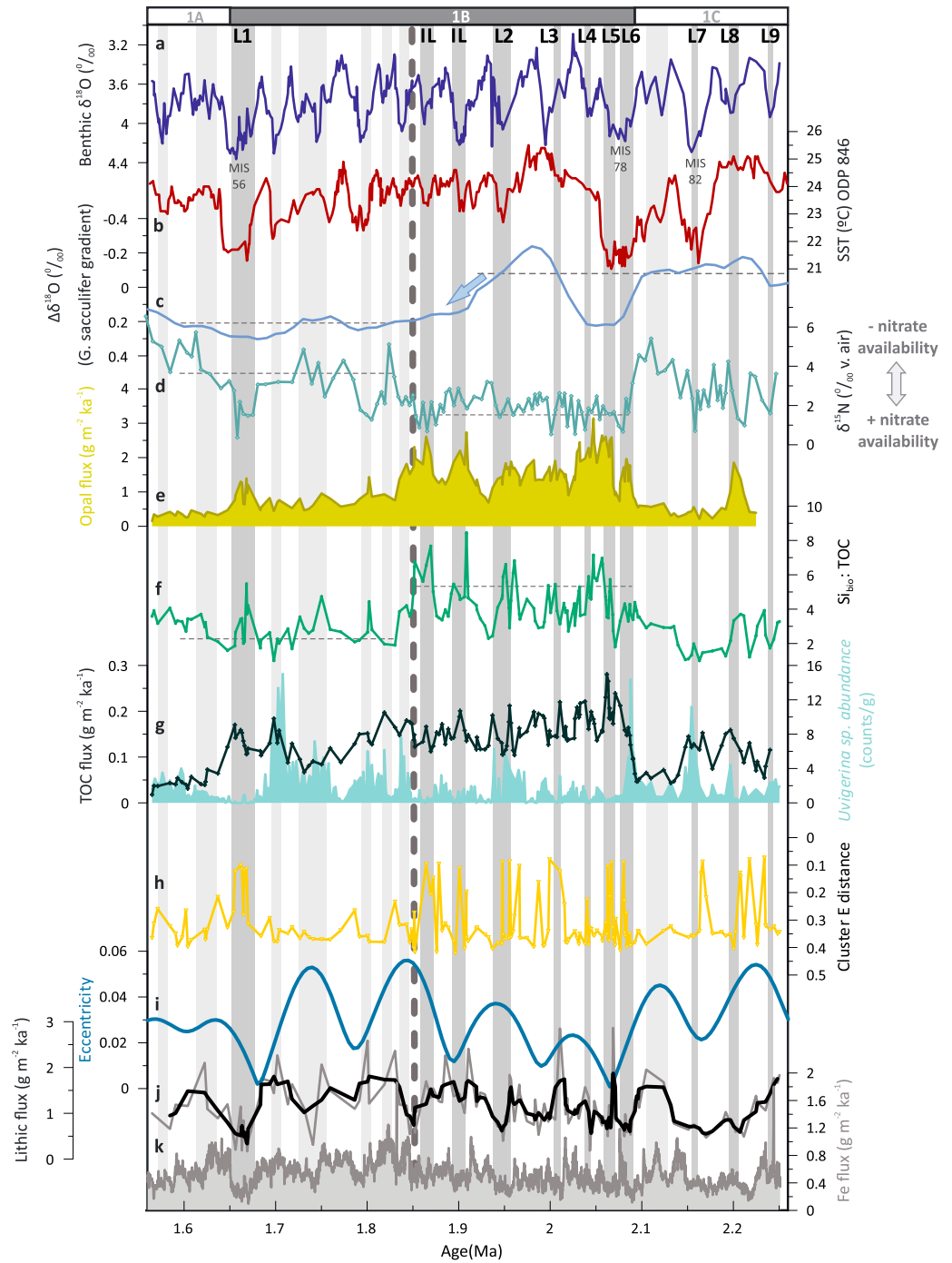
The mineralogical composition of the lithic fraction is dominated by six main mineral phases that remain constant in composition over the studied period (1.56–2.26 Ma; Figure S6 and Table S1 in the supporting information). The most abundant phases are feldspar (42.15%), opaques (25.45%), and quartz (19.43%), and the minor mineral components are epidote (6.50%), volcanic glass (4.52%), and amphibole (1.95%).

## 6. Discussion

### 6.1. Changes in Atmospheric Transport

Since terrigenous sediment comes to the studied location primarily through the atmosphere, its characteristics should reflect the ITCZ position and intensity of the wind belt system, as well as changes in the aridity of the source area. Previous studies have found that eolian dust in the EEP comes from the arid areas of western South America [Nakai et al., 1993], mostly from the Atacama desert [Molina-Cruz, 1977] or from the Andean region [Janecek and Rea, 1985; Chuey et al., 1987; Rea, 1990]. Moreover, Atacama desert became hyperarid in the Pliocene as a consequence of a global climate cooling [Hartley and Chong, 2002]. This episode of hyperaridity produced a sedimentary hiatus in the Atacama region from 3.37 Ma, which would be coeval to a major development of Antarctica ice sheets and to an enhancement of the cold ocean upwelling in the eastern Pacific during the Pliocene-Pleistocene transition [Sáez et al., 2012]. Thus, these cooling stages could trigger the extreme hyperarid conditions in the Atacama region with an absence of sediment production and accumulation [Sáez et al., 2012].

Deposition of lithic material, including iron, was relatively low during the time interval prior to 1.85 Ma (Figures 5j and 5k). During this period, the grain size distribution results at Site 1240 show the dominance of giant (>60 μm) and relatively poorly sorted coarse grains (Figure 3c, clusters E and F). In some extreme cases, within the period previous to 1.85 Ma, the fine dominant mode between 4 and 6 μm completely disappears or become very scarce. These are the samples represented by a low cluster E distance, which means a higher similarity with this cluster (Figure 5h), and happen particularly during glacial periods and coinciding with LDOs and also during the strong event at MIS 56. In contrast, after 1.85 Ma, the samples displayed a characteristic trimodal distribution with a principal mode between 6 and 7 μm, indicating the dominance of better sorted fine grains and low variance, particularly during the glacial times (MISs 58, 60 and 62; Figures 3a, 5j and 5k 60 and 62; Figure 3a). These glacial intervals also record an increased arrival of lithic grains and iron.



**Figure 5.** Interpreted ITCZ migrations and distinctive fertilization mechanisms associated to atmosphere-ocean connections over the eastern equatorial Pacific during the studied period. (a) Benthic  $\delta^{18}\text{O}$  record ( $\text{‰}$ ). (b) SST ( $^{\circ}\text{C}$ ) ODP Site 846 [Herbert et al., 2010]. (c) Oxygen isotope difference (*G. sacculifer*) between ODP Site 851 (eastern Pacific) [Cannariato and Ravelo, 1997] and ODP Site 806 (western Pacific) [Berger et al., 1993; Jansen et al., 1993]. (d)  $\delta^{15}\text{N}$  ( $\text{‰}$  v. air) [Etourneau et al., 2013]. (e) Opal flux ( $\text{g m}^{-2} \text{ka}^{-1}$ ). (f)  $\text{Si}_{\text{bio}}/\text{TOC}$  ratio. (g) TOC flux ( $\text{g m}^{-2} \text{ka}^{-1}$ ) and *Uvigerina* spp. abundance (expressed as counts/grams dry bulk weight). (h) Cluster E distance. (i) Eccentricity [Laskar et al., 2004]. (j) Lithic flux ( $\text{g m}^{-2} \text{ka}^{-1}$ ). (k) Fe flux ( $\text{g m}^{-2} \text{ka}^{-1}$ ). The dark gray shaded bars indicate the position of the observed and interpreted glacial LDOs, labeled as L1–L9 and IL, respectively. The light gray shaded vertical bars indicate the glacial periods without LDOs. The white and gray bar on the top shows the three sedimentological units (1A, 1B, and 1C). The vertical dashed line marks the 1.85 Ma transition. Marine isotopic stages (MISs) 56, 78, and 82 are also shown.



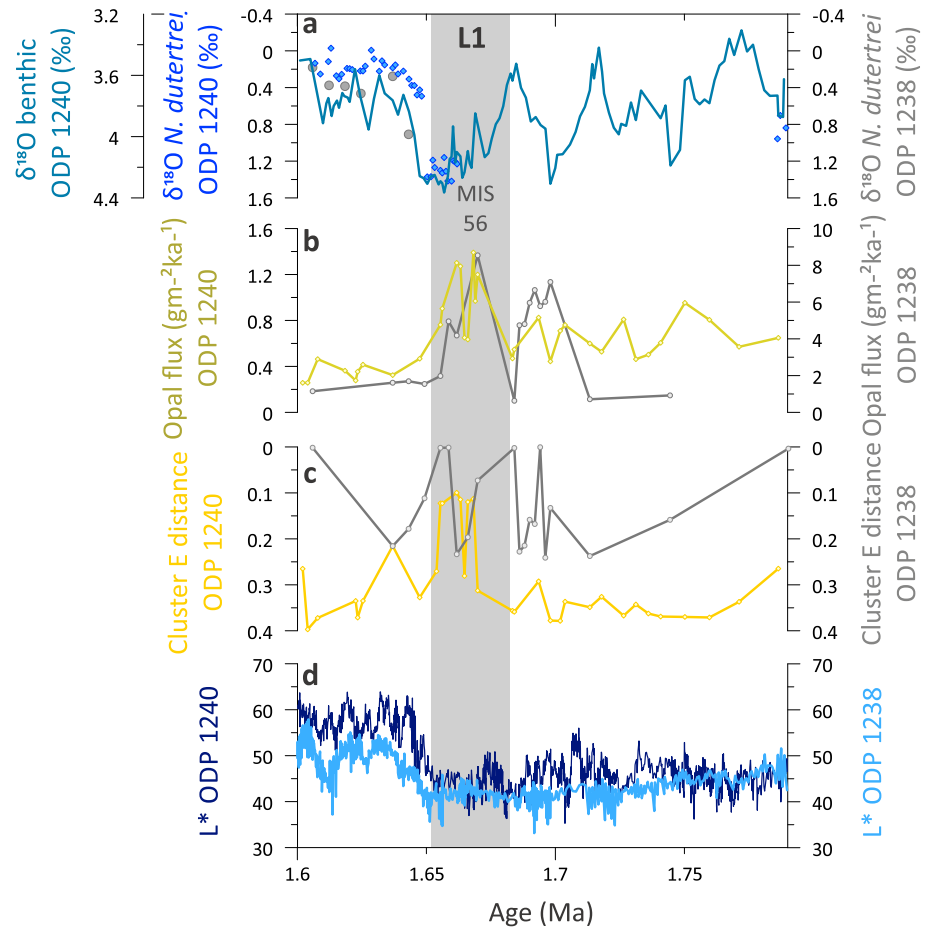
The size of dust particles transported over hundreds of kilometers is generally below 10  $\mu\text{m}$  [Tegen *et al.*, 1996]. However, the presence of eolian giant particles ( $>10 \mu\text{m}$ ) has also been documented in previous studies [Glaccum and Prospero, 1980; Betzer *et al.*, 1988; Moreno *et al.*, 2001; Jeong *et al.*, 2013]. These particles can be transported over long distances if strong upward advection of air masses lifts these dust particles to higher altitudes [Windom, 1985; Pye, 1995] or a midtropospheric wind belt induces a rapid dust transport [Jeong *et al.*, 2013]. An additional factor controlling grain size distribution is the relative contribution of wet and dry deposition [Guerzoni *et al.*, 1997]. The range of grain size particles of dust deposition by a wet event has been explored through the analysis of a series of Saharan dust samples collected in Iberia during rain events (mean Saharan dust wet deposition; Figure S7 in the supporting information), showing that a wide size range of particles can be transported and deposited but always with a strong presence of the coarser mode.

These observations would suggest that most of the samples result from a mixture of wet and dry deposition processes. Nevertheless, when samples get closer to the cluster E, deposition is dominated by wet deposition, consistent with the proximity to the particle size distribution from the Saharan dust (wet deposition; Figure S7 in the supporting information). These changes in the grain size distribution reflect the position of the ITCZ. Strong southeasterly trade winds occur south of the ITCZ, while within the ITCZ, the trade winds become weaker and wet deposition dominates [Hovan, 1995]. Consequently, it appears that during glacial periods with the occurrence of the LDOs, mostly before 1.85 Ma, the ITCZ was located at its southernmost position, just above ODP Site 1240. The presence of coarser grains, even giant particles ( $>200 \mu\text{m}$ ), and scarcity of lithic and iron contents, indicates the dominance of weak southeasterly winds and increased rainfall or wet deposition events. The lithic fraction presents a coherent trend with eccentricity [Laskar *et al.*, 2004], with minimum values at eccentricity minima (Figures 5i–5k). Low eccentricity in the glacial periods previous to 1.85 Ma would have reduced seasonal contrast, and thus ITCZ seasonal migration, anchoring it in a southerly position. This is particularly evident in glacial stages MIS 78 and 56 when intense and long glacial conditions are observed, highlighting the previously proposed relevance of the 400 kyr eccentricity cycle in the EEP for this time period [Herbert *et al.*, 2010]. In contrast, when eccentricity was higher (with an upward increase after 1.85 Ma), Earth's seasonality increased causing greater latitudinal migration of the ITCZ. Thus, the ITCZ may have been located further north, closer to its current position, with a reinforcement of the local winds and decreased rainfalls. This situation would have allowed a higher lithic input, including iron, well sorted around a finer mode. Furthermore, the overall increase in lithic contributions across the studied period, with a greater content from 1.85 Ma, also indicates more arid conditions of the source regions. This enhanced aridity has been also detected in other regions like the African continent during this time period [deMenocal, 2004]. Finally, the invariant mineralogical composition along the whole record, including glacial and interglacial phases (Figure S6 and Table S1 in the supporting information), suggests that there were no noticeable changes in the source area of the lithic material in relation to these ITCZ migrations.

In order to better characterize the geographical impact of the discussed ITCZ displacements, ODP Site 1238, located further southeast ( $1^{\circ}52.310'S$ ,  $82^{\circ}46.934'W$ ) in the EEP, was also examined for the time period of the most intense LDOs (1.6–1.79 Ma), which occurred during glacial MIS 56. If these events occurred during a weakening of the southeasterly trade winds, it should also be reflected in Site 1238. Thus, the recorded signal in Site 1238 with high fluxes of opal, coarse grains with a similar distribution to cluster E (Figure 6), even with an increased signal due to the shorter transport distance for the lithic material, supports this southward shift of the ITCZ and illustrates the wide geographical extension of the L1.

## 6.2. Atmosphere–Ocean Coupling

Primary productivity in the EEP is controlled by the availability of nutrient inputs in the system which in turn is influenced by the atmosphere–ocean coupled system. Thus, it is also sensitive to the ITCZ or equatorial front (EF) migration and the associated equatorial upwelling system. Highest values of export production occurred during glacial periods between 1.85 and 2.1 Ma and glacial time located at 1.65 Ma (MIS 56; Figures 5e–5g), when the LDOs were formed. The lithic fraction data (section 6.1) suggest that during these glacial periods, the ITCZ was located over the equator (ODP Site 1240 location) likely at its most southward position over the entire record. The dominance of the cluster E occurred primarily during periods when opal and TOC were high; thus, the interpreted weak trade winds could not stimulate this high-productivity system (Figure 5). In addition, this high productivity could not be explained through an iron fertilization process as could be expected in an iron-limited ocean region [Martin, 1990; Jickells *et al.*, 2005], since iron values are relatively



**Figure 6.** The imprint of a major southward ITCZ migration during L1 (1.6–1.79 Ma), registered further south over ODP Site 1238. (a) ODP Site 1240 benthic  $\delta^{18}\text{O}$  record ( $^{\circ}/_{\text{oo}}$ ; blue line), ODP Site 1240 *Neogloboquadrina dutertrei*  $\delta^{18}\text{O}$  record ( $^{\circ}/_{\text{oo}}$ ; blue diamonds), and ODP Site 1238 *N. dutertrei*  $\delta^{18}\text{O}$  record ( $^{\circ}/_{\text{oo}}$ ; dark gray circles). (b) Opal flux ( $\text{gm}^{-2}\text{ka}^{-1}$ ) from ODP Site 1240 (green line) and ODP Site 1238 (dark gray line). (c) Cluster E distance from ODP Site 1240 (yellow line) and ODP Site 1238 (dark gray line). (d) Luminescence ( $L^*$ ) from ODP Site 1240 (dark blue line) and ODP Site 1238 (light blue line) [Blum et al., 2005]. The gray shaded bar shows the locations of L1 and MIS 56.

low before 1.85 Ma. A comparison with a sedimentary  $\delta^{15}\text{N}$  isotope record from the same marine core [Etourneau et al., 2013] also reveals low  $\delta^{15}\text{N}$  values specially during this interval prior to 1.85 Ma transition (Figure 5d). Etourneau et al. [2013] interpreted this as a reflection of enhanced nitrate availability in the eastern equatorial Pacific system, suggesting that nutrient consumption was low relative to nutrient supply. Thus, the low  $\delta^{15}\text{N}$  values when export production was high indicate a significant supply of nutrients, including silicic acid and nitrate [Billups et al., 2013], to the eastern equatorial Pacific between 1.85 and 2.1 Ma. Since the EEP is Si and iron colimited [Brzezinski et al., 2008, 2011], diatoms tend to deplete surface waters of silicic acid before nitrate, reducing the  $\text{Si}(\text{OH})_4:\text{NO}_3$  ratio in the surface ocean [Hutchins and Bruland, 1998]. This major silicic acid uptake promotes more silicified diatoms, with heavier and larger frustules [Franck et al., 2000; Beucher et al., 2007], thus allowing for faster sinking and the formation of the LDOs during these periods prior to 1.85 Ma. The *Thalassiothrix* spp. diatoms, typical of these LDOs, have been associated to the dominance of stratified surface waters in the vicinity of the EF [Kemp et al., 2000, 2006; Pike and Stickle, 2007]. The occurrence of these laminations has also been associated to major cooling events in the eastern equatorial Pacific [Kemp et al., 1995]. This seems to be confirmed by excursions toward cooler SST during LDO deposition as evidenced by alkenone-derived SST record (Figure 5b) [Liu and Herbert, 2004; Herbert et al., 2010]. This is not true for two laminations (L3 and L8) that record higher SSTs. This may be explained by the seasonality of the coccolithophorid population. The inferred stratified conditions are consistent with the interpreted ITCZ location over equator. But, the stimulated diatom productivity also requires an extra arrival of silicic acid to the EEP, likely through advection of

nutrient-rich intermediate waters feeding the EUC. Previous studies have identified strong connections between high and low latitudes, mainly through advection of Southern Ocean intermediate water to the Equatorial Undercurrent (EUC) [Kessler, 2006; Pena *et al.*, 2013]. This Antarctic component would have provided Si-rich waters to the tropical thermocline [Calvo *et al.*, 2011], stimulating diatom production (Figure 5e) and a consequent increase in nitrate availability [Sarmiento *et al.*, 2004]. This high-latitude forcing is confirmed by the strong obliquity signal on the opal record during the interval previous to 1.85 Ma (Figure S8 in the supporting information). Consequently, prior to the 1.85 Ma transition, we interpret that the fertilization of the EEP occurred through an enhanced EUC nutrient supply, potentially of Southern Ocean origin, as also published in *Etourneau et al.* [2013].

After 1.85 Ma, according to the lithic fraction interpretation, the ITCZ changed its mean position toward a more northern location, particularly during glacial times. This situation would have triggered enhanced equatorial upwelling, less stratified surface waters, a thermocline shoaling, and a greater equatorial E-W Pacific gradient (Figure 5c), consistent with the enhancement in Walker circulation proposed in previous studies [Ravelo *et al.*, 2004; Wara *et al.*, 2005; Ford *et al.*, 2012]. The productivity proxies indicate a decrease but still relatively high values in export production (Figures 5e and 5g) and a clear change in the phytoplankton community, supported by a lowering in the  $\text{Si}_{\text{bio}}:\text{TOC}$  ratio and the disappearance of the heavy silicified diatoms that formed the LDOs (Figure 5f). This evidence and the parallel increase nitrate consumption (Figure 5d) suggest a change in the  $\text{Si}(\text{OH})_4:\text{NO}_3$  ratio consistent with a reduction in the availability of silicic acid and/or enhanced iron fertilization. The reinforcement of the upwelling system by southeasterly trade winds produced SST slightly lower after 1.85 Ma and also increased the atmospheric dust transport as is supported by the relatively high lithic and iron fluxes (Figures 5j and 5k). The exception to this situation occurred during the glacial MIS 56 (1.65 Ma), when conditions returned to those of glacial previous to 1.85 Ma, but with a more extreme expression. This southward displacement of the ITCZ may be a consequence of the extreme glaciation triggered by 400 kyr minimum eccentricity at 1.65 Ma, as already seen in numerical models [Masunaga and L'Ecuyer, 2011]. The ITCZ displacement reached further south, to the position of Site 1238, confirming the severity of the glacial MIS 56 period. On the other hand, although the most marked and important changes are observed during glacial periods before and after 1.85 Ma, the interglacial phases also show a different pattern of behavior between these two marked periods, such as TOC and opal fluxes (Figures 5e and 5g). These evidence support a tight coupling between the atmospheric changes and the upwelling system and highlight the high dynamism of the equatorial system during the studied period.

### 6.3. Implications for Carbon Fluxes to the Deep-Sea Floor

The TOC record (Figure 5g) shows the highest fluxes during the period covering lithological subunit 1B (1.65–2.08 Ma), supporting an enhanced C export to the deep ocean. Nevertheless, C fluxes appear to be slightly higher prior to the 1.85 Ma transition and, particularly, during those glacial periods with LDO formation. *Uvigerina* spp. is a detritivore and infaunal benthic foraminifera, typical of environments with a high organic carbon flux and low oxygen content [Seiglie, 1968; Murray, 1991; Rathburn and Corliss, 1994]. In general, *Uvigerina* spp. abundances parallel the TOC variability, with maximum percentages of *Uvigerina* spp. occurring during maxima in TOC. However, this relationship is not satisfied during most of the LDOs (Figures 4a, 4b, and 5g). These time intervals of maximum TOC fluxes toward the deep ocean did not stimulate the proliferation of *Uvigerina* spp., theoretically prone to high carbon fluxes. This very distinctive response of the benthic system to two primary productivity scenarios suggests different mechanisms of carbon sinking to the deep ocean. LDO layers are formed by pennate-type diatoms, such as *Thalassiothrix* spp. [Mix *et al.*, 2003]. These diatoms tend to form large grids of twisted cells, which could drag down large amounts of organic carbon and other particles to the deep-sea floor. These high fluxes of TOC would have occurred in rapid events, probably as seasonal cycles (especially during fall or early winter) [Kemp *et al.*, 2000] rather than as a continuous and homogeneous rain, and apparently prevented the development of *Uvigerina* spp. owing to the extremely high contents of TOC. These results highlight the role of vertical particle transport controlling the benthic population and also document the high efficiency of the LDOs in the deep transfer and storage of carbon and their potential to increase the storage of atmospheric  $\text{CO}_2$  in the deep ocean [Dugdale and Wilkerson, 2001; Kemp *et al.*, 2000, 2006].

## 7. Conclusions

The integrated study of both lithic and biogenic components from EEP sediments allows the identification of coupled changes in atmospheric and oceanic dynamics that occurred along the early Pleistocene (from 1.56 to 2.26 Ma) indicating major meridional shifts in the main position of the ITCZ.

Glacial periods from 1.85 to 2.26 Ma present lower iron and lithic contents, dominated by coarse and unsorted lithic particles, interpreted to reflect a southerly position of the ITCZ, approximately over the equator (ODP Site 1240). This would result in a weakening of the trade winds over the region and increasing wet dust deposition associated with more frequent rainfall events below the ITCZ. This situation is consistent with the dominance of the heavy silicified diatom that formed the LDOs, typical of stratified surface waters in the vicinity of oceanic frontal zones. The increased N availability (low  $\delta^{15}\text{N}$  values) [Tourmeau *et al.*, 2013] and opal fluxes, particularly after 2.1 Ma, support a change in the nutrient availability likely induced by a greater input of silicic acid-rich waters, potentially from Antarctic origin. The high-latitude origin of these Si-rich waters is supported by the detected obliquity pacing in the biological Si record. The almost absence of *Uvigerina* spp., a benthic species that usually takes advantage of high TOC fluxes, supports a high and rapid flux of carbon toward the deep ocean that overwhelmed the benthic ecosystem during LDO formation.

Glacial periods after 1.85 Ma present higher deposition of finer and better sorted lithic particles and also enhanced iron fluxes. These conditions could reflect the dominance of eolian dry deposition as a result of a northward migration of the ITCZ. This interpretation is supported by the evidence of high primary productivity but with remarkable differences in the nutrient balance (less N availability) consistent with conditions of enhanced upwelling and iron fertilization in the region. This situation would have enhanced the E-W gradient in the equatorial Pacific in agreement with the previously proposed strengthening of the Walker circulation after 1.85 Ma. The high resolution of the new ODP Site 1240 records at this time frame has allowed to characterize an abrupt shift in the system located at 1.85 Ma rather than a progressive and smooth long trend change. During this time, carbon flux toward the deep ocean was also high but occurred as a more homogeneous rain that efficiently stimulated the development of *Uvigerina* spp.

The glacial period centered at 1.65 Ma (MIS 56) was an exception to this 1.85 Ma boundary and became a major breakdown to this northward shift of the ITCZ. MIS 56 and also MIS 78 are characterized by the best developed LDOs and also the coldest glacial phases coincident with eccentricity minima paced by the 400 kyr cycle. The seasonal changes derived from this distinctive astronomical configuration combined with the growing ice of the North Hemisphere ice sheets are suggested to have lead the recorded migrations in the ITCZ position.

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