Anti-Atlas Moroccan Chain as the source of lithogenic-derived micronutrient fluxes to the deep Northeast Atlantic Ocean

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[1] Identifying the source of atmospheric dust is crucial to better understand the global marine biogeochemical cycle as phytoplankton growth relies on dissolved micronutrient elements available in the open ocean. Mineralogical, geochemical and Sr isotope analyses of a one year-time series (April 2003–April 2004) of deep ocean particle flux at the Madeira Abyssal Plain in the subtropical northeast Atlantic are presented. The lithogenic fraction has a high occurrence of palygorskite and smectite and an absence of kaolinite together with Sr isotopic compositions similar to the Northeast Atlantic aerosols. This indicates the Anti-Atlas Moroccan chain of Paleozoic age as the source region. The lithogenic fraction supplies 4 times more Fe during a dust event than during the spring-summer aeolian input. A continuous input of only 1% of the lithogenic iron made available over a year period, could lead to an increase in primary productivity of 40% relative to today’s value.


1. Introduction

[2] Fe supply to the open ocean impacts on the chemical cycles of carbon, sulphur, silicon and nitrogen by altering algal nutrient stoichiometry and new production rates (e.g. downward particulate organic carbon export) [Fasham, 2003]. Fe is mostly supplied to the ocean via river inputs, continental margin sediments, and aeolian deposition [Jickells et al., 2005]. Sahara dust storms represent a period of Fe loading to the proximal coastal surface ocean [Mahowald et al., 2005] and in the subtropical ocean culminate in a phytoplankton bloom during the fall-winter period [Duce et al., 1991]. Previous meteorological studies showed that all North Africa is a potential dust source [Middleton and Goudie, 2001]. The total ozone mapping spectrometer (TOMS) can identify major dust sources within Africa [Prospero et al., 2002], however the deposition area of dust originating from these sources to the open ocean remains a subject of debate [Mahowald et al., 2005]. So far, element fluxes associated with lithogenic input are determined by difference between total fluxes and those from the biogenic components [Jickells et al., 1998], relying on a sole continental origin of Aluminium (Al). However, such an assumption may lead to systematic errors in dust/Al ratios [Tindale and Pease, 1999]. We present the results of a mineralogical, chemical and Sr isotopic investigation of a one year time-series of particle flux in the subtropical northeast Atlantic in order to better understand and constrain the impact of aeolian-derived micronutrients on the biogeochemistry.

2. Sampling and Methods

[3] We present a one year time-series of deep ocean particle flux data (April 2003–April 2004) collected via sediment trap at site Kiel276 (33°N, 22°W) located in the Madeira Abyssal Plain in the northeast Atlantic (Figure 1). The physical settings of the Kiel276 station, seasonal and annual particle flux cycle and phytoplankton dynamics and the sample preparation and analysis techniques employed in this study are described in detail by Waniek et al. [2005].

[4] The mineralogical association of each sample was determined by scanning electron microscopy and energy-dispersive X-Ray microanalyses (EDX). The method is based on automatic identification and quantitative element analysis (EDAX-GENESIS) of 500–1500 individual particles in each sample. The full description of this technique is presented by Leipe et al. [1999] and Bauerfeind et al. [2005].

[5] The analytical procedure used to obtain the chemical and Sr isotope compositions from each sample (~10 mg) is described in detail by Chavagnac et al. [2006].

[6] The mineralogy, chemical composition, Sr isotope ratios and element fluxes are presented in the auxiliary material.1

3. Results and Discussion

3.1. Mineralogy

[7] Particles collected at 3050 m depth represent a mixture of aeolian and authigenic particles. Maximum particle flux is observed from January to March. The biogenic carbonate and silica represent 1.8 to 82.7% and 0.67 to 34.9% of the total particle flux, respectively (Data Set S1 of the auxiliary material). Variation in the biogenic particle flux was reported to be a direct consequence of the variability of phytoplankton biomass and primary produc-

tivity [Waniek et al., 2005]. The lithogenic particle reaches maximum flux from January to March and during a dust event, and consists of quartz, feldspar, carbonate (dolomite, magnesite) and clays among which palygorskite and smectite minerals are the most abundant (Figure 2). The ratio of illite to kaolinite, used to determine the origin of soil-derived aerosols from the Saharan dust [Caquineau et al., 2002], is found to vary over three broad source regions (Figure 1): the North and West Sahara (>2), the South and Central Sahara (0.4–0.7) and the Sahel (0.1). This indicates a latitude dependant relationship of the relative proportions of illite and kaolinite in the Sahara region [Chiapello et al., 1997] consistent with the mineralogical characteristics of Atlantic sediments [Windom, 1975] and dust collected over the Atlantic Ocean [Chester et al., 1972]. At Kiel276, kaolinite is absent but significant amount of palygorskite and illite associated with smectite are found.

3.2. Major and Trace Element Composition

The relative proportions of each major element reflect the dust mineralogy and chemistry of the geological source region. Dolomite and magnesite while being part of the lithogenic fraction, have been removed during the leaching procedure. The chemical composition (Data Sets S2 and S3 of the auxiliary material) is representative of silicate-bearing lithogenic material and refractory minerals among which quartz and biogenic silica act as diluting minerals. The chemical composition of the samples (apart from the samples 16 March–16 April 2004) is remarkably constant for Al, iron (Fe) and magnesium (Mg) with average Fe/Al of 0.59 ± 0.2 in line with Fe/Al ratios of 0.63 ± 0.11 of Saharan dust [Güiem et al., 2002]. Fe correlates linearly and positively with Al ($R^2 = 0.99$), implying that the lithogenic fraction of the particle flux originates from a single source over the time period. The two anomalous samples were sampled during a Saharan dust event (16 March till 16 April 2004) as seen by satellite (http://earthobservatory.nasa.gov/NaturalHazards/Archive/), suggesting that aeolian material originated from a much wider source area, hence imparting an atypical chemical signal. These two samples have Fe/Al ratio >1 and show no evidence of different mineralogical association, apart from higher Fe-oxides (1.25%).

Apart from the two dust-event samples, the particle flux samples exhibit flat Post-Archean average Australian sedimentary rock (PAAS [McLennan, 1989]) normalised rare earth element (REE) patterns as evidenced by $(La/Yb)_{N}=0.946–1.077$ (Data Sets S2 and S3 of the auxiliary material) (Figure 1). Only the two exceptions have HREE enrichment over LREE as shown by $(La/Yb)_{N}<0.85$. We postulate that the HREE enrichment is due to different clay proportions, and imply increasing basalt-weathering products with higher amounts of smectite. The

Figure 1. Position of the Kiel276 site and its main mineralogical, geochemical, and Sr isotope compositions. Map based on D’Almeida [1987]. The distribution of the clay mineralogy delimited by orange lines is from Molinaroli [1996]. The different sources of soil-derived aerosols from the Saharan dust are represented by coloured-fields with their typical illite/kaolinite ratio in italic. Northern Africa is characterised by illite/kaolinite ratio >1. Note that the Sahel region, which is located at the top south-end of the map, is characterised by an illite/kaolinite ratio of 0.1 [Caquineau et al., 2002]. The Sr isotopic compositions of different geological formations and aerosols are indicated in blue [Grousset et al., 1998; Krom et al., 1999; Rognon et al., 1996]. The REE patterns of lithogenic material at Kiel276 are compared with those of EUMELI (A [Tachikawa et al., 1997]) and SPM in surface waters from the northeast Atlantic (B, C, D [Kuss et al., 2001]).

Figure 2. Mineralogical composition of the particle flux (33°N, 22°W). (a) The biogenic group includes calcite, opal, organics, Ca-P mineral, and barite; the Si-bearing lithogenic group is composed of quartz, plagioclase, and clays (illite, smectite, palygorskite, chlorite); the oxide-sulphur group consists of Fe oxide, bauxite, pyrite, and Ti minerals. The carbonate group is composed of dolomite and magnesite. (b) Percentage of each mineral of the lithogenic group.
REE patterns are similar to those of deep particles in the Sargasso Sea [Sholkovitz et al., 1994], but differ from the detrital particle fraction at 21°N, 31°W (LREE enriched REE patterns with (La/Yb)$_{np}$ = 1.202–1.572) most likely because of different source regions within the Sahara [Tachikawa et al., 1997]. Note that station B exhibit HREE abundances and high Ti/Al ratio, which is interpreted as being due to specific lithogenic material [Kuss et al., 2001]. However, the lithogenic particle flux at Kiel276 exhibit similar REE features to suspended particulate material (SPM) in surface waters at station C and D from the northeast Atlantic [Kuss et al., 2001], suggesting a common REE-carrier, i.e. clays, at both locations.

3.3. Sr Isotope Composition

[10] Sr isotope composition is changing through time as a result of the $^{87}$Sr/$^{86}$Sr decay to $^{87}$Sr. The rate of change of $^{87}$Sr/$^{86}$Sr is closely approximated by Rb/Sr, implying that different geological formations of variable Rb/Sr and age, are characterised by distinctive $^{87}$Sr/$^{86}$Sr. Using Sr isotope compositions in the Saharan, it is possible to decipher three sub-provinces as potential sources of aeolian dust (Data Set S2 of the auxiliary material; Figures 1 and 3): (1) the north sources (Morocco, Algeria, Mauritian, Mali), (2) the east/ south sources (Libya, Chad, Guinea, Senegal), and (3) the Archean Saharan Shield (essentially in Mauritiania) [Grousset and Biscaye, 2005]. Here, we report for the first time that the $^{87}$Sr/$^{86}$Sr compositions of 13 lithogenic-derived particle flux samples vary between 0.7103 and 0.7121 (Data Set S2). These values are comparable to, although slightly lower than those of aerosols, Canarian loess and Mediterranean sediments (at 0.7122–0.7127 [Grousset and Biscaye, 2005]; Figure 3). East/South and Archean shield geological formations from the Sahara are unlikely to represent the source area due to the lack of kaolinite mineral and the radiogenic Sr isotope composition of Saharan aerosols (0.7147–0.7167) [Grousset et al., 1998]. The Sr isotopic compositions are not more radiogenic as Sr concentrations increase, suggesting that the source of the lithogenic fraction is a sole geological formation. Note that the Sr isotope composition of particulate flux is not altered during the settling process as the time necessary to sink from the surface to 3050 m depth does not exceed 30 days [Waniek et al., 2005]. Based on the geochemical and Sr isotope compositions, particle flux samples are co-genetic and remained a closed system since formation. We can potentially estimate the age of the lithogenic source area using a Sr isochron plot ($^{87}$Sr/$^{86}$Sr versus $^{87}$Rb/$^{86}$Sr) whereby the slope of the best linear regression line through the data points - also called isochron- is related to the age of the sample set. We obtain a Paleozoic indicative age (279 ± 89 Myr; MSWD = 43) for the source region. The Anti-Atlas Moroccan chain belt was formed during the continental collision between Eurasia and Africa during the Paleozoic. Mounji et al. [1998] report $^{87}$Sr/$^{86}$Sr compositions of Tafilt platform of the Anti-Atlas belt (calc-alkaline basalt within thick shale-dominated succession) at 0.7079–0.7096, which are close to those of our particle flux data.

[11] In summary, the suggestion that the Anti-Atlas Palaeozoic Moroccan mountain belt is the source region for the lithogenic particle flux at Kiel276 is supported by the high amount of polygorskite with illite and smectite, the lack of kaolinite, the control of clay on the REE patterns and the Sr isotope compositions (Figure 1).

3.4. Lithogenic-Derived Micronutrient Supply to the Open Ocean and Its Implication

[12] In subtropical Atlantic nitrogen fixation fuel up to 50% of export production, and is itself limited by either P or Fe. Therefore additional iron supply to this region may relieve the limitation, and enhance the primary production. Fe and P are especially known for their potential to act as limiting factors for phytoplankton growth [Falkowski, 1995; Thingstad et al., 2005]. Within the lithogenic fraction from April 2003 to April 2004 between 1.5 and 15 μmol m$^{-2}$ d$^{-1}$ of particulate Fe and up to 0.5 μmol m$^{-2}$ d$^{-1}$ of particulate P were delivered to the region (Data Set S4 of the auxiliary material; Figure 4). If we assume that 2% of the particulate Fe is soluble upon entering the water column [Jickells and Spokes, 2001], then 0.08 μmol m$^{-2}$ d$^{-1}$ and 0.005 μmol m$^{-2}$ d$^{-1}$ of average dissolved Fe and P, respectively, are delivered to the ocean. Those Fe and P fluxes increase drastically during dust events in spring 2004 (15 μmol m$^{-2}$ d$^{-1}$ of particulate Fe and 0.2 μmol m$^{-2}$ d$^{-1}$ of particulate P, respectively), and consequently 4 times more dissolved Fe (0.3 μmol m$^{-2}$ d$^{-1}$) is supplied to the region over only a short time period (Figure 4). Note however, that Fe bioavailability is still poorly understood whereby oxidation of organically complexed Fe(II) plays a crucial role on Fe uptake by micro-organisms [Rose et al., 2005; Salmon et al., 2006]. We assume that (1) only 1% of the dissolved iron is made bio-available, (2) that particulate Fe is unavailable to phytoplankton, and (3) that the uptake and in-situ remineralisation rates of Fe over 30 days are much smaller in comparison to the external inputs. Using a Redfield Ratio of C/Fe = 122/2.6 × 10$^{-5}$ [Kuss and Kremling, 1999] we obtain an additional carbon production of 0.17 g C m$^{-2}$ d$^{-1}$, which itself is rather unspectacular. Climate change scenarios proceed from the assumption that the number and duration of the dust storm events will drastically increase due to progression of arid areas and the fast growth of
deserts, especially within the African continent, leading to an increase in the bio-available Fe pool. Continuous input of just 0.3 μmol m⁻² d⁻¹ of bio-available Fe over a year period, would potentially lead to an additional production of 62 g C m⁻² y⁻¹ assuming a direct effect on primary productivity, resulting in an annual production of 210 g C m⁻² y⁻¹ (40% increase compare with today’s values for this region). However, additional Fe input enhances, first, N₂ fixation. This N is then used for primary production, reducing the overall increase in primary productivity because the Fe requirements for nitrogen fixation are high compared to primary production. Therefore the 40% rise in primary production estimated in this study most likely represents the upper limit of the effect of Fe input into the subtropical Atlantic.

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References
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Figure 4. Lithogenic derived element fluxes between April 2003 and April 2004 at 3050 m depth.


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