Elemental ratios and enrichment factors in aerosols from the US-GEOTRACES North Atlantic transects

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Abstract

The North Atlantic receives the highest aerosol (dust) input of all the oceanic basins. Dust deposition provides essential bioactive elements, as well as pollution-derived elements, to the surface ocean. The arid regions of North Africa are the predominant source of dust to the North Atlantic Ocean. In this study, we describe the elemental composition (Li, Na, Mg, Al, P, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Cd, Sn, Sb, Cs, Ba, La, Ce, Nd, Pb, Th, U) of the bulk aerosol from samples collected during the US-GEOTRACES North Atlantic Zonal Transect (2010/11) in order to highlight the differences between a Saharan dust end-member and the reported elemental composition of the upper continental crust (UCC), and the implications this has for identifying trace element enrichment in aerosols across the North Atlantic basin. As aerosol titanium (Ti) is less soluble than aerosol aluminum (Al), it is a more conservative tracer for lithogenic aerosols and trace element-to-Ti ratios. However, the presence of Ti-rich fine aerosols can confound the interpretation of elemental enrichments, making Al a more robust tracer of aerosol lithogenic material in this region.

1. Introduction

Atmospheric dust impacts global climate in a number of significant ways. Dust loading affects radiative forcing and serves as cloud condensation nuclei (Jickells et al., 2005). Dust deposition can be a significant source of bioactive trace elements (Mn, Fe, Co, Ni, Cu, Zn, Cd) in open-ocean regions far from rivers and groundwater input, and it has been suggested that primary productivity in up to 40% of the global ocean is limited by the lack of sufficient Fe (e.g., Coale et al., 1996; Boyd et al., 2000, 2007). While the primary input route of many essential bioactive trace metals to the open ocean is from aerosol deposition and wet scavenging, for a number of key elements (e.g. Fe) only a fraction of the metal associated with marine aerosols is

soluble in rainwater and seawater and therefore potentially available for uptake by primary producers. Thus, aerosol deposition and trace element solubility are key parameters in many ocean ecosystem and biogeochemical models.

It is well documented that dust emanating from northern Africa is transported across the North Atlantic basin as far as the Caribbean Sea and beyond to the Americas. Charles Darwin summarized ship-board observations of “African” dust from 1821 to 1840, including his own experience on the Beagle while in the vicinity of the Cape Verde Islands in 1833 (Darwin, 1846). More recent studies have investigated and confirmed the presence of North African dust in the Americas (e.g. Carlson and Prospero, 1972; Prospero and Carlson, 1972; Prospero et al. 1981; Duce et al., 1991; Arimoto et al., 1995; Prospero, 1999a, 1999b; Arimoto et al., 2003).

The North Atlantic Ocean receives by far the highest aerosol input of all the ocean basins. Jickells et al. (2005) estimate that 43% (193.5 Tg year⁻¹) of the total atmospheric dust deposition to the world’s oceans occurs in the North Atlantic. In contrast, only 15% of global dust deposition (the next highest input) is estimated for the North Pacific, compared with just 4% for the South Atlantic basin. The reason for such high aerosol deposition over the North Atlantic is, of course, the proximity of this basin to the arid Saharan and Sahel regions of northern Africa (often referred to simply as the ‘Sahara’). Saharan dust outbreaks occur episodically as a series of large-scale anticyclonic eddies which transport dust-laden, heated air in the Saharan Air Layer (SAL), via the easterly trade winds, at altitudes of ~1.5-6 km (Prospero and Carlson, 1972; Prospero et al., 1981). As the pulses of air move across the Atlantic the continuous fallout of particulate matter and mixing at the base of the SAL causes dust to be transferred into the marine boundary layer (~400–1200 m thickness) over the latitudinal belt 10-25 °N (Carlson and Prospero, 1972).

While some source-dependent differences in the composition of Saharan aerosols exist, these aerosols are considered relatively homogeneous, and have been characterized in terms of metal composition (e.g., Trapp et al., 2010; Gelado-Cabellero et al., 2012), size distribution (e.g., Stuut et al., 2005; Castillo et al., 2008; Buck et al., 2010^a) and fractional solubility, with particular emphasis on Fe (e.g., Baker et al., 2006; Baker and Jickells, 2006; Baker and Croot, 2008; Sholkovitz et al., 2009, 2012; Buck et al., 2010^{a, b}). As the dust-producing regions of northern Africa have low levels of industrial activity, the aerosols emitted from this region are

not nearly as impacted by human activities compared to European and North American sourced aerosols. North African mineral dust is characterized by relatively high Fe content (~ 4.5%; Guieu et al., 2002), but a growing body of research has demonstrated that the fractional solubility of Fe (and a number of other bioactive elements) in mineral aerosols from northern Africa is significantly lower than that of aerosols from continental Europe and North America (Baker et al., 2006; Sedwick et al., 2007; Sholkovitz et al., 2009, 2012; Buck et al., 2010^b; Wozniak et al., 2013).

The objectives of this paper are to report the elemental composition (in terms of elemental ratios) of aerosols collected during the US-GEOTRACES North Atlantic Zonal Transects (2010-2011) and to discuss the enrichment of various aerosol elements in contrasting regions of the North Atlantic with respect to a Saharan dust “end member” and with respect to the average upper continental crust (UCC; Taylor and McLennan, 1995). While aluminum (Al) is commonly used as a tracer for material of lithogenic origin (due to its high abundance in alumino-silicate minerals), titanium (Ti) might also be a useful lithogenic tracer due to its high abundance and low solubility. Our data confirm that Saharan dust is the dominant aerosol over much of the North Atlantic; that Al is significantly depleted and that iron (Fe) is not significantly enriched in Saharan dust relative to Ti (and relative to the average upper continental crust); that many aerosol trace elements are greatly enriched relative to a Saharan dust end-member; and that there is a source of “excess” aerosol Ti that can be observed in regions where Saharan dust is minimal. These results have an important impact on interpreting the trace element composition and biogeochemical cycling of suspended matter in the North Atlantic Ocean.

2. Methods

2.1. Sample collection, handling, and storage

Aerosol samples ($n=39$) were collected aboard the R/V Knorr during the US-GEOTRACES North Atlantic Zonal transect (Fig. 1). The transect was split into two legs: leg 1 (Lisbon, Portugal to Mindelo, Cape Verde) occurred between 15 October and 2 November 2010, and leg 2 (Woods Hole, MA, USA to Praia, Cape Verde) occurred between 6 November and 9 December 2011. Aerosol samples were collected using a high-volume aerosol sampler

(model 5170-VBL, Tisch Environmental) drawing approximately $1.2 \text{ m}^3 \text{ air min}^{-1}$ over twelve replicate acid-washed 47 mm diameter Whatman 41 (W41) ashless filter discs (total exposed area 149 cm^2). The air sampling face velocity was approximately 134 cm s^{-1} . The sampling duration averaged 17.8 h (range = 5.3–29.6 h), and the volume of air filtered averaged 1209 m^3 (range = 357–2010 m^3). The samplers were deployed on the ship's flying bridge (14 m above sea level), as high off the water as possible. Contamination from the ship's stack exhaust was minimised by controlling aerosol sampling with respect to wind sector and wind speed using an anemometer interfaced with a Campbell Scientific CR800 datalogger. The samplers were operational when the wind was $\pm 60^\circ$ from the bow and $>0.5 \text{ m s}^{-1}$. When the wind failed to meet these two criteria, the aerosol sampler stopped immediately and did not restart until the wind met both the speed and direction criteria for 5 continuous minutes. The anemometer was deployed on a 3 m pole on the flying bridge where turbulence from the wind crossing the bow did not cause the wind vane to vibrate excessively.

>>Figure 1<<

2.2. Total aerosol trace and major element determination: sample preparation and handling

All filters were stored frozen prior to processing, both on the ship and upon returning to the laboratory. For the determination of total aerosol trace and major element loadings (Li, Na, Mg, Al, P, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Zr, Cd, Sn, Sb, Cs, Ba, La, Ce, Nd, Pb, Th, U) the W41 filter discs were digested in tightly-capped 15 mL Teflon-PFA vials (Savillex) using sequential additions of: (1) 15.8 M Optima® nitric acid (1000 μL), and (2) 15.8 M Optima® nitric acid (500 μL) plus 28.9 M Optima® hydrofluoric acid (100 μL); samples were heated to 150°C during both steps (Morton et al., 2013). Solutions were dried down after each digestion step. After the final digestion and evaporation the samples were redissolved in 20 mL of 0.32 M nitric acid for analysis. All filter digestions were performed under Class-100 laminar flow conditions. Total aerosol trace metal concentrations were determined by inductively coupled plasma mass spectrometry (Thermo Element-2) at the National High Magnetic Field Laboratory at Florida State University. Blank solutions for the acid digestions were prepared by digesting W41 discs that had been deployed in the aerosol samplers for 1 h while not in operation, and the resulting concentrations were subtracted from all acid-digested filter samples. Examples of these deployment blanks ranged from 0.01–86.9% and 0.03–69.9% of the sample

concentrations for Al and Ti, respectively (this range covers the highest-loaded “North African” and the least-loaded “Marine” sample).

2.3. Reference materials

Comparing the elemental composition of aerosol or TSM samples to the average continental crust (e.g., Taylor and McLennan, 1995 or Wedepohl, 1995) is problematic due to the wide range of crustal compositions that were averaged. A common aerosol reference material would also be useful for quantifying digestion efficiency and analytical accuracy. This is especially relevant for studies requiring frequent reference material analyses, such as stable isotope ratio determinations, using ICP-MS instruments where the standard-sample-standard bracketing technique is used to account for instrumental mass fractionation and drift. For example, while Ti is recommended as a tracer of lithogenic material, it exists in a number of refractory mineral forms, e.g., rutile (TiO_2), ilmenite (FeTiO_3), and titanite (CaTiSiO_5) (Yarincik et al. 2000; Moreno et al. 2006; Castillo et al. 2008; Ohnemus et al., this issue). If recommended protocols are not followed, Ti may not be fully recovered during acid digestion of aerosol samples (Morton et al., 2013). We also note that Sholkovitz (1990) reported occasional low recovery (as low as 20%) of the heavy REE (Dy, Er, Yb, Lu, and Zr) due to HREE enriched zircon minerals in the insoluble residue from wet digestions of marine sediments using HF.

In order to quantify the digestion efficiency for refractory lithogenic elements like Ti, and to assess analytical accuracy, an appropriate reference material is essential (a full table of blanks and values for reference materials is presented in Table S1 in the Supplementary material). However, only a few Certified Reference Materials (CRMs) of natural aerosols are readily available, due to the challenge of collecting sufficiently large quantities of an aerosol material that is both homogeneous and representative of aged aerosol material such as those encountered over the open ocean (e.g., small particle size; mixed lithogenic, anthropogenic and marine composition). Currently available aerosol reference materials include the loose powder Urban Particulate Materials (1648 and 1649) and Aerosol Particulate on Filter Media (2783), certified by the U.S. National Institute of Standards and Technology (NIST). Other reference materials that are well-certified (but are not representative of aerosol dust) are often analyzed, such as the National Research Council of Canada (NRCC) marine sedimentary materials HISS, MESS and PACS, the NIST Buffalo River Sediment (2704 and 8704), and the United States Geological

Survey (USGS) powdered rock materials (e.g., Rhyolite Glass Mountain RGM-1). Some researchers have turned to generating their own aerosol reference materials, including an aerosol proxy from Asian loess soils (Hwang and Ro, 2006; Nishikawa et al., 2013) and a Saharan soil end-member (Guieu et al. 2002; 2010).

As previously described by Morton et al. (2013), we are currently assessing the “Nominal 0-3 μm Arizona Test Dust” (ATD; Powder Technology Inc.) as a consensus reference material (similar to the SAFe and GEOTRACES reference samples for dissolved trace metals in seawater; <http://es.ucsc.edu/~kbruland/GeotracesSaFe/kwbGeotracesSaFe.html>). It is a true natural aerosol material, which is collected on a canvas cloth in the Salt River Valley, Arizona (www.powdertechinc.com). It is collected in large quantities, has not been excessively processed (only oven dried and dry-sifted), is inexpensive and commercially available. Preliminary results suggest this material is homogeneous (better than 10% RSD for most elements) at the <5-10 mg level. To further establish our digestion efficiency for refractory elements (e.g., Ti, HREE) using the strong acid digestion method, ATD was also analysed by fusion flux (Rick Murray, Boston University): briefly, concentrations determined using the strong acid digestion procedure are within 5% of those concentrations reported by Murray using fusion flux. Not only are the elemental concentrations validated, but so are the elemental ratios (Table 2), which are comparable to our Saharan dust end-member and the UCC (Taylor and McLennan 1995). As the elemental ratios of the ATD fall close to the Saharan dust and UCC ratios, ATD might be a suitable candidate for a reference material both in terms of assessing digestion efficiency and for enrichment factor calculations. The ATD will become more suitable for distribution as a reference material as other laboratories contribute concentrations to our consensus reference material effort (subsamples available upon request: wlanding@fsu.edu).

>>Table 1. Elemental recoveries between acid digestions and fusion flux<<

2.4. Air Mass Back Trajectories

Three day (72 h) air mass back trajectories were simulated every 4 h for each aerosol sampling interval using the GDAS meteorology in the publically available NOAA Air Resources Laboratory Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2013; Rolph, 2013). The GDAS and REANALYSIS data sets both have global

coverage. However, the GDAS data set has a resolution of 1° of latitude, while the resolution of the REANALYSIS data set is about 2.5° of latitude. The normal form of the model was used to simulate a new trajectory every 4 h during each ~24 h sample deployment interval in order to visualize differences in the air mass provenance during each sampling period. Because the samples were collected in the marine boundary layer (~400–1200 m thickness), an arrival height of 500 m was chosen. Air masses were operationally characterized as European, North American, North African or Marine based on the predominant source region according to the back trajectories. Air masses categorized as Marine had had no interaction with continental land masses during the 3 day back trajectory simulation, but samples may contain aerosol loadings from distant (>3 days) continental sources. In addition, samples with back trajectories that did not contact the African continent during the 3-day model simulation, but had the characteristic orange color of Saharan aerosols, were classified as North African, rather than Marine.

3. Results and Discussion

3.1. Aerosol provenance.

There are a number of ways by which aerosol provenance can be identified. In this study, aerosol provenance was identified primarily from air mass back trajectories and elemental ratios, which confirmed initial assessments from the visual inspection of filters. Aerosols from four air mass regimes (Fig. 2) were identified via air mass back trajectory simulations (using the HYSPLIT model). These four regimes could be crudely identified by their distinctive coloration: European and North American aerosols appeared grey on the filters (although visual inspection alone did not allow these two regimes to be resolved from each other); North African aerosols had a distinctive orange color and high concentrations of lithogenic elements (e.g., the maximum Al loading observed was 7485 ng m^{-3} ; Fig. 3 and Table S1 in the supplemental material); Marine aerosols were not visible to the naked eye due to the low aerosol loading (e.g., $\text{Al} = 5.90 \pm 6.36 \text{ ng m}^{-3}$). Figure 3 shows the total aerosol loadings of Al and Fe (ng m^{-3}) and further demonstrates the distinctions between the air mass regimes; the greatest aerosol loadings were associated with the North African samples (10^3 ng m^{-3} Al and Fe) > North American and European samples (10^1 – 10^2 ng m^{-3} Al and Fe) > Marine (10^0 ng m^{-3} Al and Fe).

>>Figure 2<<

>>Figure 3<<

As mentioned in the Introduction, it is common to use Al or Ti as tracers for lithogenic aerosols (mineral dust) due to their high concentrations in the continental crust. Given that mineral dust deposition to the North Atlantic basin is dominated by Saharan dust, we wanted to compare our Saharan dust trace element data to what has been reported for average upper continental crust (UCC; Taylor and McLennan, 1995). There are other reports for the composition of average continental crust (e.g., Turekian and Wedepohl, 1965; Wedepohl, 1995; Rudnick and Gao, 2003). However, we have chosen to use the data from Taylor and McLennan (1995) as they report data for the upper continental crust separately from the bulk continental crust.

The ideal lithogenic tracer should have reasonably consistent elemental ratios to the other lithogenic tracers in aerosols spanning the whole basin. Using elemental ratios, normalized to Al, Chiapello et al. (1997) were able to demonstrate source-dependent variability in African dusts. Although Al is most frequently chosen as the normalizing element, other elements such as Fe (Rädlein and Heumann, 1995) and Sc (Okubo et al., 2013) have been used. Lithogenic tracers must be capable of being accurately measured on a routine basis. They must not have a significant non-crustal source(s). For example, despite having a significant crustal source, V is also enriched in heavy oil fly ash (Sholkovitz et al., 2009, and references therein) and so is not a good candidate for a lithogenic tracer.

Table 2 compares the ratios of Ti, V, Mn and Fe to Al in North African aerosols and soils from this study to published data and the UCC. In all cases, the elemental ratios in average UCC are significantly lower than in North African aerosols/soils (Grubb's test, $P = 0.05$). Therefore, Al is depleted relative to Ti, V, Mn and Fe in our North African aerosols/soils (or Ti, V, Mn and Fe are all enriched relative to Al). Indeed, the Fe/Al in Saharan soils (0.64 by mass; Guieu et al. 2002) is greater than the UCC average (Fe/Al = 0.44; Taylor and McLennan, 1995); the orange coloration of soils from this region is assumed to result from Fe-enrichment, rather than Al-depletion. In contrast, normalization of Fe and Mn to Ti yields similar elemental ratios for North African aerosols (this study) and the UCC (e.g., Fe/Ti = 9.73 and 11.7, respectively, and Mn/Ti = 0.17 and 0.20, respectively; Fig. 4); but there is a twofold difference in the Al/Ti ratios (this study = 12.6, UCC = 26.8). This demonstrates that Al is depleted relative to Ti, V, Mn and Fe in

our North African aerosols. As the Fe/Ti and Mn/Ti ratios in Saharan dust are close to the UCC ratios, Ti might be a better tracer than Al for Saharan dust across the North Atlantic basin.

>>Table 2<<

>>Figure 4<<

However, Figure 4 also shows that the Fe/Ti, Al/Ti, and Mn/Ti ratios for some of the North American and Marine samples on this transect are significantly lower than either the Saharan dust end-member ratios or the UCC ratios. This implies that there is an additional source of Ti-rich aerosols, which is especially evident in the Marine samples when the loading of Saharan dust is minimal. Those same samples therefore show high Ti/Al ratios, somewhat elevated Mn/Al ratios, but only slightly elevated Fe/Al ratios. Since we anticipated some Fe-enriched aerosols from anthropogenic sources, the higher ratios in the North American samples were not completely unexpected. Overall the Fe/Al ratios across the entire transect were all within a factor of two of the Saharan dust end-member, supporting the conclusion that Saharan dust is the dominant source of mineral dust across the entire North Atlantic Basin.

Preliminary data from size-fractionated aerosol samples (R. Shelley and W. Landing, unpublished), collected during the 2011 leg of the transect, indicates that approximately two-thirds of the Ti from the Marine samples with high Ti/Al ratios was associated with sub-micron sized aerosols. As Ti is thought to be derived primarily from crustal material, we anticipated that the majority of the aerosol Ti would be found in the super-micron size fraction. Ohnemus et al. (this issue) describe an unusual Ti mineral found in the region of the Cape Verde Islands in deep water particles, which they argue results from lateral inputs of lithogenic particles from basaltic minerals in this volcanic island region. However, if dust mobilized from the Cape Verde islands is a source of Ti-rich aerosols, the Ti should be associated with the coarse, rather than the fine, fraction. Although it is hard to imagine an anthropogenic source of fine particulate Ti to the remote central basin, excess aerosol Ti was only detected in the Marine samples, where the aerosol composition was not overwhelmed by Saharan dust. The presence of a non-crustal source of aerosol Ti illustrates that there are subtleties in the aerosol chemistry that are yet to be explained, which has implications for the use of Ti as a lithogenic tracer for aerosol studies.

We note that Ohnemus et al. (this issue) recommend the use of Ti as a lithogenic tracer in their investigations of the trace element composition of suspended and sinking particles in the water column. This recommendation is justified since aerosol Ti is significantly less soluble than aerosol Al (Buck et al., 2010^b), and Al in seawater is involved in adsorptive scavenging and, perhaps, also biological uptake (Martin-Jézéquel et al., 2000; Beck et al., 2002; Middag et al., 2009). Thus, normalizing trace element concentrations in marine particles to Ti (rather than Al) allows one to describe excesses or depletions in Al due to its involvement in biogeochemical cycles.

In addition to Ti and Al, a number of other trace elements were investigated as a more suitable lithogenic tracer than Ti or Al. The Rare Earth Elements (REE), by definition, are lithogenically-derived, and thus were considered as potential candidates. Unfortunately, in some Marine samples the REEs, such as La and Nd (as well as other potential lithogenic tracers such as Sc, Th and U), had concentrations close to or below the detection limit. Therefore, these elements were not suitable as lithogenic tracers in this study; that is not to say that they are unsuitable as lithogenic tracers *per se*. Finally, because of the apparent presence of some Ti-rich aerosols, we conclude that ratios normalized to Al (rather than Ti) are the best way to describe the enrichment of aerosol trace elements relative to the Saharan dust end member or to the UCC.

In this study, the North African samples were fairly homogeneous in terms of their trace element/Al ratios for lithogenic (Ti, Mn, Fe), mixed-source (V, Co, Nd), and pollution-derived elements (Zn, Cd, Pb) (Fig. 5; Table 3). For the mixed-source and pollution-derived elements, the aerosol trace element/Al ratios from the other source regions are enriched with respect to the North African samples, which indicates that there are sources of the enriched elements in these other regions in addition to Saharan dust. As has already been discussed, Ti, Mn, and Fe to Al ratios for the North African samples are consistent, and are all about 1.6 times higher than trace element/Al ratios for the UCC due to the depletion of Al in Saharan dust relative to the UCC (which may be a characteristic of the deflationary source of Saharan dust from arid lake deposits or desert varnish). The greatest enrichments of Ti, V, Mn, Fe, Co, and Nd relative to Al were found in many of the North American and Marine samples (Fig. 5). The enrichment patterns for Zn, Cd, and Pb relative to Al are similar, and these elements are all enriched relative to either Saharan dust or the UCC in the North American, Marine, and European samples.

>>Figure 5<<

>>Table 3<<

3.2. Enrichment Factors

As geochemical abundance data varies over several orders of magnitude, it is necessary to normalize the data to remove the physical dimension of concentration in order to give equal weighting to all the elements of interest. Elemental ratios are one way such way of normalizing the data. Taking it one step further, enrichment factors are calculated from elemental ratios, and are most often used to indicate the impacts of pollution according to the following equation:

$$EF = \frac{[TE]/[Al]_{aerosol}}{[TE]/[Al]_{UCC}} \quad \text{Eqn. 1}$$

where [TE] is the concentration of the trace element of interest, [Al] is the concentration of a lithogenic tracer (in this case, Al) and the subscripts ‘aerosol’ and ‘UCC’ refer to the aerosol sample and the UCC (e.g., Taylor and McLennan, 1995).

Enrichment factors can be used as a first approximation of aerosol source (mineral dust or anthropogenically influenced) as they reveal the degree of enrichment of an element relative to some reference element in a major source material (often Al in the UCC). Elements such as V, Zn, Cd, Sb, Pb (and others) are generally enriched in aerosols derived from oil and other coal combustion and industrial processes (e.g., metal smelters) (Grousset et al., 1995 and references therein; Prospero, 2002). Primarily lithogenic elements, e.g. Fe and Mn, have also been observed as enriched in anthropogenically-impacted aerosols (e.g. Sholkovitz et al., 2012; Fomba et al., 2013). Sea-spray generated at the seawater surface by wind and waves has also been proposed as a mechanism for enriching TMs in aerosols (Weisel et al., 1984; Arimoto et al., 2003), using TM/Na ratios based on surface seawater concentrations. While previous experiments indicated that sea-salt recycling could account for significant enrichments of V, Sb, Se and Zn (30-60%; Arimoto et al., 2003), preliminary data from size-fractionated aerosols collected during the 2010/2011 GEOTRACES North Atlantic cruises (Shelley et al., manuscript in prep.) shows that Na primarily resides in the coarse fraction (> 3 µm) while V, Sb, Se, and Zn

primarily reside in the fine fraction ($<0.5\ \mu\text{m}$). Therefore, variability in TM enrichments in North Atlantic aerosols is better explained by anthropogenic inputs (e.g., Sedwick et al., 2007; Sholkovitz et al., 2009) rather than sea-salt recycling.

Enrichment factors are most commonly calculated against Al (i.e., TEI/Al) based on the relatively high and constant abundance of Al in crustal material ($\sim 8\%$ by mass in UCC; Taylor and McLennan, 1985). This convention also assumes that all of the Al is derived from the aluminosilicate matrix, and that the abundance of Al is a relatively conservative property of mineral dust. This raises the question of whether other elements are similarly depleted/enriched. In order to investigate this, enrichment factors (EF) for each trace element were calculated relative to Al in the UCC (Fig. 6) and to Al in North African mineral dust (data shown in Table S2 in the Supplemental Material). Typically, only samples with EF values >10 are considered to show significant enrichment (e.g., Gellado-Cabellero et al., 2012).

>>Figure 6<<

A common reference material used to calculate EFs allows samples collected at different times, locations, and between different laboratories to be compared. Given that dust from the arid regions of northern Africa (predominantly the Sahel and Sahara) dominates the mineral aerosol supply to the North Atlantic basin, it might be more appropriate to calculate EFs relative to Saharan dust. Furthermore, Saharan dust has a different elemental composition from the average UCC (Guieu et al. 2002), because it is derived from different sources, i.e. arid soils, alluvial fans and/or argillaceous (clay-based mineral) formations.

The lithogenic trace elements (Ti, Fe, Nd, Th) showed EFs less than 10 with respect to Al (in the UCC) in samples from all four of the air mass regimes (Fig. 6), indicating a predominantly lithogenic source. The EFs for Sc in the North American and Marine samples ranged from 70-87. These elevated EFs for Sc suggest that it should not be treated as a “lithogenic” tracer in the North Atlantic basin.

Of the “mixed-source” trace elements (those having a significant crustal concentration, as well as anthropogenic sources), the EFs for V were elevated in the North American (EF = 35), Marine (EF = 110), and European (EF = 30) samples. This source of this enrichment has been attributed to the burning of the heavier fractions of fuel oil, which are rich in V, resulting in fly

ashes with relatively high abundances of V (Sholkovitz et al., 2009). Modest Mn enrichment ($EF \leq 5$) has previously been reported in the North Atlantic basin (Buck et al., 2010^b), and we found a few samples with EFs greater than 10 in the North American, Marine, and European samples. High-temperature combustion processes of Mn-rich fuels and steel production in North America and Europe have been proposed as non-crustal sources of Mn (Wallace and Slonecker, 1997; Pfeifer et al., 1999; Hacisalihoglu et al., 1991). Cobalt was significantly enriched relative to Al in the North American ($EF = 26$) and Marine ($EF = 67$) samples.

For “pollution-derived” elements (Ni, Cu, Zn, As, Se, Cd, Sn, Sb, and Pb) the EF relative to Al in the UCC vary from 10 to 4006 in the North American, Marine, and European samples. Interestingly, Se was the only pollution-derived element that had an EF less than 1.0 ($EF = 0.482$) in the North African samples; demonstrating that Se is less abundant in Saharan dust than the UCC. It is also important to consider that marine biogenic sources are significant for Se (Mosher and Duce, 1987), and in those samples that were not dominated by mineral dust (i.e. the non-Saharan samples) this source becomes apparent. However, within the scope of this study we are unable to distinguish the relative contributions of marine biogenic and pollution sources for Se. In contrast to Se, the EFs for As, Cd, Sb were all greater than 10 ($EF = 13.2, 27.2, 14.5$, respectively) in our North African samples. While we were most certainly not sampling pure end-member Saharan dust aerosols at the stations closest to the African coast, we are unable to conclusively determine whether the North African aerosols were polluted with As, Cd, and Sb by admixture with pollutant aerosols during off-shore transport or if these three elements are naturally high in Saharan soils. For example, a simple two end-member mixture of 3.7% European aerosols (Cd $EF=713$) with 96.3% Saharan dust (Cd $EF=1$) would yield a Cd EF of 27 (the average Cd EF we observed in our North African samples).

Table S3 compares the EFs shown in Figure 6 with those calculated relative to our Saharan dust end-member (obtained from the ten most heavily loaded aerosol samples off the coast of Africa). The EFs for the lithogenic elements (Ti, Fe, Nd), Sc, and Mn relative to this Saharan dust end-member are about twofold lower than those calculated relative to the UCC due to the Al depletion in Saharan dust. The EFs for V and Co and some of the “pollution-derived” elements (Ni, Cu, Zn, Sn, Pb) are about three times lower, while the EFs for As, Cd, and Sb are

up to a factor of 10 lower due to the anthropogenic enrichment of those elements, coupled with the depletion of Al in Saharan dust.

The advantage of using the UCC ratios to calculate EF is to allow direct comparisons with studies in other regions, but is ultimately a broad stroke approach. If the focus of research requires source apportionment of trace elements between atmospheric, sedimentary, and biogenic sources (cf. Ohnemus et al., this issue), then it is important to understand the composition of the background material that contributes to any given sample. In that case, trace element enrichment in marine particle samples collected from the eastern basin of the North Atlantic should be discussed relative to a Saharan dust end-member. Because aerosol Al is significantly more soluble than aerosol Ti (Buck et al., 2010^b), and because Al has its own biogeochemical cycles (particle scavenging and regeneration) in the ocean, it is appealing to normalize to Ti to discuss trace element enrichment in marine particle samples. However, as we note above, there appears to be a source of Ti-rich fine-fraction aerosols in our North American and Marine samples. Input of this aerosol material could confound the use of trace element/Ti ratios under conditions where the input of Saharan dust is minimal. The caveat to this is, for studies wishing to link aerosol inputs to water column observations in regions where aerosol data is scarce, it may be appropriate to use the UCC metal/Ti ratios rather than the UCC metal/Al ratios.

4. Conclusions

In this study, we have demonstrated the differences between a Saharan dust end-member versus the reported elemental composition of the UCC to discuss trace element enrichment in aerosols across the North Atlantic basin. As aerosol Ti is less soluble than aerosol Al, it is a more conservative tracer for lithogenic aerosols and trace element-to-Ti ratios may be preferred for some studies on trace element enrichment in suspended or trapped particles. However, one must be aware that Ti-rich fine aerosols can confound such interpretations. While analysts usually include CRMs or SRMs in their analytical protocol, there is a need for a common reference material that more closely mimics natural aerosol material for use in quantifying digestion efficiency and analytical accuracy. We are continuing to investigate the suitability of “Nominal 0-3 μm Arizona Test Dust” for this purpose.

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415

416 **References**

- 417 Adepetu, J.A. et al. 1988. Elemental composition of Nigerian Harmattan dust, J. Radioanal.
418 Nucl.Chem. 121: 141–147. DOI: 10.1007/BF02041455.
- 419 Arimoto, R., et al.. 1995. Trace elements in the atmosphere over the North Atlantic."J. Geophys.
420 Res. 100: 1199-1213.
- 421 Arimoto, R., Duce, R. A., Ray, B. J. and Tomza. U. 2003. Dry deposition of trace elements to
422 the western North Atlantic. Global Biogeochem. Cycles. 17.DOI: 10.1029/2001GB001406.
- 423 Baker et al. 2013. Estimation of atmospheric nutrient inputs to the Atlantic Ocean from 50°N to
424 50°S based on large-scale field sampling: Iron and other dust-associated elements. Global
425 Biogeochem. Cycles. 27:755-767.
- 426 Baker, A. R., and Croot, P. L. 2010. Atmospheric and marine controls on aerosol iron solubility
427 in seawater. Mar. Chem. 120: 4-13.
- 428 Baker, A. R., and Jickells, T.D. 2006. Mineral particle size as a control on aerosol iron solubility.
429 Geophys. Res. Lett. 33. DOI: 10.1029/2006GL026557.
- 430 Baker, A. R. et al. 2006. Trends in the solubility of iron, aluminium, manganese and phosphorus
431 in aerosol collected over the Atlantic Ocean. Mar. Chem. 98: 43-58.
- 432 Beck et al. 2002. The relationship between Al and Si in biogenic silica as determined by PIXE
433 and XAS. Nucl. Instr. Methods Phys. Res. B. 189: 180-184.
- 434 Boyd, P. W. et al. 2000. A mesoscale phytoplankton bloom in the polar Southern Ocean
435 stimulated by iron fertilization. Nature 407: 695-702.
- 436 Boyd, P. W. et al. 2007. Mesoscale iron enrichment experiments 1993-2005: synthesis and future
437 directions. Science 315: 612-617.
- 438 Buck, C. S., Landing, W. M. and Resing, J.A. 2010^a. Particle size and aerosol iron solubility: A
439 high-resolution analysis of Atlantic aerosols. Mar. Chem. 120: 14-24.
- 440 Buck, C. S., et al. 2010^b. The solubility and deposition of aerosol Fe and other trace elements in
441 the North Atlantic Ocean: Observations from the A16N CLIVAR/CO₂ repeat hydrography
442 section. Mar. Chem. 120: 57-70.
- 443 Carlson, T. N. and Prospero, J.M. 1972. The large-scale movement of Saharan air outbreaks over
444 the North Equatorial Atlantic. J. App. Meteorol. 11: 283-297.
- 445 Castillo, S. et al. 2008. Trace element variation in size-fractionated African desert dusts. J. Arid
446 Envs. 72: 1034-1045.
- 447 Chen, L., and Duce, R.A. 1983. The sources of sulfate, vanadium and mineral matter in aerosol
448 particles over Bermuda. Atmos. Env. 17: 2055-2064.

449 Chiapello, I. et al. 1997. Origins of African dust transported over the northeastern tropical
 450 Atlantic. *J. Geophys. Res: Atmos.* 102: 13701-13709.

451 Coale, K. H. et al. 1996. A massive phytoplankton bloom induced by an ecosystem-scale iron
 452 fertilization experiment in the equatorial Pacific Ocean. *Nature.* 383: 495-501.

453 Darwin, C. R. 1846. An account of the fine dust which often falls on vessels in the Atlantic
 454 ocean. *Quarterly Journal of the Geological Society of London.* 2: 26-30 (available online at:
 455 <http://darwin-online.org.uk/content/frameset?itemID=F1672&viewtype=text&pageseq=1>.
 456 Accessed on 24 Oct 2013)

457 Draxler, R.R. and Rolph, G.D., 2013. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated
 458 Trajectory) Model access via NOAA ARL READY Website
 459 (<http://ready.arl.noaa.gov/HYSPLIT.php>). NOAA Air Resources Laboratory, Silver Spring, MD.

460 Duce, R. A., et al. 1991. The atmospheric input of trace species to the world ocean. *Global*
 461 *Biogeochem. Cycles.* 5: 193-259.

462 Fomba, K. W., Muller, K., van Pinxteren, D., and Herrmann, H. 2013. Aerosol size-resolved
 463 trace metals composition in remote northern tropical Atlantic marine environment: case study
 464 Cape Verde islands. *Atmos. Chem. Phys.* 13: 4801-4814.

465 Gelado-Caballero, M. D., et al. 2012. Long-term aerosol measurements in Gran Canaria, Canary
 466 Islands: Particle concentration, sources and elemental composition. *J. Geophys. Res.: Atmos.*
 467 117. DOI: 10.1029/2011jd016646.

468 Grousset, F. E. et al. 1995. Anthropogenic vs. lithogenic origins of trace elements (As, Cd, Pb,
 469 Rb, Sb, Sc, Sn, Zn) in water column particles: northwestern Mediterranean Sea. *Mar. Chem.* 48:
 470 291-310.

471 Guieu, C., et al. 2002. Chemical characterization of the Saharan dust end-member: Some
 472 biogeochemical implications for the western Mediterranean Sea. *J. Geophys. Res.* 107. DOI:
 473 10.1029/2001JD000582.

474 Guieu, C., Loje-Pilot, M. D., Benyahya, L., and Dufour, A. 2010. Spatial variability of
 475 atmospheric fluxes of metals (Al, Fe, Cd, Zn and Pb) and phosphorus over the whole
 476 Mediterranean from a one-year monitoring experiment: Biogeochemical implications. *Mar.*
 477 *Chem.* 120: 164-178.

478 Hacisalihoglu, G. et al. 1991. Trace-element composition of the Black Sea aerosols. *Deep Sea*
 479 *Res.* 38: S1255-S1266.

480 Hwang, H., and Ro, C.-U. 2006. Single-particle characterization of "Asian Dust" certified
 481 reference materials using low-Z particle electron probe X-ray microanalysis. *Spectrochim. Acta*
 482 *Part B.* 61: 400-406.

483 Jickells, T. D., et al. 2005. Global iron connections between desert dust, ocean biogeochemistry
 484 and climate. *Science.* 308: 67-71.

485 Jochum, K.P., Nohl, U., Herwig, K., Lammel, E., Stoll, B. and Hofmann, A.W. 2007. GeoReM:
 486 A new geochemical database for reference materials and isotopic standards. *Geostand Geoanal.*
 487 *Res.* 29:333-338.

488 Kandler, K. et al. 2007. Chemical composition and complex refractive index of Saharan Mineral
 489 Dust at Izaña, Tenerife (Spain) derived by electron microscopy. *Atmos. Environ.* 41: 8058–8074.
 490 DOI: 10.1016/j.atmosenv.2007.06.047.

491 Martin-Jézéquel, V., Hildebrand, M. and Brzezinski, M.A. 2000. Silicon metabolism in diatoms:
 492 Implications for Growth. *J. Phycol.* 36:821-840.

493 Middag, R., de Baar, H.J.W., Laan, P. and Bakker, K. 2009. Dissolved aluminium and the silicon
 494 cycle in the Arctic Ocean. *Mar. Chem.* 115: 176-195.

495 Moreno, T., et al. 2006. Geochemical variations in aeolian mineral particles from the Sahara–
 496 Sahel Dust Corridor. *Chemosphere.* 65: 261-270.

497 Morton, P. L., et al. 2013. Methods for the sampling and analysis of marine aerosols: results
 498 from the 2008 GEOTRACES aerosol intercalibration experiment. *Limnol. Oceanog.: Methods.*
 499 11: 62-78.

500 Mosher, B. W. and Duce, R.A. 1983. Vapor phase and particulate selenium in the marine
 501 atmosphere. *J. Geophys. Res.: Oceans* 88: 6761-6768.

502 Nishikawa, M., et al. 2013. Preparation and chemical characterisation of an Asian mineral dust
 503 certified reference material. *Anal. Methods.* 5: 4088-4095.

504 Ohnemus, D.C., and Lam, P.J. 2013. Cycling of lithogenic marine particulates in the US
 505 GEOTRACES North Atlantic Zonal Transect. *Deep Sea Res. II.* This issue.

506 Okubo, A., Takeda, S. and Obata, H. 2013. Atmospheric deposition of trace metals to the
 507 western North Pacific Ocean observed at coastal station in Japan. *Atmos. Res.* 129–130: 20-32.

508 Pfeifer, G.D., Harrison, R.M., and Lynam, D.R. 1999. Personal exposures to airborne metals in
 509 London taxi drivers and office workers in 1995 and 1996. *Sci. Total Environ.* 253-260.

510 Prospero, J. M. 1999^a. Long-range transport of mineral dust in the global atmosphere: Impact of
 511 African dust on the environment of the southeastern United States. *PNAS.* 96: 3396-3403.

512 Prospero, J. M. 1999^b. Long-term measurements of the transport of African mineral dust to the
 513 southeastern United States: Implications for regional air quality. *J. Geophys. Res.* 104: 15917-
 514 15927.

515 Prospero, J. M. 2002. The chemical and physical properties of marine aerosols: An introduction.
 516 In: *Chemistry of marine water and sediments.* Gianguzza, A., Peizzetti, E., and Sammartano, S.
 517 (eds). Berlin, Springer. Pp. 35-77.

518 Prospero, J. M., and Carlson, T.N. 1972. Vertical and areal distribution of Saharan dust over the
519 Equatorial North Atlantic Ocean. *J. Geophys. Res.* 77: 5255-5265.

520 Prospero, J. M., Glaccum, R.A. and Nees, R.T. 1981. Atmospheric transport of soil dust from
521 Africa to South America. *Nature*. 289: 570-572.

522 Rädlein, N. and Heumann, K.G. 1995. Size fractionated impactor sampling of aerosol particles
523 over the Atlantic Ocean from Europe to Antarctica as a methodology for source identification of
524 Cd, Pb, Tl, Ni, Cr, and Fe. *Fresenius' J. Anal. Chem.* 352: 748-755.

525 Rolph, G.D., 2013. Real-time Environmental Applications and Display sYstem (READY)
526 Website (<http://ready.arl.noaa.gov>). NOAA Air Resources Laboratory, Silver Spring, MD.

527 Rudnick, R.L., and Gao, S. 2003. Chapter 3.01. Composition of Continental Crust in *Treatise on*
528 *Geochemistry*. Vol 6. Elderfield, H. (ed). Oxford: Elsevier.

529 Sedwick, P. N., Sholkovitz, E.R. and Church, T.M. 2007. Impact of anthropogenic combustion
530 emissions on the fractional solubility of aerosol iron: evidence from the Sargasso Sea. *G³*. DOI:
531 10.1029/2007GC001586.

532 Shelley, R. U. et al 2012. Controls on dissolved cobalt in surface waters of the Sargasso Sea:
533 Comparisons with iron and aluminum. *Global Biogeochem. Cycles* 26. DOI:
534 10.1029/2011gb004155

535 Sholkovitz, E. R. 1990. Rare-earth elements in marine sediments and geochemical standards.
536 *Chem. Geol.* 88: 333-347.

537 Sholkovitz, E.R., Sedwick, P.N. and Church, T.M. 2009. Influence of anthropogenic combustion
538 emissions on the deposition of soluble aerosol iron to the ocean: Empirical estimates for island
539 sites in the North Atlantic. *Geochim. Cosmochim. Acta.* 73: 3981-4003.

540 Sholkovitz, E., R., et al. 2012. Fractional solubility of aerosol iron: Synthesis of a global-scale
541 data set. *Geochim. Cosmochim. Acta.* 89: 173-189.

542 Stuut, J.-B. et al. 2005. Provenance of present-day eolian dust collected off NW Africa. *J.*
543 *Geophys. Res.* 110. DOI: 10.1029/2004JD005161.

544 Taylor, S. R. and McLennan S. M., 1985. *The Continental Crust: Its Composition and Evolution*.
545 Boston, Mass.: Blackwell Scientific.

546 Taylor, S. R. and McLennan, S.M. 1995. The geochemical evolution of continental crust. *Rev.*
547 *Geophys.* 33: 241-265.

548 Trapp, J. M., Millero, F. J. and Prospero, J.M. 2010. Temporal variability of the elemental
549 composition of African dust measured in trade wind aerosols at Barbados and Miami. *Mar.*
550 *Chem.* 120: 71-82.

551 Turekian and Wedepohl, 1965 Distribution of the elements in some major units of the earth's
552 crust. *Bull. GSA* 72, 175-192

553 Viana, M. et al. 2002. Influence of African dust on the levels of atmospheric particulates in the
554 Canary Islands air quality network. *Atmos. Environ.* 36: 5861–5875. DOI:10.1016/S1352-
555 2310(02)00463-6.

556 Wallace, L., and Slonecker, T., 1997. Ambient air concentrations of fine (PM 2.5) manganese in
557 US national parks and in California and Canadian cities: the possible impact of adding MMT to
558 unleaded gasoline., *J. Waste Manage.* 47: 642-652.

559 Wedepohl, H. K. 1995. The composition of the continental crust. *Geochim. Cosmochim. Acta.*
560 59: 1217-1232.

561 Weisel, C. P., Duce, R. A., Fasching, J. L., and Heaton, R. W. 1984. Estimates of the transport of
562 trace metals from the ocean to the atmosphere. *J. Geophys. Res.* 89: 11607-11618.

563 Wozniak, A. S., et al. 2013. Relationships among aerosol water soluble organic matter, iron and
564 aluminum in European, North African, and Marine air masses from the 2010 US GEOTRACES
565 cruise. *Mar. Chem.* 154: 24-33.

566 Yarincik, K. M., Murray, R. W., Peterson, L. C. 2000. Climatically sensitive eolian and
567 hemipelagic deposition in the Cariaco Basin, Venezuela, over the past 578,000 years: Results
568 from Al/Ti and K/Al. *Paleoceanog.* 15: 210-228.

Figure 1. The 2010/11 US-GEOTRACES North Atlantic Zonal Transect cruise track, with aerosol sample collection locations (red dots = leg 1, Lisbon, Portugal – Mindelo, Cape Verde and black dots = leg 2 Woods Hole, MA, USA – Praia, Cape Verde) and air mass regimes indicated.

Figure 2. Examples of three day air mass back trajectory simulations from each of the four air mass regimes (North American, European, Marine and North African), with an arrival height of 500 m. A new trajectory was simulated every 4 h during each ca. 24 h sampling interval.

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 601 Figure 4. Elemental ratios (by mass) of four lithogenically-derived aerosol metals (Al, Ti, Mn
 602 and Fe). The source air mass regime is indicated on the x-axes and by the red lines on the plots.
 603 The orange lines indicate the median North African ratio (NAf; this study), and blue lines
 604 represent the ratio in mean UCC (Taylor and McLennan, 1995). The median ratio is used for the
 605 North African mineral dust to avoid the undue influence of outliers in the data. Note that the y-
 606 axes (metal ratios, by mass) have different scales and are log scales.

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609 Figure 5. Examples of metal:Al ratios (by mass), showing from left to right:
 610 top row (lithogenic metals) = Al, Fe, Nd; middle row (mixed-source metals; metals with both
 611 lithogenic and pollution sources) = V, Mn, Co; bottom row (pollution-derived metals) = Zn, Cd,
 612 Pb.

613 Source air mass regimes are indicated on the x-axes and by the red lines on the plots. The orange
 614 lines indicate the median North African ratio (NAf; this study), and blue lines represent the ratio
 615 of mean UCC (Taylor and McLennan, 1995). The median, rather than mean, ratio is used for the
 616 North African mineral dust to avoid the undue influence of outliers in the data. Note that the y-
 617 axes (metal ratios, by mass) have different scales; all are log scale. The missing data in the Cd/Al
 618 plot is a result of Cd being below the detection limit in these two samples.

Figure 6. Average enrichment factors (± 1 standard deviation) by source region (starting top left: North American, European, Marine and North African) of a selection of lithogenic (Ti, Fe, Nd, Th), mixed-source (Sc, V, Mn, Co) and pollution-derived (Ni, Cu, Zn, As, Se, C, Sn, Sb, Pb) elements. Plots show enrichment factors normalized to Al, using the UCC ratios (Taylor and McLennan, 1995). Therefore, an EF of unity is the UCC ratio. Note that the y-axis is a log scale. Enrichment factors of 10 (EF > 10: significant enrichment) are indicated by a solid, horizontal line on each plot.

629 Table 1. Comparison of elemental concentrations and recoveries from acid digestions (Shelley;
630 this study) and fusion flux (R. Murray, Boston University) for a suite of elements ($\pm 1SD$) for
631 Arizona Test Dust (ATD) and NIST Buffalo River Sediment 2704 (BRS)

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Sample	Laboratory	Method	n	Na	Mg	Al	P	Ti	V	Mn	Fe
Acid blank (ng/vial)			3	17.6 $\pm$ 4.7	26.7 $\pm$ 2.1	44.4 $\pm$ 31.6*	18.9 $\pm$ 0.5	9.7 $\pm$ 4.0	0.30 $\pm$ 0.03	0.47 $\pm$ 0.07	7.29 $\pm$ 2.55
D.L (3xSD; ng/vial)				14.2	6.4	94.7	1.6	12.0	0.08	0.20	7.66
* n=2											
ATD	Shelley (FSU)	Acid digestion	5	11100 $\pm$ 300	11100 $\pm$ 400	69600 $\pm$ 1870	875 $\pm$ 56	3220 $\pm$ 50	72.7 $\pm$ 1.1	764 $\pm$ 12	33600 $\pm$ 600
ATD	Murray (BU)	Fusion Flux	6	11800 $\pm$ 200	11300 $\pm$ 200	69100 $\pm$ 1210	896 $\pm$ 30	3330 $\pm$ 50	78.7 $\pm$ 5.6	728 $\pm$ 10	32300 $\pm$ 520
BRS	Shelley (FSU)	Acid digestion	4	4870 $\pm$ 230	10600 $\pm$ 400	55300 $\pm$ 1500	913 $\pm$ 38	4260 $\pm$ 150	91.3 $\pm$ 2.3	562 $\pm$ 20	39800 $\pm$ 800
	Certified			5470 $\pm$ 140	12000 $\pm$ 200	61100 $\pm$ 1600	998 $\pm$ 28	4570 $\pm$ 180	95 $\pm$ 4	555 $\pm$ 19	41100 $\pm$ 1000
	% recovery			89%	88%	91%	91%	93%	96%	101%	97%

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Table 2. Comparison of elemental ratios (by mass) of a selection of trace metals in North African aerosols

Ti/Al	V/Al	Mn/Al	Fe/Al	Type	Sampling location	Reference
0.08	0.003	0.013	0.77	Aerosols	At sea	This study (GEOTRACES)
0.12	0.005	0.012	0.66	Aerosols	At sea	Buck et al. (2010 ^b)
		0.010	0.58	Aerosols	At sea	Baker et al. (2013)
0.09			0.57-0.66	Aerosols	Gran Canaria	Gelado-Caballero et al. (2012)
		0.012	0.70	Aerosols	Miami/Barbados	Trapp et al. (2010)
0.08			0.58	Aerosols	Tenerife	Kandler et al. (2007)
0.08-0.10			0.53	Aerosols	Cape Verde	Kandler et al. (2007)
0.08-0.13			0.5-0.64	Soil	Chad/Niger	Moreno et al. (2006)
0.07			0.54	Aerosols	At sea	Stuut et al. (2005)
			0.63	Soil	N. Africa	Guieu et al. (2002)
0.06			0.88	Aerosols	Tenerife	Viana et al. (2002)
	0.002	0.011	0.51	Aerosols	Barbados	Arimoto et al. (1995)
	0.004	0.010	0.61	Aerosols	Bermuda	Arimoto et al. (1995)
	0.002	0.012	0.70	Aerosols	Tenerife	Arimoto et al. (1995)
0.08	0.001		0.71	Aerosols	Nigeria	Adepetu et al. (1988)
0.08±0.02	0.003±0.001	0.011±0.001	0.65±0.11			Mean ± st dev of above
0.04	0.0007	0.007	0.44	UCC	Global mean	Taylor & McLennan (1995)

Table 3. Comparison of elemental ratios (by mass) of examples of lithogenic (Al, Ti, Fe, Nd, Th), mixed-source (Sc, V, Mn, Co) and pollution-derived (Ni, Cu, Zn, As, Se, Cd, Sn, Sb, Pb) elements normalized to (a) Ti and (b) Al, in North African aerosols (this study; $n = 10$; median value shown), UCC (Taylor and McLennan, 1995) and Arizona Test Dust (ATD; Powder Technology).

(a) Element	North African	UCC	ATD	(b) North African	UCC	ATD
Al	12.8	26.8	21.6	1.00	1.00	1.00
Ti	1.00	1.00	1.00	0.0783	0.0373	0.0462
Fe	9.65	11.7	10.4	0.769	0.435	0.513
Nd	0.00863	0.00867	0.0111	0.000663	0.000323	0.000516
Th	0.00256	0.00357	0.00431	0.000207	0.000133	0.000199
Sc	0.00342	0.00367	0.0246	0.000266	0.000137	0.000114
V	0.0355	0.0200	0.0226	0.00275	0.000746	0.00105
Mn	0.165	0.200	0.238	0.0128	0.00746	0.0110
Co	0.00422	0.00333	0.00537	0.000340	0.000124	0.000248
Ni	0.0128	0.00667	0.0149	0.00100	0.000249	0.000687
Cu	0.00844	0.00833	0.0188	0.000672	0.000311	0.000870
Zn	0.0263	0.0237	0.0462	0.00203	0.000883	0.00214
As	0.00246	0.000500	0.00690	0.000194	1.87E-05	0.000319
Se	0.00205	0.0167	0.00386	0.000159	0.000622	1.69E-05
Cd	0.000212	3.27E-05	0.000366	1.7E-05	1.22E-06	1.69E-05
Sn	0.00122	0.00183	0.00355	9.62E-05	6.84E-05	0.000164
Sb	0.000374	6.67E-05	0.00145	2.97E-05	2.49E-06	6.69E-05
Pb	0.00729	0.00667	0.0114	0.000588	0.000249	0.000526

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