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Short communication

Stable isotope ratio measurements of Cu and Zn in mineral dust (bulk and size fractions) from the Taklimakan Desert and the Sahel and in aerosols from the eastern tropical North Atlantic Ocean

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ABSTRACT

Accurate characterization of the stable isotope composition of Cu and Zn in major global mineral dust sources and in aerosols is central to the application of these isotope systems to the studies of global geochemical processes and cycles. We test here for the first time Cu and Zn isotope ratios within a well-defined source-receptor setting on the continent–ocean interface and determine the isotope composition of (i) bulk surface soil dust samples from the Sahel region, (ii) individual size fractions of surface dust samples from the Taklimakan Desert, and (iii) aerosols collected in the equatorial eastern North Atlantic region. This is achieved reducing the blank contribution during the ion exchange step using small resin and acid volumes and using a second ion exchange passage to purify the Cu fraction. We find no significant correlation between size fractions and isotope ratios in the two samples analyzed from the Taklimakan Desert. Mass balance calculations suggest that isotope ratios of bulk samples are within the analytical precision of the $<4\ \mu m$ size fraction and can be used to characterize atmospheric long range transport of Cu and Zn in mineral dust from the Taklimakan Desert. The $<1\ \mu m$ size fractions of two aerosol samples collected over the equatorial eastern North Atlantic region have Cu and Zn isotope ratios that are different to Sahel surface soil dust suggesting important non-crustal sources, in line with calculated enrichment factors, and possibly of anthropogenic origin. Using previously reported $\delta^{66}Zn$ values for anthropogenic emission from Europe, preliminary calculations suggest that up to 55% of Zn arriving at the sampling points in the equatorial eastern North Atlantic region could be of anthropogenic origin.

1. Introduction

Stable isotope ratios are emerging as a powerful tool for studying the global biogeochemical cycles of trace elements including copper (Cu) and zinc (Zn) and the human impact on them [1–3]. Of particular interest is the application in the aquatic environment due to the importance of these elements as micronutrients for phytoplankton [4–7] and in the urban atmospheric environment due to their pulmonary toxicity [8,9].

Central to the development of these stable isotope systems is the accurate characterization of the isotopic signature of possible aerosol sources (e.g., mineral dust) and of the aerosols themselves using multicollector plasma source mass spectrometry (ICP-MC-MS). There are two major challenges to this. First, volume and mass of aerosols and mineral dust available for analysis are often small and element concentrations are low. Sample contamination therefore represents a significant problem and blank contributions as small as 0.2% can affect analytical accuracy [10]. Second, significant spectral and non-spectral interferences affect the isotope ratio analysis of Cu and Zn [11,12] and interfering elements need to be removed quantitatively from the Cu and Zn fractions analysed by a mass spectrometer [13,14].

Gioia et al., developed successfully an ion exchange procedure optimized for Zn isotope ratio analysis in aerosols [8].

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The procedure lowered the Zn blank for silicate based samples compared to previously published methods [10,15] by reducing resin and acid volume. However, the small amount of resin affected the baseline resolution and cleanliness of the Cu fraction and consequently, accurate and precise isotope ratio data for Cu have not been reported for aerosols, global mineral dust sources or particle size fractions of mineral dust.

To address this problem, we aimed to test the prospect of using a second ion exchange step to clean up the Cu fraction from interfering elements and of using this modified procedure to tackle two key questions in the low temperature isotope geochemistry of Cu and Zn, i.e. (i) whether significant Cu and Zn isotope ratio variability exists between size fractions of a bulk dust sample and (ii) whether isotope variability in aerosols collected over the open ocean trace sources and/or shed new insights into their biogeochemical cycles in the remote ocean atmosphere. We measured precise Cu and Zn isotope ratios in (i) particulate size fraction of surface dust collected from the Taklimakan Desert (i.e., size fractions of <4 μm, 4–16 μm, 16–32 μm, 32–63 μm, and >63 μm), (ii) bulk Sahel soil dust and (iii) in two aerosol samples (<1 μm diameter fractions) collected in the equatorial eastern North Atlantic region.

The Sahel and Taklimakan Desert were chosen as they are major sources of dust in the atmosphere and play a key role in the supply of nutrient trace elements to the world oceans [16,17].

2. Methodology

2.1. Reagents, reference materials, mineral dust and aerosol samples

Mineral acids used were either purified in house by sub-boiling distillation in quartz stills (HNO_3 and HCl) or bought commercially (HF, 40% Suprapur®, Merck, Germany). Dilute acid solutions were prepared using 18.2 MΩ grade water (Millipore system, USA). All solutions and samples were handled in Class 10 laminar flow hoods in a Class 1000 clean laboratory.

A mixed element solution containing Ba, Cr, Cu, Fe, Mg, Ti, V, and Zn was used during the assessment of the ion exchange procedure. These elements affect isotope ratio measurement of Cu and Zn by the formation of argides, oxides or double charged species during plasma source mass spectrometry [11–13]. The concentrations of the admixed elements were 2 μg/ml for Ba, Cr, Cu, Ti, V, and Zn and 20 μg/ml for Fe and Mg to simulate element abundance found in real dust samples [18]. Two single element solutions of Cu and Zn, denoted as IMP Cu and Romil Zn, were used for quality control of the isotope measurement. (For more details regarding the preparation of the standards, see [11,12].)

The analytical procedures were tested using an in-house granite, HRM-24, a certified zinc ore standard, BCR-027, a certified granite standard, G-2, and a composite surface soil sample (denoted thereafter as SHD-mix) representing mineral dust reaching the North Atlantic region from the Sahel region and prepared by homogenizing 20 bulk surface soil samples collected en route between Bamako and Timbuktu.

Two surface dust samples collected from the Taklimakan Desert were separated into five size fractions (<4 μm, 4–16 μm, 16–32 μm, 32–63 μm, and >63 μm; denoted as TK-074 and TK-103). The surface samples were collected by scratching off 1–2 cm thick dried clay mud crust from the hydrocephalus depressions near the Taklimakan Desert [19]. The two coarser size fractions were separated by wet-sieving, and the three finer fractions (<4, 4–16, and 16–32 μm) were separated using a settling method. The <1 μm diameter fractions of two aerosol samples were collected during the cruise M55 of the German SOLAS program in the equatorial eastern North Atlantic region (denoted as tm20w and tm25w) [20,21].

2.2. Digestion and leaching of solids and aerosol filters

Solids were digested using a mixture of concentrated HNO_3 and HF (1:4) in closed PFA vials (Savillex, MN, USA) on a hot plate at 140 °C for 48 h with 15 min of ultrasonic treatment every 24 h. Digested solutions were evaporated to dryness, re-dissolved and re-fluxed, first in 300 μl of concentrated HNO_3 and then in 300 μl of 7 M HCl. The solutions were dried down and re-dissolved in 2 ml of 7 M HCl for subsequent analysis.

Filters were acid washed before aerosol collection and processed after collection following a previously developed method [20]. In summary, the filters were first washed in 20 ml 0.5 M HNO_3 for 3 h in an ultrasonic bath and then rinsed three times in 10 ml 0.5 M HNO_3. The combined solutions were evaporated to dryness. Approximately 600 μg of material was washed off of each filter and then digested as described above. The dried solutions were re-dissolved in 2 ml 0.5 M HNO_3. Filters after rinsing showed similar element concentrations as unused filters (below 0.2 μg Cu and Zn/g of filter) and this was amounting to less than 2% blank contribution from the filter. Comparing the weights of unused filters and rinsed filters suggested that the removal of dust from the filters was quantitative.

2.3. Ion exchange chromatography for the separation of Cu and Zn

The Bio-Rad AG MP-1 resin (100–200 mesh, washed thoroughly with 0.5 M HNO_3 after purchase), Bio-Rad polypropylene columns (2 ml of resin support and 10 ml reservoir) and in-house made Teflon columns (0.2 ml of resin support and 3 ml reservoir) were used for the ion exchange chromatography. Recovery of Cu and Zn was determined based on their concentrations in the solutions before and after the column passage.

2.4. Concentration and isotope ratio measurements

Elemental concentrations were determined in the aerosols using inductively coupled plasma quadrupole mass spectrometry (ICP-Q-MS, Varian MS-810, USA) and during the analytical procedure development using inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista-Pro Axial, USA). Details of the elemental analysis procedures are given elsewhere [22]. The precision for elemental concentrations was below 8% and 12% for ICP-Q-MS and ICP-OES, respectively. The recovery of the trace elements during the digestion was tested using the certified values for G-2 and was quantitiative for all elements studied here [22].

Isotope ratios of Cu and Zn were determined using multi collector inductively coupled plasma mass spectrometry (ICP-MC-MS, Nu Instruments Limited, UK) equipped with a Nu DSN-100 Desolvation Nebulizer System and PFA nebulizer. The instrument settings are given in Table 1. Data collection used three blocks with 20 measurements each, a 5 s integration time and 15 s sample admission delay. The wash out time between samples was 180 s using two subsequent 0.1 M HNO_3 acid solutions. Isobaric interferences of ^{64}Ni were monitored using intensity measurements of ^{62}Ni and were negligible throughout the study. Instrumental mass bias effects were corrected using standard sample bracketing for Cu and a ^{64}Zn–^{67}Zn double spike for Zn [23,24]. Copper and Zn isotope ratios are reported as $\delta^{66}Zn_{Lyon}$ and $\delta^{65}Cu_{NIST976}$ using the δ-notation:

$$\delta^{66}Zn_{Lyon} = \left\{ \left[\frac{(^{66}Zn/^{64}Zn)_{sample}}{(^{66}Zn/^{64}Zn)_{Lyon}} \right] - 1 \right\} \times 1000$$

Table 1
Operation conditions of the Nu Plasma ICP-MC-MS during the study period.

Plasma settings	
Coolant Ar flow	13 L/min
Auxiliary Ar flow	1.0 L/min
Nebulizer Ar flow	30 L/min
Extraction voltage	6000 V
Torch power	1300 W
Reflected power	0 W
Cones	Ni sample and Ni skimmer cone
Nebulizer parameters	
Spray chamber temperature	~101 °C
Desolvator temperature	~116 °C
Ar sweep gas flow	2.8–3.8 L/min
Sensitivity	Cu: ~90 V/μg/ml and Zn: ~135 V/μg/ml
Sample uptake rate	115–135 μl/min

$$\delta^{65}\mathrm{Cu}_{\mathrm{NIST976}} = \left\{ \left[\frac{(^{65}\mathrm{Cu}/^{63}\mathrm{Cu})_{\mathrm{sample}}}{(^{65}\mathrm{Cu}/^{63}\mathrm{Cu})_{\mathrm{NIST976}}} \right] - 1 \right\} \times 1000$$

2.5. Back trajectories modeling of aerosol samples

Air masses reaching the aerosol sampling sites during the M55 cruise were characterized using 5-day kinematic back trajectories arriving at 10, 500, and 1000 m above mean sea level (MSL). The trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT). The meteorological data used for the computation of the trajectories is taken from archive data (http://ready.arl.noaa.gov/archives.php).

3. Result and discussion

3.1. Separation of the Zn and Cu fractions using ion exchange columns

The ion exchange procedure to separate the Zn and Cu fractions is shown in Table 2. The smallest resin volume enabling the baseline separation of the Cu and Zn peaks was 0.6 ml resulting in a bed height of ca. 1.2 cm. This volume was established experimentally testing different amounts of resin between 0.2 and 1 ml (data not shown). Fig. 1 shows the elution profiles for the synthetic multi-element solution and the in-house HRM-24 granite. Whilst the Cu and Zn fractions are quantitatively separated, we find that only the Zn fraction is free of the problematic elements. The Cu fraction contained significant concentrations of Ba, Cr, Ti, V, Mg, and Fe after the first passage through the column (< 5% of the total matrix elements) and these would affect subsequent isotope measurements [12,13].

The Cu fraction was subsequently passed through a second, smaller column with less acid and resin volumes. These columns were made in-house from heat-shrink Teflon tubes and have 0.2 ml of resin support (2.2 cm long) and 3 ml reservoir (2.7 ml long). We added 0.15 ml of AG MP-1 resin. The Cu fraction collected after the first passage was dried down, re-dissolved in 0.3 ml of 7 M HCl and loaded onto the second column. Then 3.5 ml of 7 M HCl was used to elute the Cu fraction. The Cu fractions following the second ion exchange passage were free from interfering matrix elements (see Fig. 1). The recoveries for the HRM-24 granite were quantitative for both elements (98 ± 5% for Zn, $n=3$ and 96 ± 4% for Cu, $n=3$).

The procedural blank for our two-step ion exchange procedure was 2.4 ng for Cu. This is significantly lower for silicate samples than those reported for the one-step ion exchange procedure by Maréchal et al. (10 ng, [15]) and Chapman et al. (35 ng, [10]) but slightly higher than that reported for the two-step ion exchange procedure using TRU spec resin by Archer and Vance (≤ 0.5 ng, [25]). The Zn blank after one-step column passage is 2.9 ng, similar to the blank achieved by Gioia et al. (2.8 ng, [8]) and Archer and Vance (1 ng, [25]) but significantly lower to the blank achieved by Maréchal et al. (50 ng, [15]) and Chapman et al. (28 ng, [10]). Our results suggest that the blank from the ion exchange procedure is related with the resin volume as it increases from below 2.9 ng for Zn using 0.6 ml of resin to above 10 ng using 1.6 ml of resin. This highlights the challenge posed by ‘cleaning’ resins.

Table 2
Details of the two stage ion exchange procedure used during this study to separate Zn and Cu from the matrix solutions.

Stage	Acid	Volume used (ml)
Stage 1—Separation of Cu and Zn fraction from matrix		
Conditioning	7 M HCl	4
Sample loading	7 M HCl	1
Matrix elution	7 M HCl	1.5
Cu elution	7 M HCl	10
Fe elution	2 M HCl	7
Zn elution	0.1 M HCl	7
Stage 2—Purifying of the Cu fraction		
Conditioning	7 M HCl	2
Sample loading	7 M HCl	0.3
Matrix elution	7 M HCl	0.3
Cu elution	7 M HCl	3.5

3.2. Accuracy and precision of the Cu and Zn isotope measurements

Accuracy and precision of the Cu and Zn isotope ratio measurements following our ion exchange procedure were assessed using two well-characterized synthetic element solutions from our laboratory (i.e., IMP Cu and Romil Zn, [11,26], pure and spiked with contaminant elements), certified (for concentrations) reference materials BCR-027 (blende ore) and G-2 (granite), and the in-house standard HRM-24 (granite). The total amount of Cu and Zn processed was comparable to that expected in aerosols and dust fractions, i.e. around 100 ng of Zn and Cu per sample. Possible isotope fractionation during the ion exchange separation procedure was tested comparing the isotopic compositions of the synthetic element solutions before and after the passage through the ion exchange columns.

Table 3 shows the $\delta^{65}\mathrm{Cu}_{\mathrm{NIST976}}$ and $\delta^{66}\mathrm{Zn}_{\mathrm{Lyon}}$ values determined for the various samples using the improved procedure of this study alongside previously published values [10,11,23,27]. We do not find significant isotope fractionation during the passage of the ion exchange column and the $\delta^{65}\mathrm{Cu}_{\mathrm{NIST976}}$ and $\delta^{66}\mathrm{Zn}_{\mathrm{Lyon}}$ values of IMP Cu, Romil Zn, G-2 and BCR-027 agree within error with published data using a variety of different analytical procedures. The in-house standard HRM-24 shows values for $\delta^{65}\mathrm{Cu}_{\mathrm{NIST976}}$ of +0.23 ± 0.05‰ (2SD and $n=3$) and for $\delta^{66}\mathrm{Zn}_{\mathrm{Lyon}}$ of +0.26 ± 0.05‰ (2SD and $n=3$). These ratios fall well within the range observed for granites and andesite [3,27]. Repeated measurement of IMP Cu and Romil Zn over the study period (36 months) showed an external precision of ± 0.05‰ pamu, which is similar to previous studies [3,23]. The subsequently analyzed aerosol and soil dust samples (see discussion below) showed a similar external precision of ± 0.05‰ pamu, which confirms that our method produces precise and accurate Cu and Zn isotope ratio determinations in mineral dust and aerosols samples.

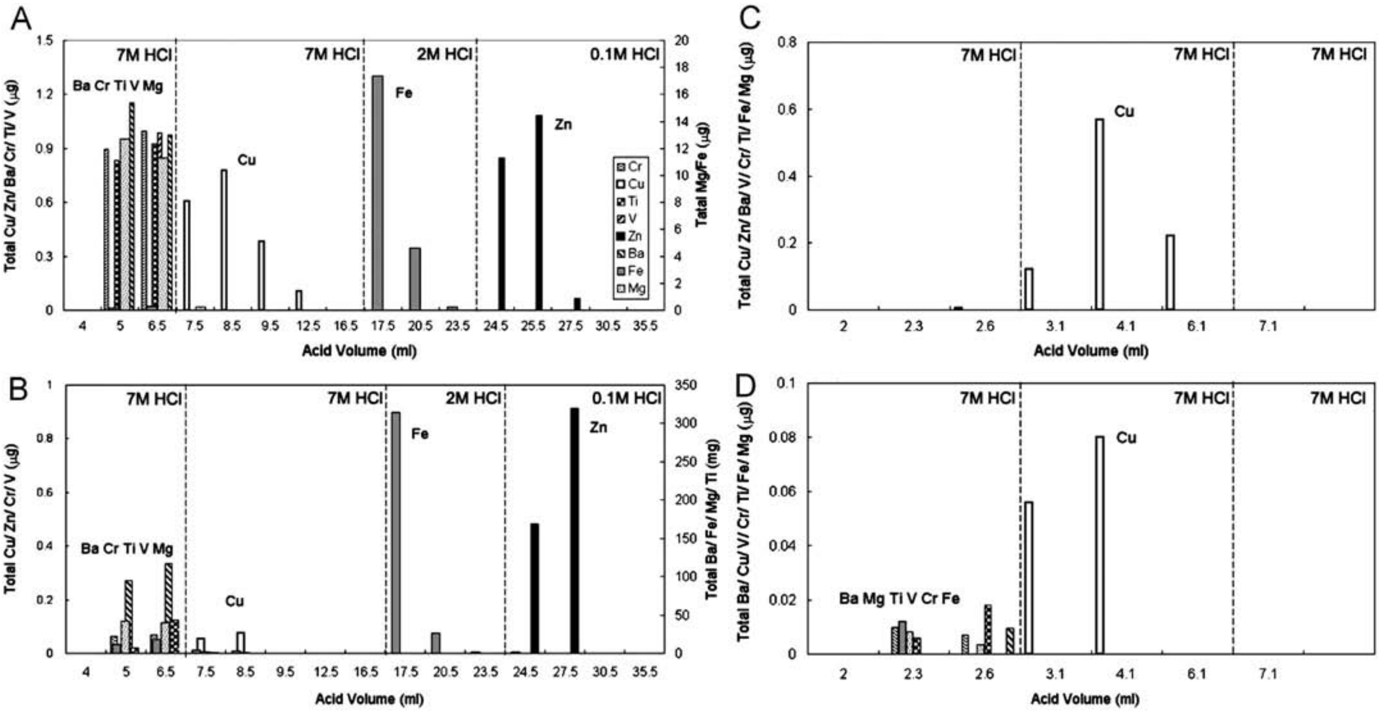

Fig. 1. Elution curves of Cu, Zn and contaminant elements (Ba, Cr, Fe, Mg, Ti, and V). Shown are the elution curves after the first (panels A and B) and after the second (panels C and D) ion exchange passage of the synthetic mixed-element solution (panels A and C) and of the HRM-24 granite (panels B and D). Panels A and B demonstrate that the Zn fraction is separated from all interfering elements after the first stage ion exchange, but the Cu fraction still contains contaminant elements. Plots C and D show the contaminant elements are separated from the Cu fraction, which results in accurate and precise isotope ratio measurement. The *y*-axis shows the element mass eluted from the ion exchange column in micrograms.

Table 3
$\delta^{65}Cu_{NIST976}$ and $\delta^{66}Zn_{Lyon}$ values determined for single and multi element synthetic solutions and for natural samples during the course of this study (see text for details). Shown are the concentration data and enrichment factor calculation for the composite Sahel soil dust sample (SHD-mix) and for the aerosols samples (tm20w and tm25w).

Sample ID	Comment	Ion exchange chromatography	Cu isotope ratio			Zn isotope ratio			Concentration		Enrichment factor	
			n	$\delta^{65}Cu_{NIST976}$ (‰)	± 2SD (‰)	*n*	$\delta^{66}Zn_{Lyon}$ (‰)	± 2SD (‰)	[Cu] (µg/g)	[Zn] (µg/g)	EF_{Cu}	EF_{Zn}
IMP Cu/Romil Zn		No	16	+0.20	0.05	27	−9.18	0.12	–	–	–	–
		Yes	15	+0.17	0.05	35	−9.21	0.10	–	–	–	–
	Mason et al. (2004)	No	22	+0.20	0.10	–	–	–	–	–	–	–
	Mason et al. (2004)	No	–	–	–	6	−9.18	0.08	–	–	–	–
	+ Ba, Cr, Fe, Mg, Ti, and V	Yes	16	+0.20	0.05	4	−9.14	0.09	–	–	–	–
BCR–027	This study	Yes	6	+0.38	0.09	9	+0.31	0.07	–	–	–	–
	Arnold et al. (2010)	Yes	–	–	–	4	+0.25	0.06	–	–	–	–
	Chapman et al. (2006)	Yes	10	+0.52	0.15	8	+0.33	0.07	–	–	–	–
G-2	This study	Yes	3	+0.27	0.09	6	+0.43	0.05				
	Moeller et al. (2011)	Yes	–	–	–	3	+0.44	0.09				
HRM-24		Yes	3	+0.23	0.05	3	+0.26	0.05	–	–	–	–
tm20w		Yes	3	−0.02	0.10	3	+0.03	0.04	165	234	11.8	6.5
tm25w		Yes	3	−0.14	0.09	3	+0.17	0.10	326	1333	9.0	6.9
SHD-mix		Yes	6	−0.24	0.11	6	+0.43	0.10	9.0	21.6	1.8	1.2

3.3. *Isotopic variability of particle size fraction of a potential dust source*

We applied our method to test isotopic variability between different size fractions of mineral dust. The variability of the isotopic (and thus geochemical) signature within the size fraction is crucial to know because usually the < 4 µm fraction is transported over long distances in the atmosphere and the isotopic signature of the bulk sample may not be representative of transported dust [17,28].

We determined Cu and Zn isotopic abundances and elemental concentrations in size fractions separated from two surface samples from the Taklimakan Desert (TK-074 and TK-103) (Table 4, Fig. 2). Copper and Zn concentrations were determined using ICP-Q-MS for the < 4 µm, 16–32 µm, and > 63 µm size fractions only due to limited sample availability. The lowest Cu concentrations are found in the middle size fractions (16–32 µm). The Zn concentrations decrease with increasing size fraction, i.e., from 321 and 389 µg Zn/g in the < 4 µm fraction to 41.5 and 84.1 µg Zn/g in the > 63 µm fraction, respectively. The Cu and Zn isotope ratios were determined in all of the five size fractions. There is no visible trend defined between δ^{65}Cu values and size fractions. In contrast, the δ^{66}Zn values show a distinct pattern, with isotope ratio values decreasing from the < 4 µm to the 16–32 µm size fraction and increasing again in the > 63 µm size fraction. The middle size fraction (16–32 µm) is the isotopic lightest (+0.08 ± 0.08‰ for TK-074 and +0.13 ± 0.05‰ for TK-103). The largest fraction (> 63 µm) is the isotopic heaviest (+0.38 ± 0.06‰ for TK-074

Table 4
Concentration and δ-values for Cu and Zn of individual size fractions separated from two Taklimakan desert dust samples. The size distribution is shown in percentage and *n* represents the number of repeats during the analysis of Cu and Zn isotope ratios.

Sample ID	Size fraction	Concentration (μg/g)		Cu isotope ratio (‰)		Zn isotope ratio (‰)		n	Size distribution (%)
		[Cu]	[Zn]	$\delta^{65}Cu_{NIST976}$	2SD	$\delta^{66}Zn_{Lyon}$	2SD		
TK-074	< 4μm	67.7	389	+0.03	0.12	+0.23	0.05	4	39.5
	4–16μm	–	–	−0.02	0.08	+0.14	0.08	4	40.9
	16–32μm	26.9	184	+0.20	0.09	+0.08	0.08	4	11.0
	32–63μm	–	–	−0.12	0.11	+0.17	0.09	4	4.1
	> 63μm	85.6	41.5	+0.37	0.10	+0.38	0.06	4	4.5
TK-103	< 4μm	77.5	321	+0.20	0.16	+0.28	0.08	4	18.8
	4–16μm	–	–	+0.31	0.10	+0.14	0.04	4	32.5
	16–32μm	20.7	147	+0.06	0.12	+0.13	0.05	4	24.6
	32–63μm	–	–	−0.06	0.09	+0.35	0.07	4	14.9
	> 63μm	26.6	84.1	−0.07	0.09	+0.48	0.06	4	9.3

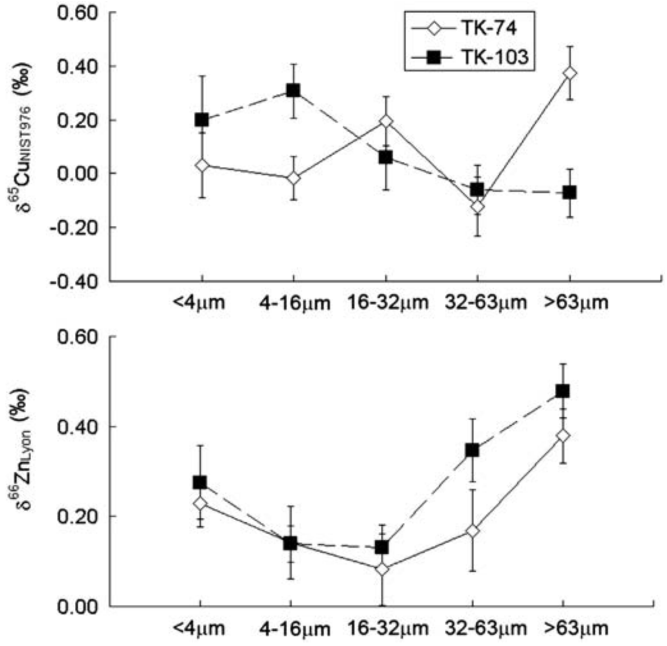

Fig. 2. Isotope ratios of Cu and Zn in different particle size fractions (< 4 μm, 4–16 μm, 16–32 μm, 32–63 μm, and > 63 μm) of two surface samples collected from the Taklimakan Desert (TK-074 and TK-103). Error bars given in ± 2SD.

and +0.48 ± 0.06‰ for TK-103). The size fractions 4–16 μm and 16–32 μm between the two samples are indistinguishable at 95% level (between +0.08 ± 0.08‰ and +0.14 ± 0.08‰).

Given the small yet significant isotopic variability of different particle size fractions, we tested whether the isotopic difference found between the < 4 μm fraction and the other size fractions affects the validity of using bulk samples to estimate source signatures. This is of importance as particle size separation cannot be easily done and often geochemical (isotopic and elemental) characterization of atmospheric mineral dust sources is done using bulk samples [28]. Consequently, we conducted a mass balance calculation using the experimentally determined isotope ratios and concentrations of the particle size fractions. To account for the missing concentration data for the particle size fractions 4–16 μm and 32–63 μm (Table 4), we conducted the mass balance calculations attaching maximum and minimum values for the three measured Cu and Zn concentrations (see Supporting Material for calculations). The results suggest that the isotope ratio of the bulk sample reflects well the < 4 μm fraction within the analytical precision, thus analysis of bulk samples is likely representative of the Cu and Zn isotope ratios of the dust fraction transported over long distance from the Asian continent.

3.4. Isotopic ratios of Sahel soil dust and aerosols collected in the equatorial eastern North Atlantic Ocean

To test the potential of precise and accurate isotope ratio determinations to improve our understanding of the atmospheric cycling of Cu and Zn between continent and ocean, we measured the Cu and Zn isotopes in Sahel surface soil dust, the potential natural sources to the equatorial eastern North Atlantic Ocean, and in two aerosol samples collected off shore the African continent in 2002.

Air mass back trajectories for both samples from the tropical Atlantic (Fig. 3) are consistent with dust being transported over source regions in Mauritania/Mali and possibly Algeria. We calculated enrichment factors for Cu and Zn ($EF_{Cu,Zn}$) to evaluate non-crustal sources using aluminum (Al) as reference element and upper continental crust as reference reservoir [29]. The enrichment factors (Table 3) calculated for the two aerosol samples are significantly higher than the Sahel dust samples (EF_{Cu} value of 11.8 and 9.0, and an EF_{Zn} value of 6.5 and 6.9, respectively). This suggests a significant contribution from non-crustal sources, most likely from anthropogenic emissions from Europe [30] and possibly also from sea spray since the samples were collected less than 15 m above the sea surface. Enrichment factors below two calculated for the bulk Sahel soil dust sample (Table 3) are in line with the enrichment factors determined for eolian dust collected in Emetteur Kati, Mali (near Bamako, Mali) [31,32] and in South Algeria [33].

The Sahel soil dust sample has isotope values for $\delta^{65}Cu_{NIST976}$ of −0.24 ± 0.11‰ (2SD and $n=6$) and for $\delta^{66}Zn_{Lyon}$ of +0.43 ± 0.10‰ (2SD and $n=6$). Aerosol sample tm20w has a similar Cu isotope ratio (−0.14 ± 0.09‰, 2SD, and $n=3$) but a lighter Zn isotope ratio (+0.03 ± 0.04‰, 2SD, and $n=3$) and aerosol sample tm25w has a heavier Cu isotope (−0.02 ± 0.10‰, 2SD, and $n=3$) and a lighter Zn isotope (+0.17 ± 0.10‰, 2SD, and $n=3$) signature than Sahel soil dust (Table 3). The difference in average isotope signatures between Sahel soil dust and the two aerosols is larger for Zn ($\Delta Zn_{dust-aerosol}=+0.33 \pm 0.07$‰) than for Cu ($\Delta Cu_{dust-aerosol}=-0.16 \pm 0.06$‰) and the observed difference suggests significant contributions from other sources than the Sahel soil dust only. This is in line with observed enrichment factors. Previous work on Zn isotopes in the atmospheric environment suggests that anthropogenic emissions can account for isotopic light Zn in the atmosphere [8,9,34,35]. Assigning a $\delta^{66}Zn_{Lyon}$ value for industrial Zn emission from Europe of ca. −0.3‰ (estimated roughly using observed isotope signatures in urban aerosols and in rainwater in France [9,35])

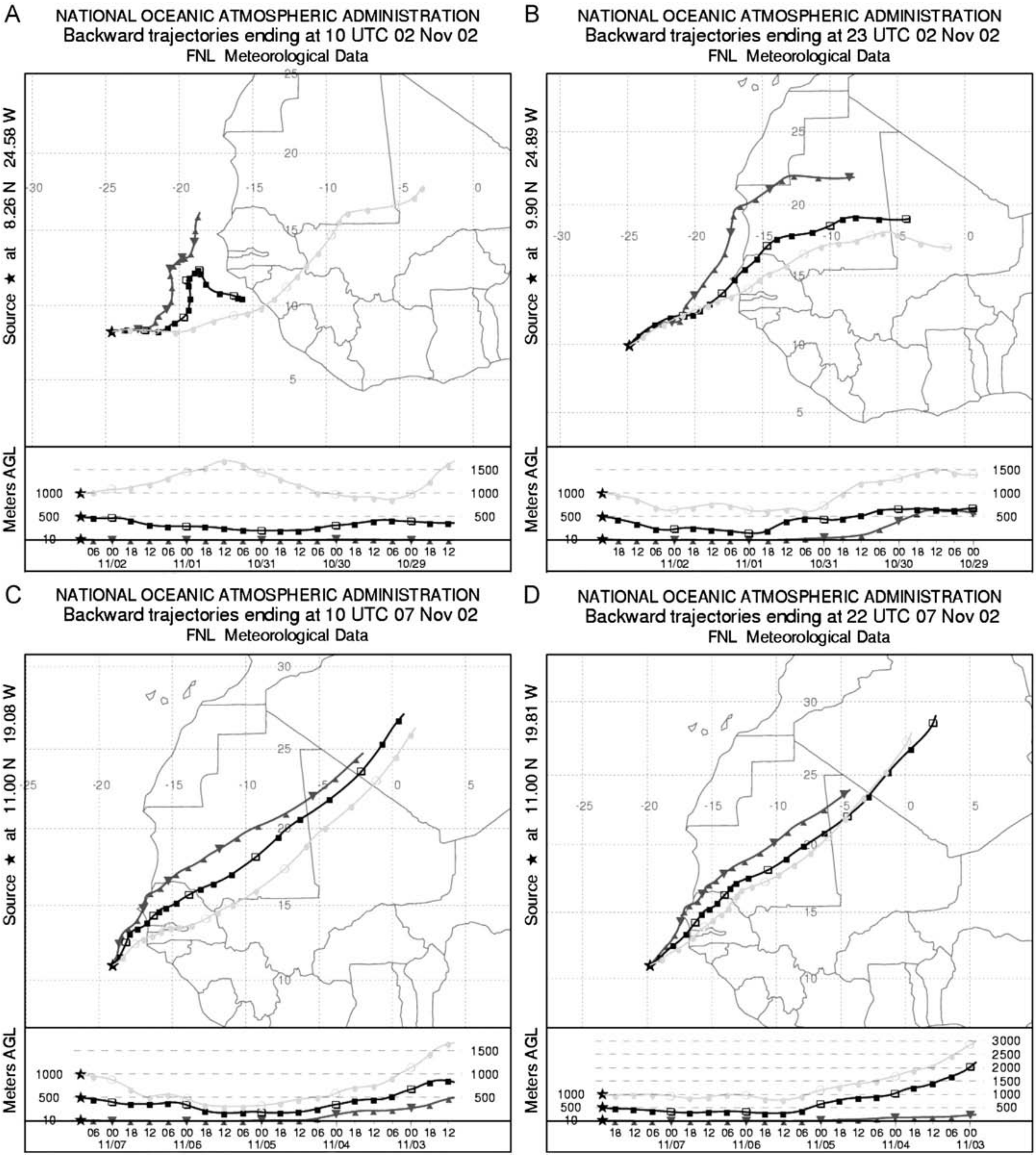

Fig. 3. Back trajectories for the air masses arriving at the sampling stations during cruise M55 of the SOLAS program. The models cover the trajectories at three different heights (10, 500, and 1000 m) during the last five days before the sampling. (A) and (B) show the starting (8.26°N 24.58°W) and ending (9.90°N 24.89°W) longitude and latitude of sample tm20w and (C) and (D) show the starting (11.00°N 19.08°W) and ending (11.00°N 19.81°W) longitude and latitude of sample tm25w.

for preliminary calculations suggests that up to 55% of Zn arriving at the sampling points in the equatorial eastern North Atlantic region could be of anthropogenic origin. However, a more thorough characterization of the anthropogenic Zn sources coming from North Africa is warranted.

4. Conclusions

We tested an ion exchange procedure adapted to the task of separating matrix free Cu and Zn fractions in low volume and low concentration mineral dust and aerosol samples. We determined for the first time the isotopic composition of Cu and Zn in (i) five size fractions separated from two bulk surface dust samples collected from the Taklimakan Desert, (ii) bulk Sahel soil dust, and (iii) aerosol samples collected in equatorial eastern North Atlantic region. We find distinct isotope variability between the different size fractions for $\delta^{65}Cu_{NIST976}$ and $\delta^{66}Zn_{Lyon}$ values. Tentative mass balance calculation suggests that the isotope ratio of the bulk dust sample is within the analytical precision of that measured in the $<4\ \mu m$ fraction and isotopic signature of bulk dust samples is likely be representative for the dust signature transported for long distance in the atmosphere.

A composite sample consisting of 20 surface soil dust samples collected from the Sahel region in Mali has a $\delta^{65}Cu_{NIST976}$ of $-0.24 \pm 0.11‰$ and a $\delta^{66}Zn_{Lyon}$ of $+0.43 \pm 0.10‰$. Two aerosol samples collected in the equatorial eastern North Atlantic region off West Africa ($\delta^{65}Cu_{NIST976} = -0.02 \pm 0.10‰$ and $\delta^{66}Zn_{Lyon} = +0.03 \pm 0.04‰$; $\delta^{65}Cu_{NIST976} = -0.14 \pm 0.09‰$ and $\delta^{66}Zn_{Lyon} = +0.17 \pm 0.10‰$) have different isotopic signatures than the Sahel soil dust. Calculated enrichment factors and back trajectory analyses suggest that other sources, likely of anthropogenic origin contribute to the aerosol samples. Our study demonstrated the potential of Zn and Cu isotopes to provide important insights into the biogeochemical cycles of these key trace elements at the continent–ocean interface.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at xlink:href="http://dx.doi.org/10.1016/j.talanta.2013.03.062">10.1016/j.talanta.2013.03.062.

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