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Sr–Nd–Hf isotopic fingerprinting of transatlantic dust derived from North Africa

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ABSTRACT

Long-range transport of African dust plays an important role in understanding dust-climate relationships including dust source areas, dust pathways and associated atmospheric and/or oceanic processes. Clay-sized Sr–Nd–Hf isotopic compositions can be used as geochemical fingerprints to constrain dust provenance and the pathways of long-range transported mineral dust. We investigated the clay-sized Sr–Nd–Hf isotopic composition of surface samples along four transects bordering the Sahara Desert. The transects are from Mali, Niger/Benin/Togo, Egypt and Morocco. Our results show that the Mali transect on the West African Craton (WAC) produces lower ε_{Nd} ($\varepsilon_{Nd\text{-}mean} = -16.38$) and ε_{Hf} ($\varepsilon_{Hf\text{-}mean} = -9.59$) values than the other three transects. The Egyptian transect exhibits the lowest $^{87}Sr/^{86}Sr$ ratios ($^{87}Sr/^{86}Sr_{mean} = 0.709842$), the highest ε_{Hf} ($\varepsilon_{Hf\text{-}mean} = -0.34$) and ε_{Nd} values of the four transects. Comparison of the clay-sized Sr–Nd–Hf isotopic values from our North African samples to transatlantic African dust collected in Barbados demonstrates that the dust's provenance is primarily the western Sahel and Sahara as well as the central Sahel. Summer emission dust is derived mainly from the western Sahel and Sahara regions. The source of transatlantic dust in spring and autumn is more varied than in the summer and includes dust not only from western areas, but also south central areas. Comparison of the Sr–Nd–Hf isotopic fingerprints between the source and sink of transatlantic dust also suggests that a northwestward shift in dust source occurs from the winter, through the spring and into the summer. The isotopic data we develop here provide another tool for discriminating changes in dust archives resulting from paleoenvironmental evolution of source regions.

1. Introduction

Dust particles play an important role in many atmospheric and oceanic processes such as scattering and absorbing radiation and modifying cloud properties including condensation and ice nuclei (DeMott et al., 2010; Zimmermann et al., 2008). These processes influence both the Earth's climate and the course of many biogeochemical systems (Dale et al., 2015; Doherty et al., 2012; Gross et al., 2015; Knippertz and Todd, 2012). North Africa is the world's largest source of mineral dust, producing an estimated 0.8TG per year and accounting for ~70% of the global dust budget (Huneeus et al., 2011; Laurent et al., 2008). Mineral dust emission from North Africa is primarily from the hyper-arid Sahara and the semi-arid Sahel by the action of persistent easterly and northeasterly winds resulting in great quantities of African dust being transported across the Atlantic. When deposited in the ocean this dust is thought to be a primary source of iron, an important limiting nutrient that can become biologically available to phytoplankton (Gross et al., 2015; Jickells et al., 2005; Mahowald et al., 2013; Martin, 1990). African dust also is transported to the southern United States, Caribbean, and South America where it may increase productivity by providing important soil nutrients (Chien et al., 2016; Perry et al., 1997; Prospero et al., 1981).

Dust transport from around the Sahara is the result of strong aridification in source regions (Caquineau et al., 2002; Prospero and Lamb, 2003). During the winter, periods of drought in the Sahel initiate the main dust corridor over the North Atlantic (Prospero and Lamb, 2003). Volumetrically, spring is the time when the greatest quantity of dust is transported (Gama et al., 2015) with March as the leading month. During the summer the

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intertropical convergence zone (ITCZ) shifts to the north, as does the locus of dust transport, and mineral dust can be lofted to higher altitudes by dry convection and transported from the Sahel and central Sahara (Engelstaedter and Washington, 2007) across the Atlantic towards North America. Comparitively little dust is transported during the fall (Gama et al., 2015). These cyclic shifts in dust transport are due not only to seasonal shifts in the ITCZ, but also to climatically-controlled changes, including increased wind speeds, increased aridity, expansion of dust source areas, reduced vegetation coverage, etc. (Prospero and Lamb, 2003).

As noted above, transatlantic dust plays an important role in both terrestrial and oceanic biogeochemical cycles and climate. To constrain the far-reaching impacts of transatlantic dust, it is essential to identify the source of the dust and employ this information to understand feedback mechanisms between wind systems and dust source changes as influenced by climate. Hence, a reliable indicator for dust provenance would assist in studying the trans-continental transport of mineral dust (Aarons et al., 2013; Pourmand et al., 2014; Rickli et al., 2010). One promising method to better decipher dust provenance and transport is to compare isotopic fingerprints from source sediments to aerosol samples from dust outbreaks captured on atmospheric filters (Pourmand et al., 2014; Rickli et al., 2010; Újvári et al., 2015; Zhao et al., 2014, 2015). Several studies have established the usefulness of Sr, Nd, Hf and Pb isotopic ratios as conservative fingerprints for discriminating dust source areas when comparing isotope data from different aerosol samples (Aarons et al., 2013; Abouchami et al., 2013; Grousset and Biscaye, 2005; Pourmand et al., 2014; Rickli et al., 2010). However, isotopic fingerprints of potential North African dust sources are few and, as a result, knowledge of the potential source areas to unravel the provenance and origin of transatlantic aerosols is currently limited (Aarons et al., 2013; Pourmand et al., 2014; Rickli et al., 2010; Scheuvens et al., 2013). Further, because differences in isotopic composition might also result from differences in the particle size distribution of mineral phases in source sediments and aerosols, it is necessary to compare similar size fractions. In this paper we concentrate on Sr–Nd–Hf isotopic compositions from the clay-sized fraction, a common size fraction in aerosol samples (Glaccum and Prospero, 1980; Perry et al., 1997; Schütz and Sebert, 1987) that has shown promise for isotopic fingerprinting of dust (Aarons et al., 2013; Pourmand et al., 2014; Rickli et al., 2010). Clay-sized fractions (<2 μm) may be lofted to a height of several kilometers and transported over long distances (Glaccum and Prospero, 1980; Murray et al., 2012; Schütz and Sebert, 1987). The fine particles derived from source rocks of different geologic ages tend to maintain their Sr, Nd and Hf radiogenic isotopic composition. That is, the isotopic fingerprints from dust provenance to dust archived in ice and sediment cores are preserved (Aarons et al., 2013; Blakowski et al., 2016; Lupker et al., 2010; Pourmand et al., 2014; Rickli et al., 2010; Újvári et al., 2015; Zhao et al., 2014, 2015).

One potential problem for the Nd–Hf isotopic fingerprint is the zircon effect with Hf – zircon has a very low Lu/Hf ratio, resulting in very unradiogenic $^{176}Hf/^{177}Hf$ (Patchett et al., 1984). However, the clay fractions are too fine (<2 μm) to contain any significant amount of zircon (Zhao et al., 2014) and the high-density mineral zircon is preferentially depleted with transport distance from the dust source (Aarons et al., 2013). Therefore, the clay-sized $^{87}Sr/^{86}Sr$, ε_{Nd} and ε_{Hf} values may be used to ascertain potential dust source areas from North Africa and to fingerprint the provenance of transatlantic dust. The goal of this paper is to develop a more comprehensive source to sink tracer for transatlantic dust by examining the Sr–Nd–Hf isotopic data from potential Saharan source regions. To accomplish this goal we examined four transects from around the Sahara – from Egypt, Morocco, Mali and Niger/Benin/Togo and will address the following questions. First,

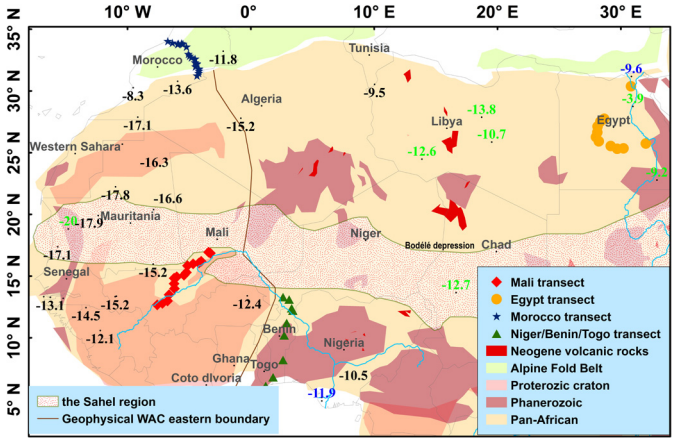

Fig. 1. Map of geology and sample location for each of the four North African transects. Schematic geological map modified from Guiraud et al. (2005) and Youbi et al. (2013). Black and green ε_{Nd} are from Grousset et al. (1998), Grousset and Biscaye (2005), and blue ε_{Nd} are from Bayon et al. (2015). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

what are the characteristics of clay-sized Sr–Nd–Hf isotopic compositions from the four North African transects we investigate? Second, can clay-sized Sr–Nd–Hf isotopic fingerprints effectively identify transatlantic dust sources? We will compare our African source data to published Sr–Nd–Hf aerosol data from Barbados (Pourmand et al., 2014), an island where individual massive dust outbreaks have been traced from the surface of Africa (Bou Karam et al., 2014).

2. Materials and methods

Fifty eight surface sediment samples collected from North Africa were used to monitor Sr–Nd–Hf isotopes for potential dust provenance areas (Fig. 1, Table S1, Supplementary material). These surface materials are from four transects – two Sahara to Sahel transects, mainly in Mali and Niger/Benin/Togo, and two North African transects, one from Morocco and one in Egypt. Details of the sampling and a more thorough description of the four transects may be found in Balsam et al. (2011) and Lyons et al. (2010). The Mali and Niger/Benin/Togo transects are distributed mainly in the Sahel region and most of the samples are from the semi-arid desert and tree Savannah. In addition, our data interpretation includes published Sr–Nd–Hf values from around Africa (Grousset et al., 1998; Grousset and Biscaye, 2005) and published analyses of aerosol samples from Barbados (Pourmand et al., 2014) during various seasons from 2003 to 2011 (Barbados, 13.165°N, 63.183°W). Barbados is an ideal location to study long-travelled transatlantic dust because the island is the easternmost point of the Americas in the Caribbean and is situated approximately 4800 km west of the western-most point of Africa.

Our sample analyses included several steps. First, the organic matter and carbonates from all samples were individually removed using excess hydrogen peroxide (30%) and 1 M acetic acid for 8 h (Yang et al., 2000). Second, the clay-sized (<2 μm) particles were separated using Stokes' Law and recovered by centrifuging (Ji et al., 1999). Third, 100 mg of the clay-sized material was dissolved in a HF–HNO_3 acid mixture at 120 °C for more than 72 h on a hot plate. Six parallel clay-sized samples were dissolved in highly pressurized, steel-jacketed Parr bombs for 72 h using a two-phase acid attack to guarantee the complete dissolution of whole-rock samples containing refractory zircon. Once dissolved, established ion exchange procedures (Yang et al., 2010) were employed. (For details of the method refer to Supplementary material.) In addi-