URANIUM AND THORIUM CONCENTRATIONS IN WIND-BORNE SAHARAN DUST OVER THE WESTERN EQUATORIAL NORTH ATLANTIC OCEAN

Harold S. RYDELL and Joseph M. PROSPERO
University of Miami,
Rosenstiel School of Marine and Atmospheric Science,
10 Rickenbacker Causeway,
Miami, Florida 33149, USA

Received 13 December 1971
Revised version received 3 February 1972

The average uranium and thorium concentration in 15 samples of wind-borne Saharan dust collected at Barbados, West Indies, is 3.6 and 12.4 ppm, respectively; these values are approximately one-third greater than that of average crustal material. The thorium–uranium weight ratio of the dust is 3.5, about the same as that of the crust; the $^{234}$U/$^{238}$U activity ratio is 1.08 and the $^{230}$Th/$^{234}$U activity ratio, 0.97. We conclude that the presence of large amounts of African dust in Atlantic sediments would not significantly affect the validity of the assumptions inherent in the $^{234}$Pu/$^{238}$Th and $^{230}$Th/$^{238}$Th dating methods.

1. Introduction

Marine sediment is a composite of many genetically different constituents. Once these diverse materials have become incorporated in marine sediment, it is very difficult or impossible to identify the component fractions, with the exception of biological material, and to separate them for analysis.

Traditionally it has been assumed that essentially all of the detrital fractions of pelagic sediments were originally transported to the oceans by rivers and thence by ocean currents. However, there is an increasingly large body of evidence which suggests that a significant fraction of the detrital component of sediments in some oceanic regions consists of wind-transported material. For the most part, this evidence is inferred from the configuration of the concentration gradients of certain mineral species in the sediments when viewed with respect to the disposition of land masses and the major wind systems [1–3]. Qualitative support for the eolian hypothesis was obtained from a number of studies of the concentration of air-borne mineral dust collected from aboard ships on the Atlantic, Pacific, and Indian Oceans [4–8]. However, because these studies were of a short duration and were all performed at sea level, and because of a lack of knowledge of removal rates from the atmosphere, it is not possible to make a quantitative estimate of the mass of material transported from the continents to the seas by winds.

Recently, Prospero and Carlson [9] established that the quantity of dust transported annually from North Africa to the Caribbean area by the trade winds between 10°N and 25°N was in excess of 50 megatons; this calculation was based on five years of essentially continuous sea level aerosol studies at Barbados, West Indies, [9–12] and on extensive aircraft measurements made during the Barbados Oceanographic and Meteorological Experiment [13]. To visualize this mass in terms of sedimentation rates, assume that an equal quantity of material was deposited en route; then the effective sedimentation rate in the 15° latitude band between Africa and Barbados would be approximately 0.5 g of dry sediment per thousand years, a rate commensurate with the measured carbonate-free sedimentation rates in this region [14].

Thus, analyses of wind-borne dust can provide the foundation for some unique geochemical measurements of the interaction of the atmosphere and hydrosphere and should establish elemental and isotopic parameters
for this material prior to permanent inclusion and alteration in the water-sediment column. In this paper we report on the analyses of dust for uranium (238U) and thorium (232Th) and two of their daughter products, 234U and 230Th. These nuclides are important because two of the commonly used methods for the absolute dating of oceanic sediments are based on the relative concentrations of these nuclides. In the 230Th/231Pa and 230Th/232Th dating methods [15, 16], a uranium correction is made to distinguish between the unsupported authigenic 230Th and 231Pa (the datable part) and the allogenic (old terrestrial part). The allogenic 230Th and 231Pa is presumed to be contained in detrital particles and to be in radioactive equilibrium with the parent uranium nuclides, 238U and 235U, respectively.

If wind-borne dust does constitute a major portion of marine sediment in some areas and if considerable radioactive disequilibrium exists in the dust, then the dates obtained by these methods would be rendered inaccurate.

2. Procedures

The airborne dust collections were made at the University of Miami Marine Aerosol Studies Station, Barbados, West Indies (13.6N, 59.0W), where essentially continuous aerosol sampling has been carried out since August 1965 [10–13]. It has been shown conclusively that this material is derived from the arid regions of West Africa, over 4500 km to the east [13]. Aerosols were collected using a mesh technique; a detailed description of the aerosol facility and the procedures employed there is presented by Delany et al. [10].

In addition to the Barbados dusts, we analyzed several samples of air-borne dust collected at a coastal site in the Miami area during westerly (offshore) winds.

Isotopic uranium and thorium analyses were done by alpha particle spectrometry using a solid state detector and a multichannel analyzer. After total dissolution of the samples, uranium and thorium were concentrated and separated by a procedure employing co-precipitation, solvent extraction, ion exchange, and electrodeposition. 232U and 234Th tracers were used to correct for analytical losses. These are procedures similar to those used by other workers [17–19].

3. Results and discussion

Before discussing our results we will describe briefly the mineralogical and chemical composition of the dust. X-ray diffraction and optical studies of Barbados dusts show the dominant mineral to be quartz which comprises about one-third of the sample on a bulk weight basis; many of the quartz grains are coated with desert varnish (ferruginous oxides) thereby giving the dust a characteristic deep red-brown coloration [12]. Layered silicates (kaolinite, chlorite, muscovite) also are present in abundance. All samples contain sufficient quantities of amorphous material [12] to produce a pronounced diffuse X-ray scatter background. Thirty representative dust samples analyzed for 26 elements (Prospero, unpublished data) were found to have a composition essentially identical to that of average crustal material [2].

Miami dust collected during westerly (offshore) win is largely calcite with lesser amounts of aragonite and minor amounts of feldspar and quartz [21]. In addition the Miami dusts contain large quantities of organic matter and unidentified amorphous material.

Our uranium and thorium results are presented in table 1. For Barbados dust, the average U and Th content is 3.6 and 12.4 ppm, respectively, and the Th/U ratio is 3.5. Miami westerly dust has 5.5 ppm U and 1.65 ppm Th, yielding a Th/U ratio of 0.3. Krauskopf [20] gives the average U and Th contents (in ppm) for the earth's crust as 2.7 and 9.6, and for shale as 3.2 and 11, respectively; therefore, the ratio of Th/U for crust would be 3.6 and for shale 3.4. Thus, the Barbados samples show a small enrichment, approximately 30% of U and Th compared to average crust, but the Th/U ratio is about the same.

We considered the possibility that a bias could be introduced in our results because of the low capture efficiency of our collectors for particles below several microns diameter; consequently, our dust samples are not truly representative of the actual airborne material since it is known that some compositional characteristics, such as the mineralogy [12], are size dependent. In order to ascertain whether a significant size dependence existed for uranium and thorium, we removed a

* During the summer easterlies, the composition of Miami dust is identical to that of Barbados dust, indicating again the influence of the African dust transport phenomenon [21].
<table>
<thead>
<tr>
<th>Location</th>
<th>Date</th>
<th>Year</th>
<th>U (ppm)</th>
<th>Error  ±</th>
<th>Th (ppm)</th>
<th>Error  ±</th>
<th>U-238</th>
<th>Error  ±</th>
<th>Th-230††</th>
<th>Error  ±</th>
<th>Th**</th>
<th>Error  ±</th>
</tr>
</thead>
<tbody>
<tr>
<td>B (bulk sample)</td>
<td>24-26/6</td>
<td>67</td>
<td>2.95</td>
<td>0.17</td>
<td>11.44</td>
<td>1.23</td>
<td>1.06</td>
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<td>0.11</td>
<td>3.87</td>
<td>0.47</td>
</tr>
<tr>
<td>B (&lt; 2 μm)</td>
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<td>67</td>
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<td>0.16</td>
<td>14.14</td>
<td>0.84</td>
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<td>1.19</td>
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<td>8.5</td>
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<td>0.73</td>
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<td>3.4</td>
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<td></td>
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<tr>
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<td>7-12/8</td>
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<td>3.96</td>
<td>0.11</td>
<td>13.26</td>
<td>0.45</td>
<td>1.00</td>
<td>0.04</td>
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<td>0.15</td>
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<tr>
<td>* D (aqueous)†</td>
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<td>68</td>
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<td>&lt;0.01</td>
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<tr>
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<td>0.68</td>
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<td>1.01</td>
<td>0.05</td>
<td>0.37</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Mean B: 3.58  U-238: 12.41  Th: 0.97  Mean M: 5.49  U-238: 1.65  Th: 0.85

Error 1σ radiometric count. B - Barbados dust, M - Miami dust.
* Analyses by Willard S. Moore.
** Weight ratio.
† Based on total dissolved and suspended solids (6.81g).
†† Activity ratio.
aliquot of sample B-6/24-26/67 and, using an aqueous sedimentation technique, separated the less than 2μm diameter size fraction which we then analyzed.* The data in Table 1 show that the composition of the small size fraction is not significantly different from that of the bulk sample or of the other B samples analyzed.

We also established that no error was introduced in neglecting to analyze the supernatant liquid from the mesh wash water which normally is discarded after the dust is recovered. This phase contains dissolved salts, mostly sea salt, and the extremely fine particulates still in suspension after the one-day settling period. We analyzed the supernatant liquid from sample D (aqueous) 8/12/68 which was collected aboard OSS DISCOVERER, on station 100 km east of Barbados, concurrently with Barbados sample B 8/7-12/68. The mineralogical composition of these two dust samples is identical. The salt content of the D sample was equivalent to that of about 200 ml of sea water, while the uranium content (0.36μg) was approximately equal to that of 100 ml of sea water. The average uranium concentration of sea water is 3.3μg l⁻¹ [22, 23] Because of the low uranium concentration, the counting statistics are too poor for the measured ²³⁴U/²³⁸U ratio of 1.9 to be meaningful. Thus we conclude that in disregarding the aqueous phase we are not introducing any significant bias into our results.

The uranium concentration in Miami westerly dust is higher than the 1–4 ppm that would be expected for Pleistocene to Recent marine carbonates [19]. This enrichment may be due to the presence of non-carbonate material such as organic matter, mineral dust, and atmospheric pollutants. The high uranium concentration may also be attributed to the use of phosphate fertilizers which typically have a high uranium content. These possibilities seem plausible as the samples were collected when the wind was from the mainland and probably bore dust derived from the agricultural and urban areas of Dade County.

In some respects, the Miami westerly dust may be considered to be a “contaminated” sample of local marine carbonate. Pleistocene and Recent corals and oolites from the Miami area have been studied by Osmond et al. [19], for the purpose of dating the Pleistocene Key Largo and Miami Oolite formations by the ²³⁰Th/²³⁴U method. The age determined by Osmond for these formations is about 130,000 yr bp. Our sample RSMAS M491, which, on the basis of having the lowest U and Th content, would seem to be the least “contaminated” example of dust from the local lithology, is strikingly similar to the data of Osmond et al. [19], and yields a ²³⁰Th/²³⁴U age of approximately 135,000 yr.** Despite the good agreement in ages, we would not advocate dust analysis as a means of dating Pleistocene marine carbonate formations! However, the isotopic composition of dusts may be useful as an indicator of provenance.

As mentioned above, the inclusion of significant amounts of terrestrial dust in marine sediments could conceivably cause problems in absolute age dating by the ²³⁰Th/²³¹Pa and ²³⁰Th/²³²Th methods if these dusts exhibited large departures from equilibrium. In closed geological systems older than about 10⁵ yr, ²³⁰Th and ²³⁴U will have achieved radioactive equilibrium with their parent, ²³⁸U; that is, their alpha activity ratio would be 1.00. However, in open systems exposed to weathering and the circulation of groundwater, separation of these nuclides can occur, giving rise to a state of radioactive disequilibrium [24–27]. Consequently, the activity ratio of ²³⁴U to ²³⁸U in many natural waters, including most rivers, is greater than 1.00, that of the oceans being 1.15 [26, 28, 29].

Our analyses show a considerable variation in the degree of disequilibrium between ²³⁴U/²³⁸U and ²³⁰Th/²³⁴U. However, the average for the activity ratio ²³⁴U/²³⁸U is 1.08 and for ²³⁰Th/²³⁴U is 0.97 for Barbados dust. Since a ²³⁰Th/²³⁴U ratio of 1.0 is assumed in correcting for U-supported ²³⁰Th in dating by the ²³⁰Th/²³¹Pa and ²³⁰Th/²³²Th methods, we would conclude that the influx of dust from Africa into the equatorial Atlantic and Caribbean would not, in itself, significantly affect the dates obtained for marine sediments. The average 8% excess of ²³⁴U is probably the result of weathering processes occurring near the source area in Africa. The excess ²³⁴U is possibly associated with the desert varnish coating depos-

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* Air-borne particulates frequently exist as loosely-bound agglomerates; consequently, after dispersing our samples in water, we find that 40% to 50% of the dust weight consists of particles in the less than 2μm diameter size range [12].

** Ideally, marine carbonates intended for dating should contain only radiogenic ²³⁰Th and no ²³²Th.
ited by secondary processes; it is unlikely that the excess $^{234}\text{U}$ is derived from sea-spray salts as the samples are washed prior to analysis.

Because of the small sample sizes ($\sim 2g$), $^{231}\text{Pa}$ could not be measured, but a rough estimate can be made. On the basis of the average $^{230}\text{Th}/^{234}\text{U}$ activity ratio of 0.97 and the $^{234}\text{U}/^{238}\text{U}$ ratio of 1.08, the net disequilibrium between parent $^{238}\text{U}$ and its eventual daughter $^{230}\text{Th}$ is about 5%. Since the activity ratio $^{238}\text{U}/^{235}\text{U}$ (21.8) is constant in nature, it can be assumed that if $^{231}\text{Pa}$ is in equilibrium with its parent, $^{235}\text{U}$, then there would be a 5% deficiency of $^{231}\text{Pa}$ relative to $^{230}\text{Th}$ in African dust. Again a discrepancy of this magnitude, if existent, would not greatly influence the correction for the allogenic component of radio-elements in dating of marine sediments.

Probably a greater source of potential dating errors than the disequilibrium in dust is (a) the post depositional mobility of uranium [18, 30, 31] and (b) the separation of $^{235}\text{Th}$ and $^{231}\text{Pa}$ in oceanic regions where manganese nodules and encrustations are common [32].

Acknowledgements

We thank W.S. Moore for permission to use his data in this report, R. Nees and C. Dorta for their technical assistance, and Judge G.L. Taylor, Barbados, for the continued use of his coastal land site for our field operations.

A portion of this research was supported by the Office of Naval Research Contract N00014-67-A-0201-0013, Atomic Energy Commission Contract AT-(40-1)-3622, and National Science Foundation Grants GA-25916, GA-20112 and GA-22033.

Contribution no. 1465 from the Rosenstiel School of Marine and Atmospheric Science.

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