

Measurement of ^{236}U at the GEOTRACES East Pacific Zonal Transect

M. Villa-Alfageme^{1}, E. Chamizo², M. López-Lora², T. Kenna³, N. Casacuberta⁴, P. Masqué⁵, M. Christ⁴*

¹Applied Physics Dept.II, ETSIE. Universidad de Sevilla. 41012 Sevilla, Spain

²Centro Nacional de Aceleradores (CNA). Universidad de Sevilla. Junta de Andalucía. Consejo Superior de Investigaciones Científicas. Sevilla, Spain

³Lamont-Doherty Earth Observatory. Columbia University. NY. USA

⁴Ion Beam Physics.ETH Zürich. Switzerland

⁵School of Natural Sciences. Centre for Marine Ecosystems Research. Edith Cowan University. Joondalup. WA. Australia

Abstract

During October-December 2013 U.S. GEOTRACES sampled the East Pacific Zonal Transect (EPZT). The transect went from Peru (12°S, 77°W) to Tahiti (17°S, 149°W) and included the in-depth analysis of the Peru Margin upwelling and oxygen minimum zone (OMZ), and the large hydrothermal plume (HP) originating from the southern East Pacific Rise. Respectively St. 11 (12°S,94°W) and St. 18 (15°S,113°W). That area might have been influenced by the US and French nuclear weapon testing sites at the Pacific Ocean. Several water profiles were collected for the analysis of ^{236}U . Surface samples, i.e. above 400 m, were measured on the 1 MV AMS system at the Centro Nacional de Aceleradores (CNA, Sevilla, Spain) because the $^{236}\text{U}/^{238}\text{U}$ atom ratio (AR) was at the order of 10^{-10} , and the maximum sensitivity achieved on this system is 7×10^{-11} . In deeper samples the expected AR was at the 10^{-12} - 10^{-11} level, and for that reason they were measured on the 600 KV Tandy facility at the ETH Laboratory of Ion Beam Physics (Zürich, Switzerland), with a lower background (at the order of 10^{-14}).

We present here the results for stations 11 and 18. Our results show that: i) Samples above 1000 m presented ^{236}U concentrations from $0.02 \cdot 10^6$ to $7 \cdot 10^6$ at kg^{-1} , lower than the activity concentrations at the Equatorial North Atlantic (NA), from $2 \cdot 10^6$ to $6 \cdot 10^6$ at kg^{-1} , above 1000 m. The data indicated the presence of anthropogenic ^{236}U , but no additional sources than global fallout were identified here. In contrast, deep samples in the North Atlantic showed the presence of ^{236}U from European nuclear reprocessing plants. ii) Most of the samples between 600 and 2000 m presented very low values, close to the lithogenic/natural ratios (i.e. at the 10^{-12} level). To the best of our knowledge, these ratios are the lowest ones measured so far in seawater. Below 2000 m it might be detected a slight increase in the ^{236}U concentration in both OMZ and HP stations. iii) Regarding the biogeochemical behaviour, similar $^{236}\text{U}/^{238}\text{U}$ profiles were obtained in the upper 1300 m in both OMZ and HP. The analysis of other radionuclides sampled during the cruise, e.g. ^{237}Np and ^{129}I , and of additional EPZT profiles will provide insights of the origin of ^{236}U fluctuations in depth.

Introduction

Uranium-236 is a long-lived radioisotope ($T_{1/2} = 2.35 \cdot 10^7$ y) that decays by alpha emission to ^{232}Th . It is mainly produced in nuclear reactors through the capture of a thermal neutron by ^{235}U or ^{239}Pu (followed by alpha decay of ^{240}Pu). It is also naturally produced in much more inferior amounts by neutrons associated to cosmic radiation and by the so-called nucleogenic component (i.e. neutrons produced by the spontaneous fission of ^{238}U or in the (α, n) reactions on light elements). These processes lead to natural abundance levels that range from 10^{-14} to 10^{-10} $^{236}\text{U}/^{238}\text{U}$ atom ratios [Steier

et al., 2008]. However, ^{236}U in the environment mainly has an anthropogenic origin, leading to isotopic ratios in seawater between 10^{-9} and 10^{-6} in the environment ([*Steier et al.*, 2008; *Wendel et al.*, 2013; *Winkler et al.*, 2012] and references therein).

A total amount of 35 kg of mobile ^{236}U coming from natural sources has been estimated ([*Casacuberta et al.*, 2014; *Christl et al.*, 2015; *Steier et al.*, 2008] and references therein). It is estimated that about 10^6 kg of ^{236}U has been produced in nuclear reactors worldwide. Atmospheric nuclear weapons tests contributed to the total inventory with a quantity that has been calculated to range between 900 and 1400 kg [*Casacuberta et al.*, 2014; *Sakaguchi et al.*, 2009]. The nuclear fuel reprocessing plants (NFRP), Sellafield and La Hague, carried out important liquid releases discharges, approximately between 115-250 kg of ^{236}U , to the North Sea. The contribution of these sources is not well defined, but they dominate some areas of the Atlantic Ocean [*Christl et al.*, 2015].

Up to now, due to the difficulties in the measurement of low $^{236}\text{U}/^{238}\text{U}$ ratios, the availability of data on ^{236}U in the environment was limited. After the improvement of the analytical detection techniques, AMS [*Marsden et al.*, 2001], ICP-MS [*Ketterer et al.*, 2003] or TIMS [*Richter et al.*, 2010], ^{236}U concentrations data in several environmental compartments have become available in recent years. Furthermore, recent studies demonstrated the potential use of ^{236}U as an oceanic circulation tracer [*Casacuberta et al.*, 2016; *Christl et al.*, 2012; *Sakaguchi et al.*, 2012], and to study the signal of fallout in corals [*Winkler et al.*, 2012], peats [*Quinto et al.*, 2013] and ice cores [*Wendel et al.*, 2013].

However, it is uncertain the contribution of specific sources as Sellafield and La Hague in different areas and depths of the Atlantic Ocean. Thus, it is important to build a database that provides data of ^{236}U distribution in order to broaden the information of the different sources to the Ocean. In this context, very few data from the Pacific Ocean waters are available [*Sakaguchi et al.*, 2009].

In this work, we present ^{236}U data from the Equatorial Pacific. This area is not expected to be affected by releases from nuclear fuel reprocessing plants, but it might be potentially affected by the past US and French nuclear tests carried out in the Marshall islands and Mururoa and Fangataufa atolls during the Pacific Proving Grounds (PPG) and the French Nuclear Weapons Testing, respectively [*Nomura et al.*, 2017].

Materials and Methods

Samples

The U.S. GEOTRACES East Pacific Zonal Transect (EPZT) was occupied from October-December 2013. The transect from Peru to Tahiti included the Peru Margin, upwelling and oxygen minimum zone (OMZ), St. 11 ($12^{\circ}\text{S}, 94^{\circ}\text{W}$), and the large hydrothermal plume (HP), St. 18 ($15^{\circ}\text{S}, 113^{\circ}\text{W}$), originating from the southern East Pacific Rise (Fig. 1). 125 samples were collected.

Radiometric technique

In a first step, 3 pg of ^{233}U ($T_{1/2} = 1.59 \cdot 10^5$ y) spike were added to the samples to quantify the $^{236,238}\text{U}$ concentrations by the isotope dilution. Actinides were co-precipitated at Lamont-Doherty Earth Observatory (LDEO) as follows. 4 L of seawater samples were acidified with 1 mL of HNO_3 (65%) per litre of sample, mixed and let settled for, at least, one hour for their homogenisation. Fe^{3+} was

then added to the samples and uranium was extracted from the bulk of the sample by rising the pH to about 8.5 adding 45% NH_3 . After complete precipitation and settling of the $\text{Fe}(\text{OH})_3$ particles, the supernatant was discarded and the resulting precipitate taken to dryness. Subsequently, at CNA-Universidad de Sevilla, $\text{Fe}(\text{OH})_3$ precipitate was dissolved with 8M HNO_3 and UTEVA® resins in a vacuum box were used for the final uranium purification following the method described in *López-Lora et al.* [In review]. AMS sources were prepared by adding 1 mg of Fe^{3+} to the uranium solutions for its coprecipitation with $\text{Fe}(\text{OH})_3$. Precipitates were transferred to quartz crucibles, dried and heated at 650°C to get iron oxides. Finally samples were mixed with 3 mg of Nb powder and pressed into suitable aluminium cathodes.

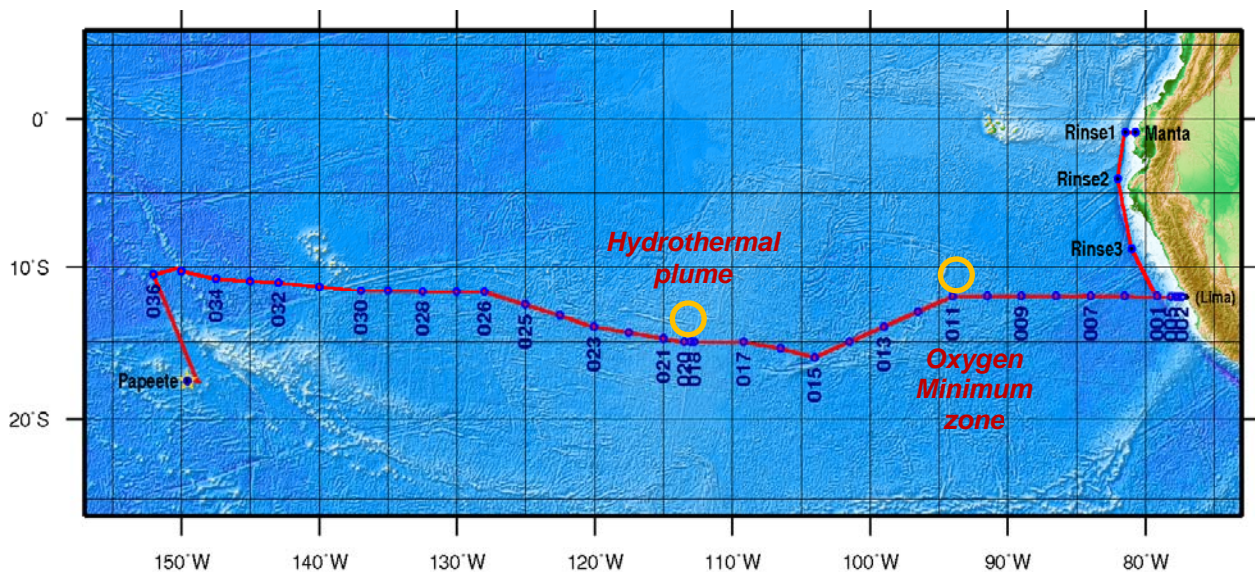


Figure 1. U.S. GEOTRACES East Pacific Zonal Transect. Geographical distribution. Discussed sections, 11 (Oxygen Minimum Zone) and 18 (Hydrothermal Plume), are marked in yellow.

Measurement

AMS determinations were performed on the 1 MV CNA AMS system and on the 600 kV ETH AMS facility. Details about the technique can be found in [*Chamizo et al.*, 2015]. Briefly, uranium isotopes are extracted from the Cs^+ sputtering ion-source as negative oxide ions (UO^-). These anions are analysed by a first 90° sector magnet and directed to the terminal of the tandem accelerator, which contains the stripper gas (He gas in both facilities). Negative oxide ions brake up and are stripped to 3+ charge state in the so-called stripping process. These ions are analysed by additional cinematic filters at the exit of the accelerator. Finally, the minor isotopes ($^{233,236}\text{U}^{3+}$) are counted from the total energy signal provided by a gas ionization chamber. The abundant natural isotope ^{238}U is measured as a beam-current in a Faraday Cup.

Surface samples, i.e. above 400 m, were measured at the CNA because the $^{236}\text{U}/^{238}\text{U}$ atom ratio (AR) was at the order of 10^{-10} , and the maximum sensitivity achieved on this system is 7×10^{-11} . In deeper samples the expected AR was at the 10^{-12} - 10^{-11} level, and for that reason they were measured at the ETH facility, which features with a lower background (at the order of 10^{-14}) obtained with an additional sector magnet before the final detection system. Details about the current status of the 1 MV CNA system are given in *Scognamiglio et al.* [2016] and about the 600 kV ETH facility in *Christl et al.* [2013]

Results and Discussion

Figure 2 shows that samples above 1000 m presented ^{236}U concentrations from $0.02 \cdot 10^6$ to $7 \cdot 10^6$ at kg^{-1} , which are lower than the concentrations at the Equatorial North Atlantic (NA), from $2 \cdot 10^6$ to $6 \cdot 10^6$ at kg^{-1} . The data indicated the presence of anthropogenic ^{236}U , but no additional sources than global fallout were identified here. In contrast to the deep samples in the North Atlantic, that showed the presence of ^{236}U from nuclear reprocessing plants. The inventories are presented in Table 1 and compared for both Pacific and Atlantic Ocean for similar latitudes, these data in the Pacific Ocean are lower than at North Atlantic Ocean, and seem to correspond exclusively to fallout.

The profiles and inventories show that at 94° and 113° western longitude there is no contribution of the local fallout from the Pacific Proving Grounds (PPG) and the French Nuclear Weapons Testing that were carried out by US at the Marshall islands and by France at Mururoa and Fangataufa atolls.

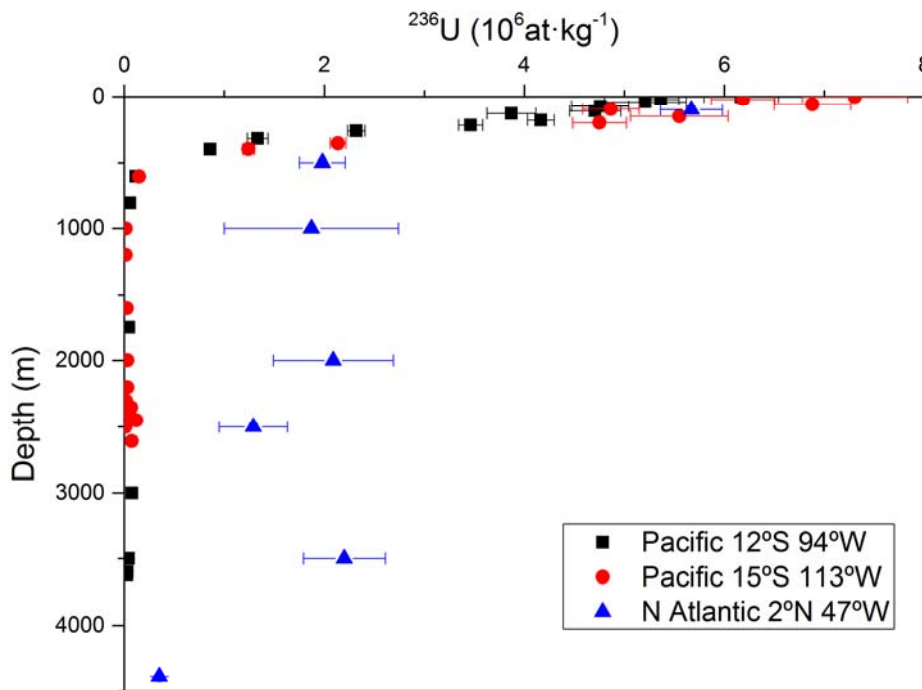


Figure 2. ^{236}U concentrations in i) the two stations from the EPZT. Station 11 ($12^\circ\text{S } 94^\circ\text{W}$) and station 18 ($15^\circ\text{S } 113^\circ\text{W}$) and ii) a North Atlantic Station at a close latitude ($2^\circ\text{N } 47^\circ\text{W}$).

Figures 3 and 4 showed that most of the samples between 600 and 2000 m presented very low $^{236}\text{U}/^{238}\text{U}$ atom ratios, close to the lithogenic/natural ratios (i.e. at the 10^{-12} level). To the best of our knowledge, these AR are the lowest ones measured so far in seawater.

Below 2000 m Figure 4 shows the differences between the Hydrothermal Plume, 113° longitude station, in contrast to the Oxygen Minimum Zone, 94° longitude station. Figure 6 shows the bathymetric profile of the transect and the topography of the bottom ocean in both locations. The hydrothermal plume is originated from a sharp peak around 2500 m; whereas the ocean bottom at the Oxygen minimum zone is flatter and deeper.

Site	LAT °N	LONG °W	at m ⁻²	Uncert
Pacific Ocean	12	94	1.45E+12	1E+11
	14.9	113	1.72E+12	1E+11
North Atlantic	18.6	58	1,57E+13	2,94E+12
	2.5	41	7,21E+12	1,68E+12

Table 1. ²³⁶U inventories deep depths in two stations from the EPZT, station 11 (12°S 94°W) and station 18 (15°S 113°W) [this work] and in two stations from the North Atlantic at similar latitudes [Casacuberta et al., 2014].

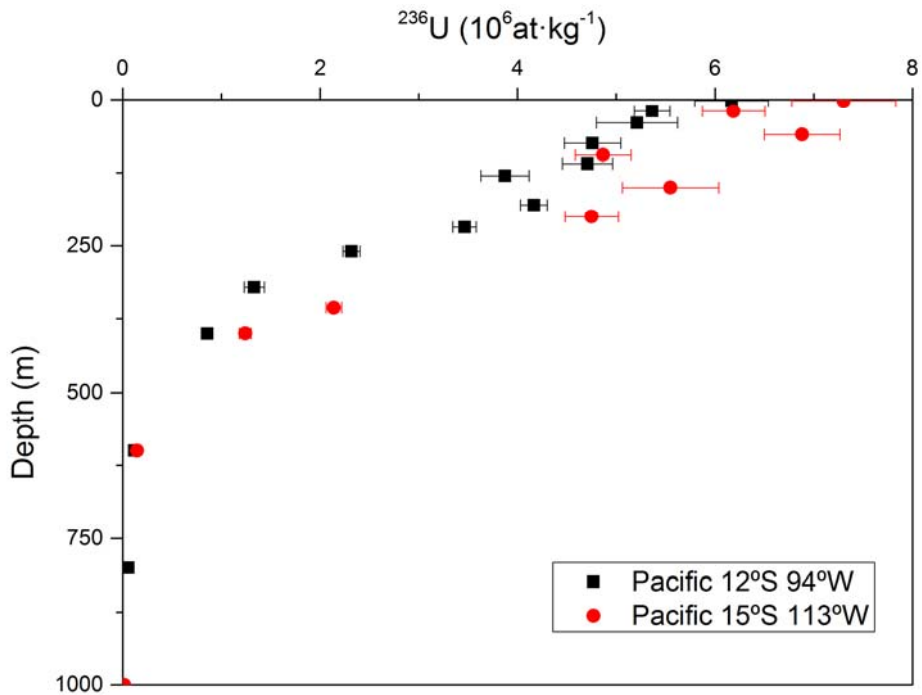


Figure 4. ²³⁶U concentrations in the first 1000 m in two stations from the EPZT. Station 11 (12°S 94°W) and station 18 (15°S 113°W).

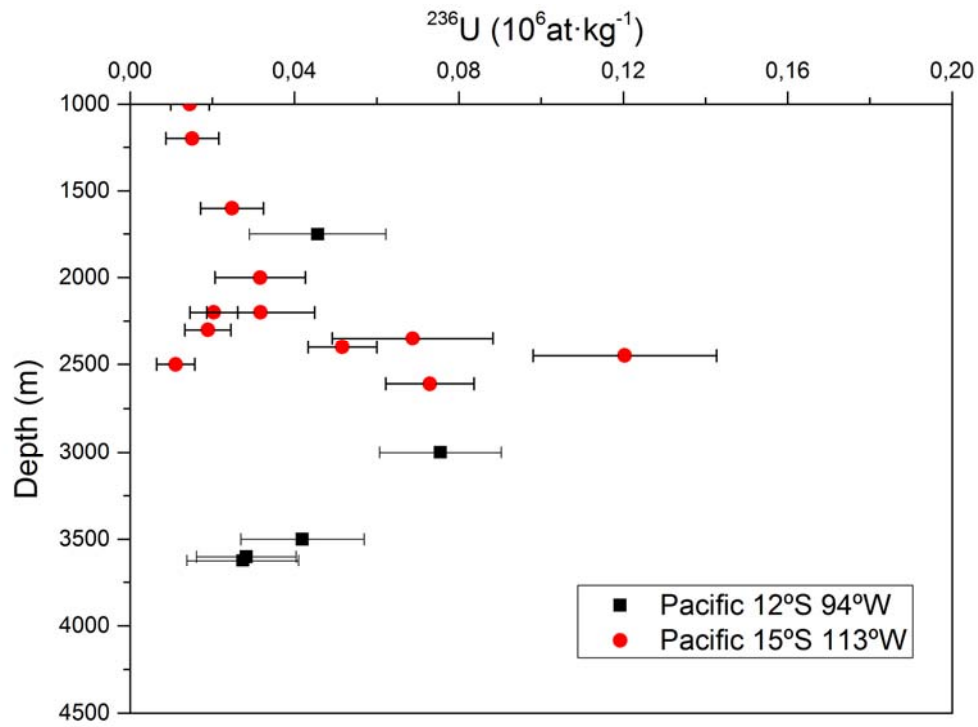


Figure 5. ^{236}U concentrations in deep depths in two stations from the EPZT. Station 11 (12°S 94°W) and station 18 (15°S 113°W).

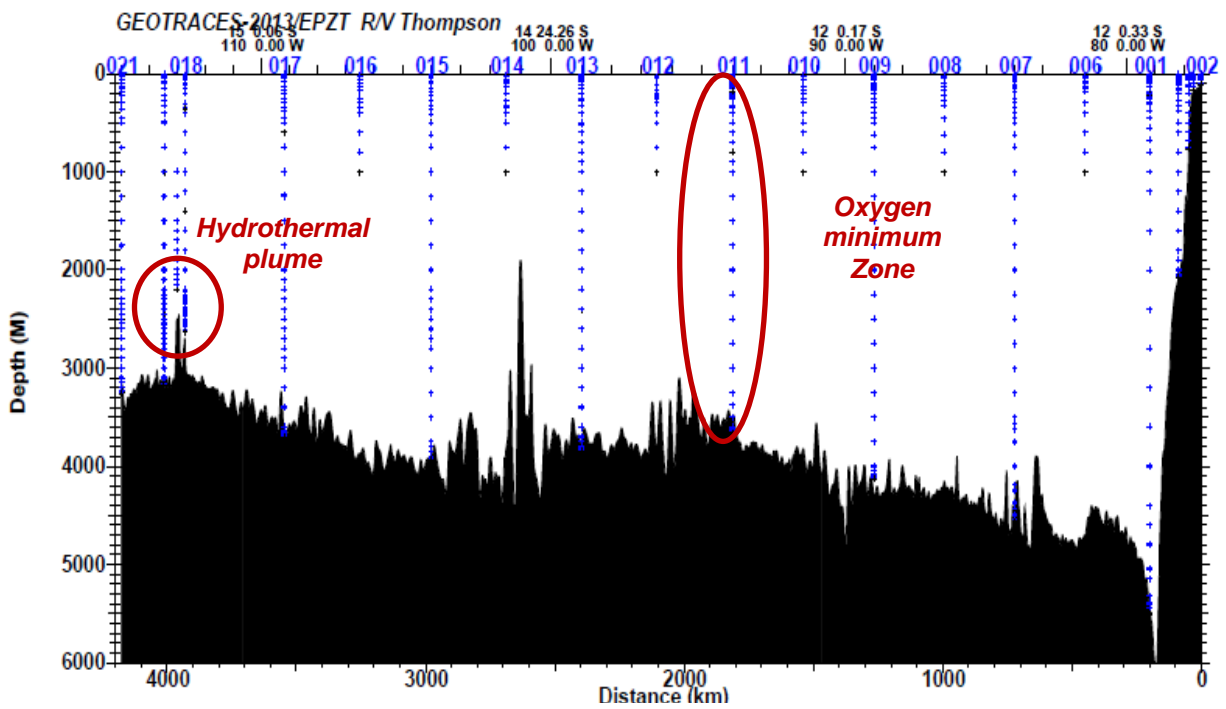


Figure 6. U.S. GEOTRACES EPZT Sample distributions: Stations 1-21.

Conclusions

These results show that the AMS ^{236}U technique allows the measurement of $^{236}\text{U}/^{238}\text{U}$ down to the lithogenic AR. In the profiles analyzed from the EPZT around the Equatorial Pacific, ^{236}U concentrations and inventories show that the main source of ^{236}U in these locations is global fall-out and no additional sources were identified. These results are key because the profiles are not affected by anthropogenic contributions from the nuclear reprocessing fuel plants (NRFP) and allow the examination of ^{236}U typical water conservative profiles.

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