# Improvement of 137Cs analysis in small volume seawater samples using the Ogoya underground facility

| | |
|---|---|
| 著者 | Hirose Katsumi, Aoyama M., Igarashi Y., Komura K. |
| journal or publication title | Journal of Radioanalytical and Nuclear Chemistry |
| volume | 276 |
| number | 3 |
| page range | 795-798 |
| year | 2008-06-01 |
| URL | http://hdl.handle.net/2297/10967 |

doi: 10.1007/s10967-008-0634-6

## LOG NUMBER OF PAPER: 221

## TITLE OF PAPER:

# Improvement of $^{137}$Cs analysis in small volume seawater samples using the underground facility (Ogoya)

## AUTHORS and ADDRESSES OF EACH AUTHOR:

K. Hirose[1,2], M. Aoyama[1], Y. Igarashi[1] and K. Komura[2,1]

1. Geochemical Research Department, Meteorological Research Institute, Nagamine 1-1, Ibaraki 305-0052, Japan

2. Low Level Radioactivity Laboratory, Kanazawa University, Wake, Nomi, Ishikawa 923-1224, Japan

## CORRESPONDING AUTHOR'S FAX AND E-mail ADDRESS:

Katsumi Hirose, Dr.

FAX: +81-29-853-8728

E-mail: khirose@mri-jma.go.jp

# Improvement of $^{137}$Cs analysis in small volume seawater samples using the underground facility (Ogoya)

K. Hirose

khirose@mri-jma.go.jp

M. Aoyama

maoyama@mri-jma.go.jp

Y. Igarashi

yigarash@mri-jma.go.jp

Geochemical Research Department, Meteorological Research Institute, Nagamine 1-1, Ibaraki 305-0052, Japan

K. Komura

komura@yu.incl.ne.jp

Low Level Radioactivity Laboratory, Kanazawa University, Wake, Nomi, Ishikawa 923-1224, Japan

Key words: $^{137}$Cs, seawater, underground facility, gamma-spectrometry, ammonium phosphomolybdate, ultra low level

# Improvement of $^{137}$Cs analysis in small volume seawater samples using the underground facility (Ogoya)

K. Hirose[1,2], M. Aoyama[1], Y. Igarashi[1] and K. Komura[2,1]

1. Geochemical Research Department, Meteorological Research Institute, Nagamine 1-1, Ibaraki 305-0052, Japan

2. Low Level Radioactivity Laboratory, Kanazawa University, Wake, Nomi, Ishikawa 923-1224, Japan

$^{137}$Cs in seawater is one of the most powerful tracers of water motion. Large volumes of samples have been required for determination of $^{137}$Cs in seawater. This paper describes improvement of separation and purification processes of $^{137}$Cs in seawater, which includes purification of $^{137}$Cs using hexachloroplatinic acid in addition to ammonium phosphomolybdate (AMP) precipitation. As a result, we succeeded the $^{137}$Cs determination in seawater with a smaller sample volume of 10 L by using ultra low background gamma–spectrometry in the underground facility (Ogoya). $^{137}$Cs detection limit was about 0.1 mBq (counting time: $10^6$ s). This method is applied to

determine $^{137}$Cs in small samples of the South Pacific deep waters.

## INTRODUCTION

Most of the $^{137}$Cs with a half-life of 30 years has been injected into the world ocean surface waters via global fallout from the 1961-62 large-scale atmospheric nuclear testing.[1] $^{137}$Cs is one of the most useful traces of water motion in the ocean because the ocean input process is well characterized; the major input of $^{137}$Cs in the ocean occurred in 1962-64 as approximately a single injection and the geographic distribution of $^{137}$Cs injection was re-constructed from fallout and inventories in the soil and in the water column data.[2] The spatial distribution and temporal changes of $^{137}$Cs in seawater reflect motion of seawater such as advection and diffusion because most of the $^{137}$Cs exists as a dissolved form in seawater. The data of $^{137}$Cs in seawater has been accumulated as databases such as HAM and GLOMARD.[3,4] However, oceanic $^{137}$Cs has not been comprehensively used as an oceanic tracer comparing with CFCs[5] (chloro-fluoro carbons) because there are only a few cases depicted cross section of oceanic $^{137}$Cs distribution such as Geochemical Ocean Sections Study (GEOSECS).[6]

Recently $^{137}$Cs has been applied to validation of a global ocean circulation model.[7] In order to achieve comprehensive use of $^{137}$Cs in the field of oceanography, it is necessary to improve analytical methods of $^{137}$Cs in seawater such as reduction of sample volumes.

Recently, Aoyama et al.[8] have improved the ammonium phosphomolybdate (AMP) procedure for determination of $^{137}$Cs in seawater, which includes a reduction of the amount of AMP and achievement of high sensitivity of $^{137}$Cs determination by using high-efficiency well-type Ge-detectors. Furthermore, ultra low background γ–spectrometry using Ge detectors with high efficiency and low background materials in an underground facility (Ogoya Underground facility: OUL) can realize higher sensitive determination of $^{137}$Cs.[9-11] A detection limit of $^{137}$Cs at the OUL is 0.18 mBq for a counting time of 10000 minutes.[11] However, there is a residual problem of underground γ–spectrometry for $^{137}$Cs measurements in the underground facility. AMP adsorbs trace amounts of potassium when Cs is extracted as AMP/Cs compound from seawater because K is a major component in seawater and radioactive potassium ($^{40}$K) contains 0.0118 % of total in the natural materials. Trace amounts of $^{40}$K caused elevation of background corresponding to energy range of $^{137}$Cs due to Compton scattering γ-rays from $^{40}$K. If $^{40}$K can be removed in AMP/Cs compound samples, the full performance of underground γ–spectrometry for $^{137}$Cs measurements may be improved.

In this paper, we describe a method to remove $^{40}$K from the AMP/Cs compound and application of new method to samples collected in the South Pacific.

## EXPERIMENTAL

### *Sampling and materials*

Seawater samples were collected in the around the world BEAGLE cruise of RV Mirai, Japan Agency for Marine-Earth Science and Technology (JAMSTEC) conducted in 2003-2004, using a CTD-rosette multi-bottle sampler, which collected seawater of each 12 liters at 36 different depth layers. The detail of water sampling was described in elsewhere.[12] All of water samples were filtered with a membrane filter (pore size of 0.45 μm). 5 to 20 liters samples were used for $^{137}$Cs analysis.

All reagents used for $^{137}$Cs assay are special (G.R.) grade for analytical use. All experiments and sample treatments were carried out at ambient temperatures. We confirmed that the background $^{137}$Cs activity in the CsCl reagent was less than 0.03 mBq g$^{-1}$ by using ultra low background γ–spectrometry at the OUL. The $^{137}$Cs activity in the AMP employed was less than 0.01 mBq g$^{-1}$. There was no serious contamination of $^{137}$Cs from other reagent, too.

### *γ–spectrometry*

$^{137}$Cs measurements were carried out by γ–ray spectrometry using well-type Ge detectors coupled with multi-channel pulse height analyzers. The performance of the well-type Ge detectors was described elsewhere.[11] Detector energy calibration was done using γ-ray sources containing $^{137}$Cs, while the geometry calibration was done using the "reference" material[13] with the same tube and the very similar density.

### *Methods*

Seawater samples of 5 to 20 liters were transferred in a tank of appropriate size. A pH in seawater samples was adjusted to 1.6 by adding 14 M $HNO_3$. In order to prepare insoluble AMP/Cs complex, CsCl of 0.26 g was added in each acidified seawater and well-mixed using a stirrer. AMP powder of 4 g was added and dispersed in acidified seawater. After the solution was well mixed for 1 hour using the stirrer, the insoluble AMP/Cs complex was allowed to settle for 6 to 24 hours. The AMP/Cs complex was collected onto a No. 5B paper filter and washed with 100 ml of 1 M $HNO_3$ solution. The precipitate was dried in ambient temperature for several days. The AMP/Cs complex was weighed to determine the weight yield. Finally, the AMP/Cs complex was put into a Teflon tube of 4 ml volume and subjected to $\gamma$–spectrometry. A detail of analytical procedure is described in elsewhere.[8,11]

For deep waters, the AMP/Cs precipitates were dissolved in an alkali solution. pH in solution was adjusted to be ca. 8.1 by adding 2M HCl and adjusted the volume of solution to ca. 70-100ml. Precipitation of $Cs_2Pt(Cl)_6$ was performed to add hexachloroplatinic acid (1g/5ml D.W.) at pH = 8.1 and kept in a refrigerator during a half-day. The $Cs_2Pt(Cl)_6$ precipitate was collected onto a filter and washed the compound with the solution (pH = 8.1). The $Cs_2Pt(Cl)_6$ precipitate was dried for several days in room temperature. The $Cs_2Pt(Cl)_6$ precipitate was weighted to determine a weight yield. After the transfer of the $Cs_2Pt(Cl)_6$ precipitate into a Teflon tube of 4ml volume, $^{137}Cs$ was determined by the underground $\gamma$-spectrometry.

Previous experiments[8] have shown that significant contamination of $^{137}Cs$

from air and reagents in the laboratory is not a concern.

### *Chemical yields*

Previous experiments[8,11] have shown that the chemical yields of insoluble AMP/Cs complex in average were 98.5 % for 20 liter samples of seawater. During the process to remove $^{40}$K from the AMP/Cs precipitation, a yield of $^{137}$Cs was 93±13 %. We confirmed that a yield of stable Cs in this process is larger than 99.8 % by ICP-MS measurement (Fujikawa, per comm.). Therefore, the large uncertainty of the RI recovery is due to smaller net counts of $^{137}$Cs. Since a part of $Cs_2Pt(Cl)_6$ precipitate remained on the filter, the average weight yields of insoluble the $Cs_2Pt(Cl)_6$ precipitate were above 90%.

## RESULTS AND DISCUSSION

### *Purification of $^{137}$Cs*

Hexachloroplatinic acid forms an insoluble salt with Cs in a weak alkali solution. In the late 1950s, $Cs_2Pt(Cl)_6$ precipitation method has been used for determination of $^{137}$Cs in seawater with β-counting because of underdevelopment of γ-spectrometry.[14] To remove $^{40}$K in the AMP/Cs compound, we carried out further purification with $Cs_2Pt(Cl)_6$ precipitation method. The result of $\gamma$-spectra before and after $Cs_2Pt(Cl)_6$ purification is shown in Fig. 1. After the purification of $Cs_2Pt(Cl)_6$ precipitation, $^{40}$K concentrations decreased less than 20 % of that in the AMP/Cs compound. As a result, a clearer peak of $^{137}$Cs was found in $\gamma$-spectra from underground $\gamma$-spectrometry (Ogoya). The $^{137}$Cs concentrations in the South Pacific deep waters are summarized in Table 1.

### *Vertical profile of $^{137}$Cs in the South Pacific*

According to worldwide database of $^{137}$Cs concentrations in seawater, the smallest number of data exists in the South Pacific. The BEAGLE expedition in 2003/2004[12] provided the detail distributions of chemical constituents including chemical tracers such as $^{137}$Cs as shown in Fig. 2. The $^{137}$Cs concentrations in the mid-latitude of the central South Pacific ranged from 1.3 to 1.5 Bq $m^{-3}$, which are in fair agreement with previous estimates (1.4 to 1.7 Bq $m^{-3}$ in 2000 estimated from the temporal trend of the $^{137}$Cs concentrations in the surface water).[15] The $^{137}$Cs concentrations in the South Pacific exponentially decreased to around 1500 m depth with increasing depth (Fig. 2). On the other hand, there is no reliable data of the $^{137}$Cs concentrations in the South Pacific deep waters (>1000 m depth). Now we report the first sight of the $^{137}$Cs concentrations in the South Pacific deep waters. The level of the $^{137}$Cs concentrations in the central South Pacific deep waters was in the range of 0.03 to 0.07 Bq m$^{-3}$, which was slightly higher than that in the middle layer (around 2000 m depth). It is difficult to reproduce the $^{137}$Cs concentrations in the deep waters (>2000 m ) from the present model,[7] although the $^{137}$Cs concentrations from surface to 1500 m depth can be explained by the model including vertical mixing and diffusion. According to knowledge of oceanography, the bottom water in the Pacific is formed due to deep convection in the Antarctic Sea as the Circumpolar Deep Water, CDW. The CDW is transported from the Antarctic Sea to the north. Detection of the $^{137}$Cs in deep waters in the western South Pacific Ocean is evidence that the CDW was transported in the mid latitude region of the South Pacific during the past four decades.

## CONCLUSION

Improvement of the $^{137}$Cs analytical method, including AMP adsorption and $Cs_2Pt(Cl)_6$ purification, and the underground γ–spectrometry, allows us to preciously determine the $^{137}$Cs concentration in seawater with smaller sampling volumes (around

10 liters). $^{137}$Cs detection limit was about 0.1 mBq (counting time: $10^6$ s). We can depict fine structures of the spatial $^{137}$Cs distribution in the ocean, especially in deep waters. Therefore, the $^{137}$Cs in the ocean is an effective tracer to verify the global circulation model and to detect long-term change of water masses such as decadal variability. The $^{137}$Cs concentrations in the central South Pacific deep waters provided evidence on the formation of bottom waters in the Antarctic Sea and intrusion of bottom waters from the Antarctic Sea to the central South Pacific bottom waters.

## ACKNOWLEDGMENTS

Authors thank the captain and the crew of RV Mirai, JAMSTEC, and Masao Fukasawa for water sampling. Authors also thank Itsoo Koshino for his help of $^{137}$Cs analysis and the experiment, and anonymous reviewers for constructive comments and suggestion. This research is supported by the fund of MEXT, JAPAN for the radioactivity survey in Japan.

## REFERENCES

1. UNSCEAR, Sources and effects of ionizing radiation, United Nation, New York,

2000.

2. M. Aoyama, K. Hirose, Y. Igarashi, J. Environ. Monitoring, 8 (2006) 431.

3. M. Aoyama, K. Hirose, ScientificWorldJOURNAL, 4 (2004) 200.

4. P.P. Povinec, K. Hirose, T. Honda, T. Ito, E.M. Scott, O. Togawa, J. Environ. Radioact., 76 (2004) 113.

5. M.J. Warner, J.L. Bullister, D.P. Wisegarver, R.H. Gammon, R.F. Weiss, J. Geophys. Res., 101 (1996) 20,525.

6. V.T. Bowen, V.E. Noshkin, H.D. Livingston, H.L. Volchok, Earth Planet. Sci. Lett., 49 (1980) 411.

7. D. Tsumune, M. Aoyama, K. Hirose, J. Geophy. Res., 108(C8) (2003) 3262.

8. M. Aoyama, K. Hirose, T. Miyao and Y. Igarashi, Appl. Radiat. Isot., 53 (2000) 159.

9. K. Komura, (2004)., Appl. Radiat. Isot., 61 (2004) 179.

10. K. Komura, Y. Hamajima, Appl. Radiat. Isot., 61 (2004)164.

11. K. Hirose, M. Aoyama, Y. Igarashi, K. Komura, J. Radioanal. Nuclear Chem., 263 (2005) 349.

12. M. Aoyama, M., M. Fukasawa, K. Hirose, R.F.C. Mantoura, P.P. Povinec, C.S. Kim, K. Komura, In: Radionuclides in the Environment, Ed., P.P. Povinec and J.A.

Sanchez-Cabeza, pp.53- 66 (2006).

13. M. Otsuji-Hatori, Y. Igarashi, K. Hirose, J. Environ. Radioact., 31 (1986) 143.

14. N. Yamagata, T. Yamagata, Bull. Chem. Soc. Japan, 31 (1958) 1063.

15. K. Hirose, M. Aoyama, J. Environ. Radioact., 69 (2003) 53.

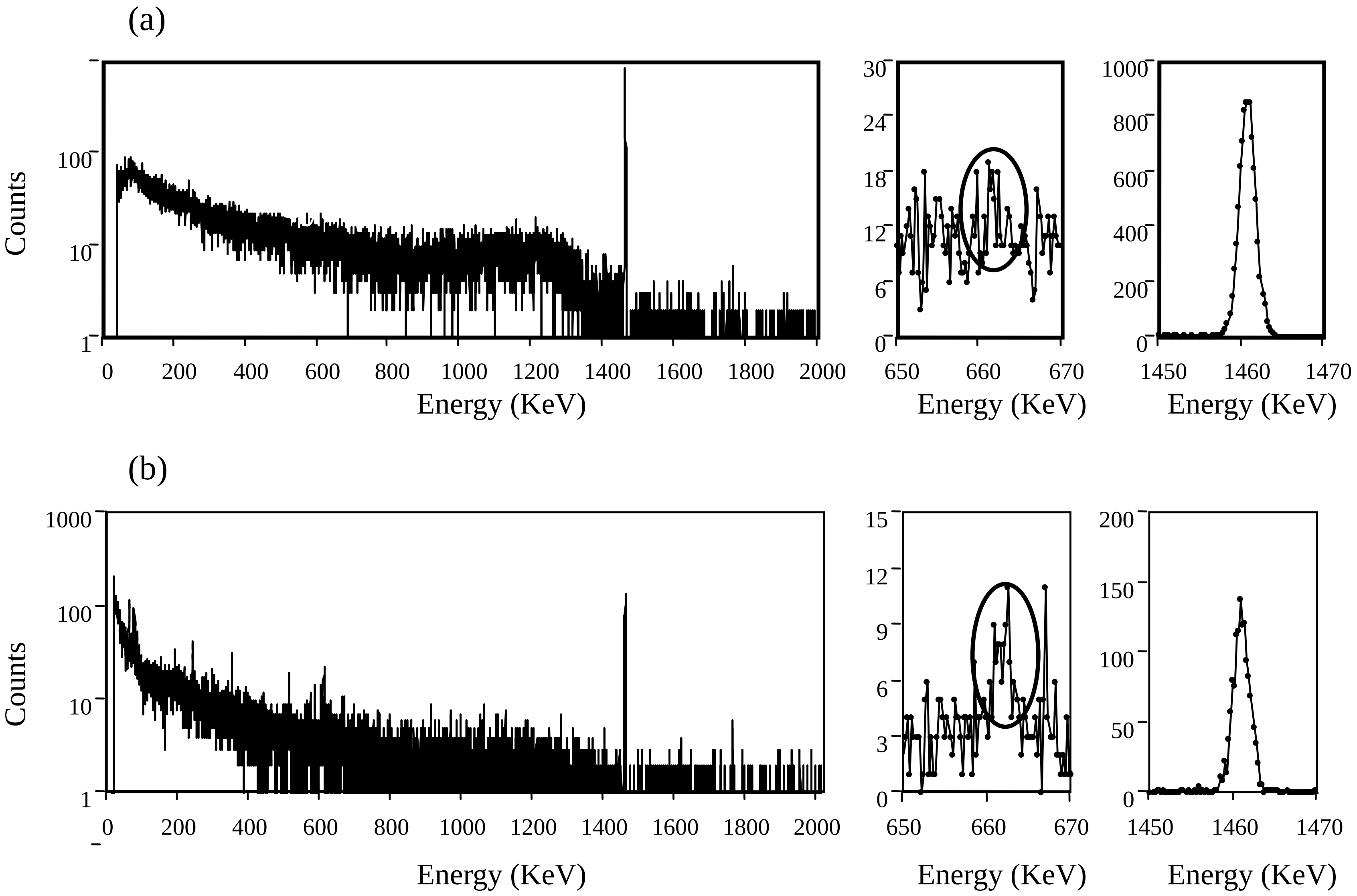
Table 1. The $^{137}$Cs concentrations in the central South Pacific deep waters (sampling location: P06_175, 32°30’S, 177°40’W)

| Depth (m) | $^{137}$Cs concentration (Bq m$^{-3}$) |
|---|---|
| 1400 | 0.020±0.005 |
| 2000 | 0.011±0.002 |
| 2400 | 0.049±0.012 |
| 3000 | 0.010±0.012 |
| 5000 | 0.031±0.017 |
| 5500 | 0.067±0.015 |
| 6500 | 0.031±0.019 |

Figure Caption

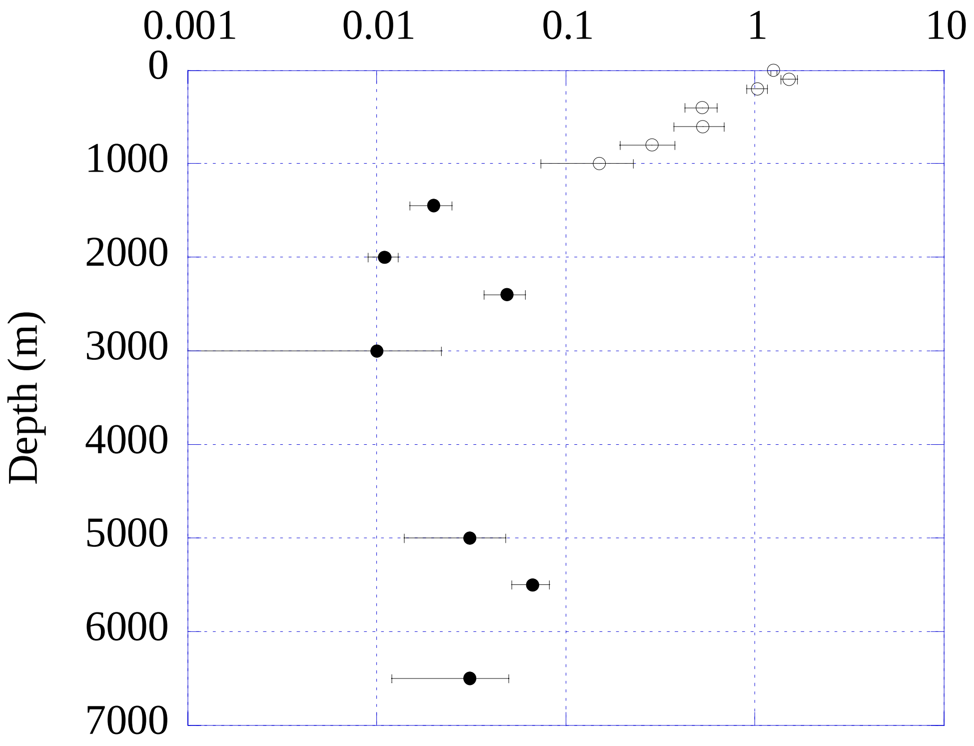
Fig. 1 $\gamma$–spectra of $^{137}$Cs fraction before (a) and (b) after $Cs_2Pt(Cl)_6$ purification, which were measured in the Ogoya underground facility, Kanazawa University. Counting times of (a) and (b) were $7.5 \times 10^5$ and $7.6 \times 10^5$ s, respectively. Left figures are full $\gamma$–spectra of a deep water sample. Central figures show an energy area including $\gamma$–ray of $^{137}$Cs. The ring means a peak area of $\gamma$-ray emitted from $^{137}$Cs. Right figures show an energy area including $\gamma$–ray of $^{40}$K.

Fig. 2 The vertical profile of the $^{137}$Cs concentrations in the central South Pacific (32°30’S, 177°40’W). Open circle is cited from ref. 12 and closed circle is obtained by this work.



Hirose Figure 1

Full depth $^{137}$Cs profile at P06_175 (32°30’S, 177°40’W) (Bq m$^{-3}$)



Hirose Figure 2