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Momoshima, Noriyuki
Radioisotope Center, Kyushu University

Inoue, F.
Graduate School of Science, Kyushu University

Ohta, T.
Research Reactor Institute, Kyoto University

Mahara, Y.
Research Reactor Institute, Kyoto University

他

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Application of ^{85}Kr dating to groundwater in volcanic aquifer of Kumamoto Area, Japan

N. Momoshima[1,*], F. Inoue[2], T. Ohta[3], Y. Mahara[3], J. Shimada[4], R. Ikawa[5], M. Kagabu[4], M.Ono[4], K. Yamaguchi[4], S. Sugihara[1], M. Taniguchi[6]

[1] Radioisotope Center, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

[2] Graduate School of Science, Kyushu University, 6-10-1Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

[3] Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka 590-0494, Japan

[4] Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan

[5] Groundwater Research Group, Geological Survey of Japan, AIST, Higashi, Tsukuba, Ibaraki,350-8567, Japan

[6] Research Institute for Humanity and Nature, 457-4 Motoyama Kamigamo, Kita-ku, Kyoto 603-8047, Japan

* Corresponding author. momoshima.noriyuki.551@m.kyushu-u.ac.jp

Tel: +81-92-642-2705

Fax:+81-92-642-2706

Groundwater age was determined by $^{85}Kr/Kr$ specific activity of gases dissolved in groundwater at Kumamoto Area, in which newly developed Kr extraction system and liquid scintillation counting technique for ^{85}Kr were applied. Apparent mean residence times observed were 8.2 ± 0.7 y and 20.7 ± 0.6 y for the groundwater taken from a well at recharge area and that from an artesian borehole at the discharge area, respectively showing a consistent age trend estimated from the observed groundwater flow system of Kumamoto Area and also that determined using environmental tritium. Similar mean residence times of ^{85}Kr and tritium were observed at the discharge area but the mean residence time of ^{85}Kr at the recharge area was younger compared to that of tritium, probably due to mixing of river water containing recent ^{85}Kr high in concentration into groundwater flow coming from the northern upland's recharge area. The mean residence time of the groundwater flow coming from northern upland area and a traveling time of the groundwater between two sampling points were estimated by a simple model assuming mixing the river water with the groundwater and a piston flow between two sampling points.

Keywords: krypton 85; liquid scintillation counting; groundwater; dating

Introduction

Krypton-85 (10.76 y half-life) is a radioactive noble gas released from nuclear reprocessing plants operated in the northern hemisphere since the 1940s [1]. Because of inert nature of ^{85}Kr only radioactive decay is an expected elimination process in the environment. In accordance with an increase use of nuclear energy from 1950s, the atmospheric ^{85}Kr concentration has been increasing globally with rapid circulation of air mass and is reflected on surface waters by dissolving component air gases. Therefore, ^{85}Kr is considered to be a good tracer for relatively young groundwater [2-5]. A constant concentration of stable Kr in the atmosphere (1.14 ppm at STP) enable us to use ^{85}Kr/Kr specific activity as a dating index, which is independent of both the recharge temperature and excess air trapped during recharge. Furthermore, it is not sensitive to partial sample loss either in sampling or analysis [6]. ^{85}Kr dating is applied recently to a few aquifer systems [7-12].

The objective of this study is to apply ^{85}Kr dating method for young groundwater at Kumamoto Area where the groundwater flow system is well understood.

Experimental

Study area

The Kumamoto Area is located in the west of Mt. Aso in central Kyushu, Japan and consists of surface alluvial deposits, four pyroclastic flow deposits, called Aso-1,

Aso-2, Aso-3 and Aso-4 in chronological order from the bottom to ground level, and a cracked lava layer, called Togawa lava, cover the impermeable basement rocks, forming a shallow unconfined (No. 1) and confined (No. 2) aquifer system. In the western area in the Kumamoto Area is covered by alluvial marine clay underlain by alternating layers of silt, sand and gravel, which constitute a semi-confined aquifer system. From the groundwater potential distribution observed in Kumamoto Area (Fig. 1), the northern upland part is a recharge area where Shira River (74km and 480km^2) across the Kumamoto Area from east to west. Because of the lack of the lacustrine deposit overlying the Aso-3 which separates the unconfined and the confined aquifers in this area, percolated rainwater and irrigation water can infiltrate directly into the No.2 aquifer system. Measurement of stable oxygen isotope content (δ^{18}O ‰) and SO_4^{2-} ion in the Shira River and the No.2 aquifer suggests that the middle stream areas of the Shira River is one source of groundwater in this area [13-14]. The groundwater recharged around this area flows toward south west and discharge out to the ground fills Lake Ezu, Suizenji Park, and many other natural spring locations within the city and the groundwater in the No.2 aquifer is the major city water resources of the Kumamoto city area which develops over the Kumamoto region [15].

Mahara [16] speculated two major flow paths under of the Kumamoto Plain originating from the groundwater reservoir located north of the Shira River, one is along the old Kase River Valley, which is buried by Aso pyroclastic flow deposits and the other is along the Tsuboi River. Groundwater does not flow along the Shira River from the groundwater reservoir because residual hills and small mountains, consisting of impermeable bedrock in the plain, cut off the groundwater flow (Fig. 1).

Sampling of groundwater

We collected dissolved gases in groundwater at two places, one is Otzu located near the south of the Shira River and the other is Ezuko at the southwest area in the Kumamoto Area (Fig. 1). On May 14-15, 2008 the Otzu groundwater was pumped up at 5 m below groundwater level with a MP-1 pump (Grund-fos Corp.) from an observation well dilled at agricultural field, the groundwater table was around 30 m above sea level and the water level was observed at 65 m depth from the ground surface. The pumped groundwater is directly introduced to the Kr extraction system [17]; the Kr extraction system recovers dissolved gasses in groundwater with a hollow fiber membrane module (SEPAREL EF-040P, Dainippon Ink and Chemicals Co. Ltd) at more than 99% extraction efficiency for Kr. The gases extracted were compressed into evacuated cylinders. The groundwater at Ezuko was collected on May 14, 2008 from one of the artesian boreholes located on a shore of Lake Ezu, which was dilled before and serves groundwater to the Lake Ezu. The water in Lake Ezu is totally supported by the discharged local groundwater from No.1 and No.2 aquifers. We installed the pump at 1.5 m below outlet mouth of the artesian borehole. Judging from tritium concentration and stable oxygen and hydrogen isotopes, the sampled groundwater is probably supplied from the No. 2 aquifer though the exact screen depth of this artesian borehole is not known. The gases collected in cylinders were brought back to laboratory for ^{85}Kr analysis. The sample description is shown in Table 1.

^{85}Kr analysis

^{85}Kr in the cylinders is analyzed using a Kr separation system [18]. At first the gas was passed through four successive 3M NaOH solution bubblers to remove CO_2 and then transferred to an activated charcoal trap at 77K, and most of O_2 and N_2 were removed from the activated charcoal trap by flowing He at 195 K. The remaining gases in the activated charcoal trap were introduced into gas chromatography and Kr was separated from other impurity gasses. The isolated Kr is sealed in a quartz glass vial with scintillator and ^{85}Kr activity was measured with a low-background liquid scintillation counter (LB-5 by ALOKA Co.). Very low detection limit of the counting system, 0.0015 Bq make us possible to apply the present analytical method to relatively old groundwater as well as young groundwater.

Results and discussion

^{85}Kr concentration in the groundwater

Amount of Kr dissolved in surface water is proportional to a partial pressure and vary with temperature. The increasing trend of atmospheric ^{85}Kr concentration did not affect on partial pressure due to very small number of ^{85}Kr molecules in the atmosphere. The Kr extraction system is equipped with a dry vacuum pump (DOP-40D, Ulvac Inc.) which keeps outside of the hydrophobic polyolefin resin tubes vacuum and enforces gas transfer from the groundwater to the outside of the tube through the tube wall by permeation. The extracted gases are compressed into a cylinder through a dry compressor (DOP-80SP, Ulvac Inc.) up to a maximum pressure of 0.5 MPa. Contamination of gases with ambient present air occurs inevitably due to mechanically

incomplete sealing of the vacuum pumps and the contamination becomes larger in accordance with an increase of total usage time of the pump. We estimated the contamination from the ambient air at close condition of a valve installed between the dry vacuum pump and the hollow fiber membrane module. We observed the contamination rate of 0.16-0.36 L min^{-1} depending upon the total usage time of the pump, which obviously increases an apparent ^{85}Kr activity in the cylinder. An apparent extraction rates, which is a sum of the contamination rate and an actual extraction rate were 0.585 L min^{-1} and 0.590 L min^{-1} at Otzu and Ezuko sampling, respectively. We assumed that the contamination by the ambient air was constant during the sampling. A specific activity (SA) of $^{85}Kr/Kr$ dissolved in groundwater is calculated by Eq. 1.

$$SA_{groundwater} = \frac{SA_{observed} \times AER - SA_{presentair} \times CR}{AER - CR} \quad (1)$$

Where $SA_{groundwater}$, $SA_{observd}$ and $SA_{presnetair}$ are the specific activity of $^{85}Kr/Kr$ of the gases dissolved in the groundwater, that of the observed one by analysis and that of the present air (ambient air), respectively. *AER* and *CR* are the apparent extraction rate and the contamination rate, respectively. The ^{85}Kr concentration in the present atmosphere is 1.54 ± 0.05 Bq m^{-3} in 2008 at Fukuoka [18] which corresponds to the specific activity of 1.35 (Bq $mL^{-1}Kr$) is used as $^{85}Kr/Kr$ of the ambient air.

We calculated changes of $SA_{groundwater}$ with *CR* for Otzu and Ezuko and are shown in Fig. 2. With an increase of the contamination rates, the $SA_{groundwater}$ become smaller values. The $SA_{groundwater}$ in Otzu is always higher than that in Ezuko at the same contamination rates. However, the $SA_{groundwater}$ in Ezuko becomes negative values at the contamination rate greater than 0.26 L min^{-1}, suggesting that the contamination rate

should be smaller than 0.26 L min^{-1} during the Ezuko sampling.

^{85}Kr age of the groundwater

To estimate a groundwater age by ^{85}Kr activity we need to know atmospheric ^{85}Kr record. An increasing trend of atmospheric ^{85}Kr concentrations is plotted in Fig. 3 [18, 19-25]. The sampling places of the atmospheric ^{85}Kr are widely distributed in the northern hemisphere. Some of the data obviously higher than the baseline ^{85}Kr concentration are removed in Fig.3. The most probable baseline change after 1977 is obtained by weighted fitting of all data with 20% smoothing coefficient and is shown in Fig.3 by dashed line and the ^{85}Kr concentration before 1975 is taken from Stute and Schlosser [23]. The atmospheric ^{85}Kr concentration baseline obtained is decay corrected to the sampling day (Mar. 14, 2008) and is plotted in Fig. 3. The ^{85}Kr/Kr specific activities of the groundwater at Otzu and Ezuko at different contamination rates are converted to year using the decay corrected ^{85}Kr concentration in Fig. 3 and are shown in Fig. 2. Judging from the total usage time of the pumps at the sampling day, we estimated the contamination rate of 0.20 L min^{-1} and 0.22 L min^{-1} in the Ezuko sampling and the Otzu sampling, respectively. An apparent ^{85}Kr residence time of 8.2 ± 0.7 y for Otzu and 20.7 ± 0.6 y for Ezuko are obtained with 2 σ errors which included activity counting error and other associated errors [18].

Comparison ^{85}Kr age with tritium age

Tritium concentrations of groundwater at Kumamoto Area were measured by

combination of electrolytic enrichment and low-level liquid scintillation counting (Yamaguchi, 2010) and the mean residence time of the groundwater was evaluated using LUMPED model [26], in which the groundwater of the wells reached to the No.2 aquifer were analyzed assuming mixing of two groundwater components. One of the components is an infiltration water from the Shira River by a piston flow and the other is the groundwater flowed from the northern upland's recharge area by an exponential flow. The exponential flow assumes a complete mixing in the aquifer.

The tritium age determined by the LUMPED model for groundwater at Kubota (130°49'4E, 32º51'4N) (the screen depth 88-98 m below ground surface) near the Otzu is 28-30 years and that at Kengun (130°44'1E, 32º46'3N) (the screen depth 21-46m below ground surface) near the Ezuko is 26-41 years. The groundwater sampling locations are shown in Fig. 1. The ^{85}Kr age at Ezuko is close to the value of the tritium age at Kengun but that at Otzu is obviously younger than the tritium age at Kubota. This could be attributed to mixing of water with high ^{85}Kr concentration at Otzu mostly supplied from the Shira River. The mixing of surface water would affect to increase ^{85}Kr concentration and to decrease tritium concentration in groundwater because these radionuclides showing an opposite historical concentration change in the atmosphere and precipitation. The major source of the groundwater at Ezuko is probably that formed by mixing of the two groundwater components at the middle stream area of the Shira River because the lack of lacustrine deposit in this area easily create interaction between the No.1 and No.2 aquifers (Fig. 4).

Model calculation of the Shira River recharge effect on ^{85}Kr age

Based on ^{18}O analysis of groundwater in Kumamoto Area, 30-40 % mixing of the Shira River water was speculated in the area of the middle stream of the Shira River [27]. The sampling location Otsu is situated in the area where mixing of Shira River water occurs. A mixing model is constructed to understand the $^{85}Kr/Kr$ observed at Otzu, in which 30-40% of the Shira River water contained recent $^{85}Kr/Kr$ is considered to be mixed into groundwater flow from the northern upland's recharge area (Fig.4) and we consider that the groundwater at Otzu moves to Ezuko through No. 2 aquifer by piston flow without additional recharge.

Mahara [16]categorized the groundwater basin in Kumamoto Area into four groups based on the correlation between the $^{3}He/^{4}He$ ratio and the ratio of the dissolved equilibrium atmospheric ^{4}He concentration to the total ^{4}He in the samples. The present well and spring are distributed within the groundwater basin of group III which is characterized by a relatively high content of dissolved He and a high $^{3}He/^{4}He$ ratio. This basin is probably overlapped by the major groundwater flow path where groundwater from the groundwater reservoir north of the Shira River flows through the old Kase River Valley, buried by Aso pyroclastic flow deposits, to the Midori River Basin. The well at Otzu is located in the upper of groundwater flow of the group III and the spring at Ezuko is downstream. Therefore, it would be reasonable assumption that Otzu and Ezuko forms continuous flow. A key diagram of water chemistry of this groundwater supports above conclusion, indicating a typical shallow groundwater of $Ca(HCO_3)_2$ type.

The $^{85}Kr/Kr$ SA of the groundwater flow from the north area at Otzu is calculated by Eq. 2.

$$SA_{Sourcewater} = \frac{SA_{groundwater,Otzu} - SA_{ShiraRiver} \times R}{(1-R)} \quad (2)$$

where $SA_{Sourcewater}$, $SA_{groundwater,Otzu}$ and $SA_{ShiraRiver}$ are ^{85}Kr/Kr SA of the groundwater flow from the north area, that observed at Otzu and that supplied from the Shira River, respectively. *R* is a fraction of the Shira River water.

The residence time of the groundwater flow from the northern upland's recharge area was obtained by fitting the $SA_{Sorucewater}$ calculated by Eq 2 to the decay corrected SA shown in Fig. 3. The residence times of 13.5 year and 18.1 year are obtained for R=0.3 and R=0.4, respectively when we assume $SA_{ShiraRiver}$ is equal to that of atmosphere at 2008. Taniguchi et al. [28] categorized the groundwater observation wells distributed in Kumamoto Area into 3 types, recharge, discharge and intermediate types depending on temperature–depth profiles and estimated recharge rates of 0.24–0.48 m y^{-1} for wells which are classified into recharge type and upward groundwater fluxes from 0.12 to 0.36 m y^{-1} for wells which are classified into the discharge type. The infiltration of the Shira River water through unsaturated formation would take a certain time to reach the groundwater table of No.2 aquifer which is flowing from the northern upland's recharge area and a time lag during this downward infiltration would be more realistic in this case because of the depths to groundwater table which is nearly 60 m below the ground surface. We calculated the residence times for the time lag of 5 years and obtained 12.7 year and 16.3 year for R=0.3 and R=0.4, respectively. The residence times decreased slightly compared to the case that $SA_{ShiraRiver}$=2008. The residence time of the groundwater flow from the northern upland's recharge area at Otzu is distributed in a range of 12.7-18.1 year.

The ^{85}Kr/Kr SA at Ezuko is calculated by Eq. 3.

$$SA_{Sourcewater} = \frac{e^{\left(\frac{\ln(2)\times T_{travel}}{HL}\right)} \times SA_{groundwater,Ezuko} - SA_{ShiraRiver} \times R}{(1-R)} \quad (3)$$

where $SA_{groundwater,Ezuko}$ is the observed ^{85}Kr/Kr at Ezuko, T_{travel} is the traveling time of the groundwater from Otzu to Ezuko, and HL is the half life of ^{85}Kr. It should be reminded that the $SA_{Sourcewater}$ and the $SA_{ShiraRiver}$ in Eq. 3 are the values at T_{travel} years ago from the present sampling date at Ezuko.

The residence time of the groundwater flow from the northern upland's recharge area were calculated as a function of the different traveling time and is plotted in Fig. 5. If we assume that the residence time of the groundwater at the Otzu has been kept unchanged during the interested period, the intersection of the estimated residence time at Otzu and the $SA_{Sorucewater}$ would give the most likely traveling time. The traveling times of 13.8 year and 14.1 year are obtained for R=0.3 and R=0.4 for the case that $SA_{ShiraRiver}$=2008, and 13.0 year and 13.4 year for R=0.3 and R=0.4 for the case $SA_{ShiraRiver}$=2003 (5 years time lag). The tritium concentration in the artesian borehole of Kengen City Water Works had analyzed by Kimura [29] and 13 years later by Mahara [16] and at 2008 by Yamaguchi [30]. The tritium concentrations were 20 TU, 9.2 TU and 1.9 TU, respectively, it decreased with almost half life in the higher tritium concentration periods; this probably supports a validity of the assumption of the piston flow between Otzu and Ezuko. The traveling time between Otzu and Ezuko is evaluated to be 13.0-14.1 year that suggests flow rate of 1.1-1.3 km y^{-1}if we assume a straight flow line connection.

Conclusion

The applicability of ^{85}Kr dating was confirmed on semi-confined shallow groundwater at Kumomoto Area. The ages obtained by radioactive tracers, ^{85}Kr and tritium showed generally consistent results indicating the usefulness of ^{85}Kr dating for young groundwater. The age index of ^{85}Kr/Kr has advantages in independency from recharge temperature and excess air trapped during recharge, and conservative nature of Kr in groundwater like tritium. However, a large sample volume, at least a few hundred liters of groundwater is necessary to obtain gas subjected to ^{85}Kr analysis and the correction of contamination of ambient air during the Kr extraction process is necessary. An improvement in Kr extraction system avoidable from contamination of ambient present air would extend applicability of this method to older age groundwater.

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Figure captions

Figure 1. Sampling location and groundwater level above sea level (m) in No. 2 aquifer [31]. Closed circles show sampling location of ^{85}Kr: 1. Otzu and 2. Ezuko and open circles that of tritium: 3. Kubota and 4. Kengun.

Figure 2. ^{85}Kr/Kr (broken line) and mean residence time (solid line) estimated at different contamination rate during Kr extraction process.

Figure 3. A change of atmospheric ^{85}Kr concentration and ^{85}Kr/Kr decay corrected to March 2008. The apparent groundwater age for Otzu and Ezuko are plotted on the decay corrected line.

Figure 4. A model adopted to analyze groundwater flow at Otzu and Ezuko. The lacustrine deposit overlying the Aso-3 is shown [31]. The groundwater at Ezuko is taken from No. 2 aquifer which located below the lacustrine deposit.

Figure 5. Residence time of the groundwater flow from the north recharge area at Otzu as a function of traveling time of the groundwater flow between Otzu and Ezuko. The residence times were calculated at various seepage conditions of the Shira River water. ○ :R=0.3, $SA_{ShiraRiver}$=2008, ● :R=0.4, $SA_{ShiraRiver}$=2008, △:R=0.3, $SA_{ShiraRiver}$=2003, ▲:R=0.4, $SA_{ShiraRiver}$=2003. The residence times for the Otzu sample are shown by horizontal lines.

Fig. 1

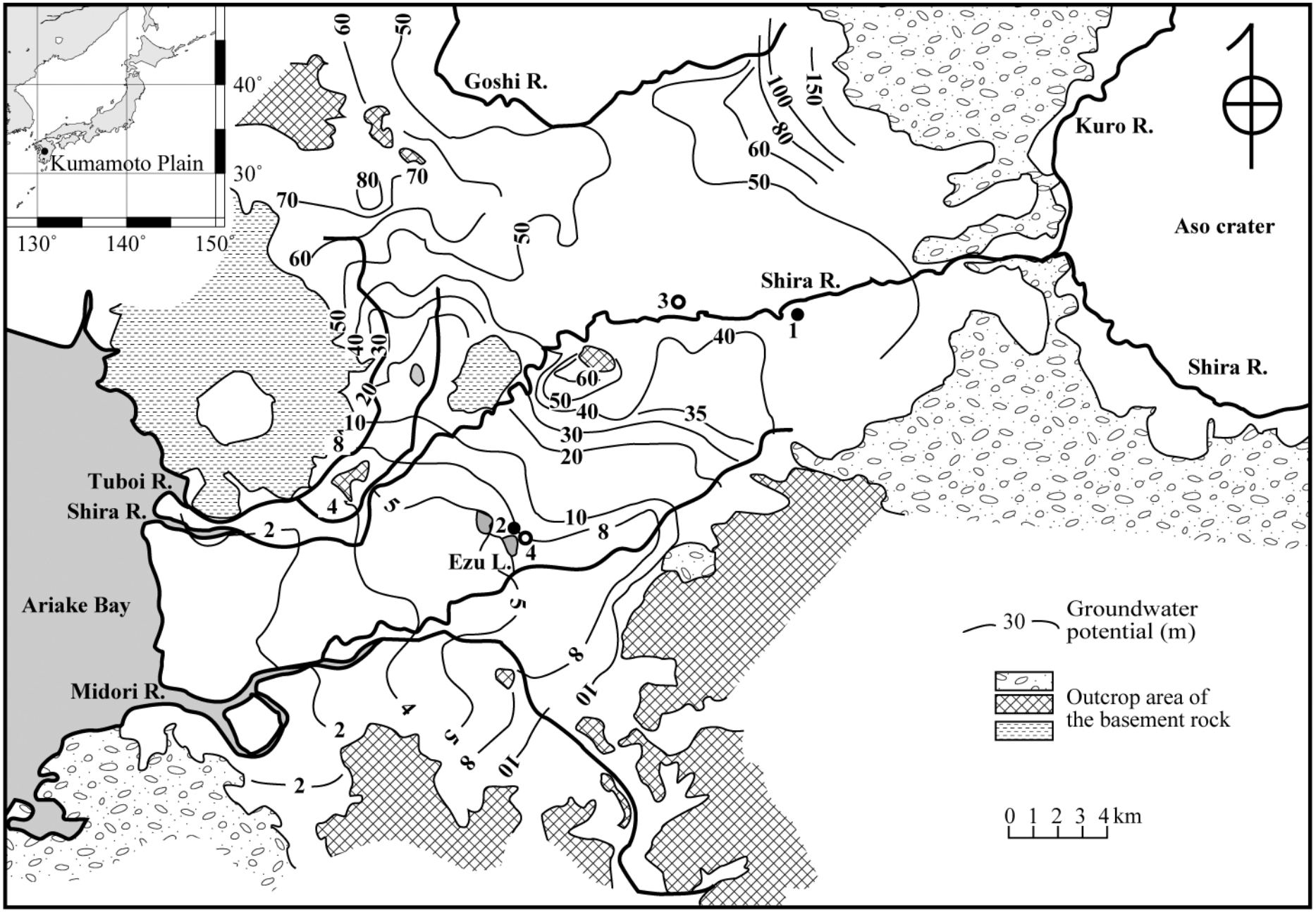
Kumamoto Plain
130°
140°
150°
40°
30°
Goshi R.
Kuro R.
Aso crater
Shira R.
Shira R.
Shira R.
Tuboi R.
Ezu L.
Ariake Bay
Midori R.
1
2
30 Groundwater potential (m)
Outcrop area of the basement rock
0 1 2 3 4 km

Fig. 2a

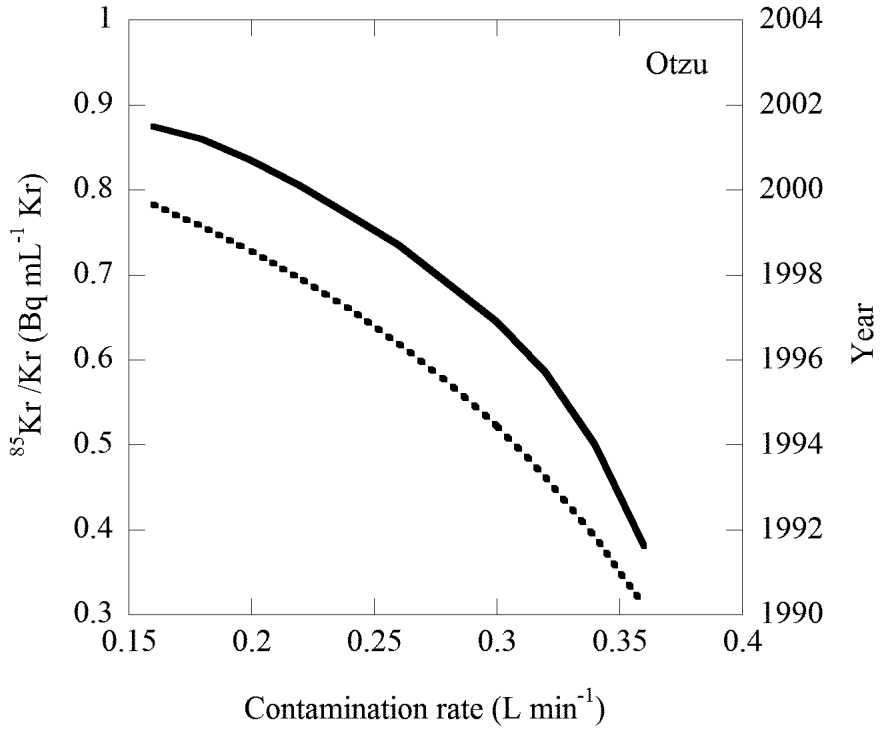
Otzu
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
2004
2002
2000
1998
1996
1994
1992
1990
0.15
0.2
0.25
0.3
0.35
0.4
^{85}Kr /Kr (Bq mL^{-1} Kr)
Year
Contamination rate (L min^{-1})

Fig. 2b

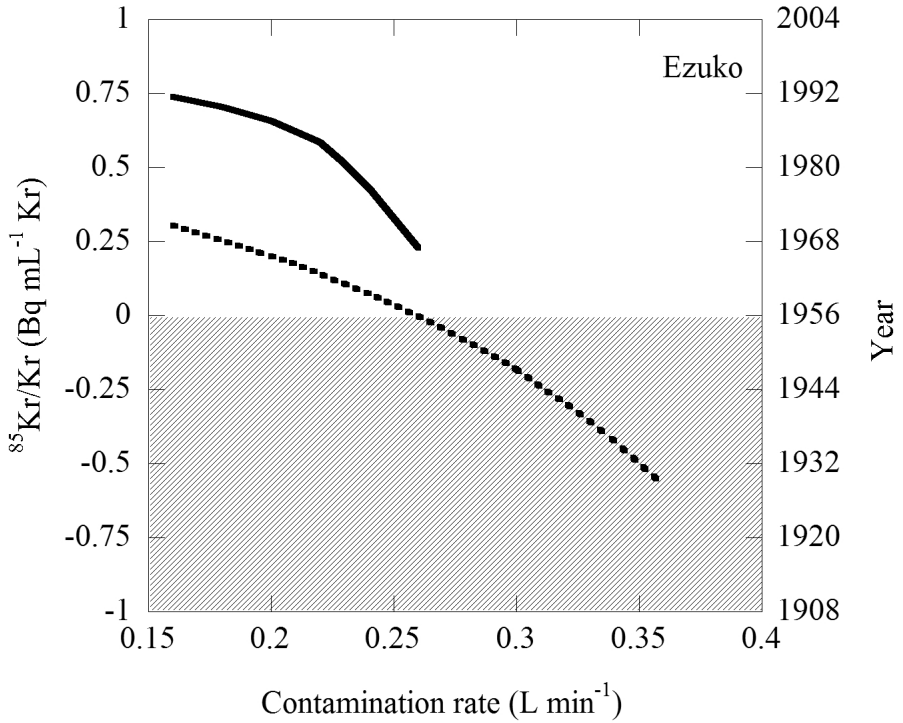
Ezuko
1
0.75
0.5
0.25
0
-0.25
-0.5
-0.75
-1
2004
1992
1980
1968
1956
1944
1932
1920
1908
Year
0.15
0.2
0.25
0.3
0.35
0.4
^{85}Kr/Kr (Bq mL^{-1} Kr)
Contamination rate (L min^{-1})

Fig. 3

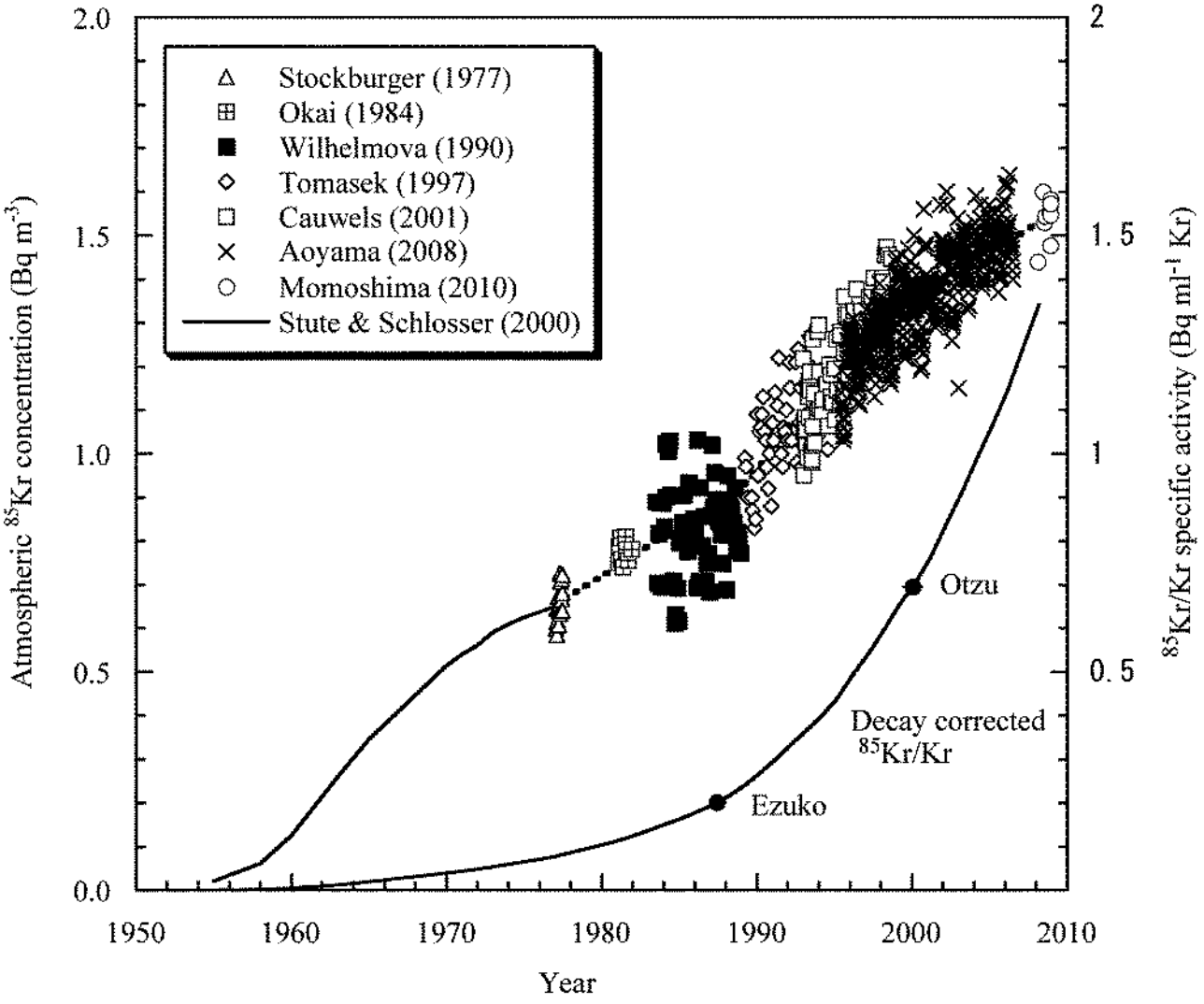
Stockburger (1977)
Okai (1984)
Wilhelmova (1990)
Tomasek (1997)
Cauwels (2001)
Aoyama (2008)
Momoshima (2010)
Stute & Schlosser (2000)
Otzu
Ezuko
Decay corrected
85Kr/Kr
Atmospheric 85Kr concentration (Bq m-3)
85Kr/Kr specific activity (Bq ml-1 Kr)
Year
2.0
1.5
1.0
0.5
0.0
2
1.5
1
0.5
1950
1960
1970
1980
1990
2000
2010

Fig. 4

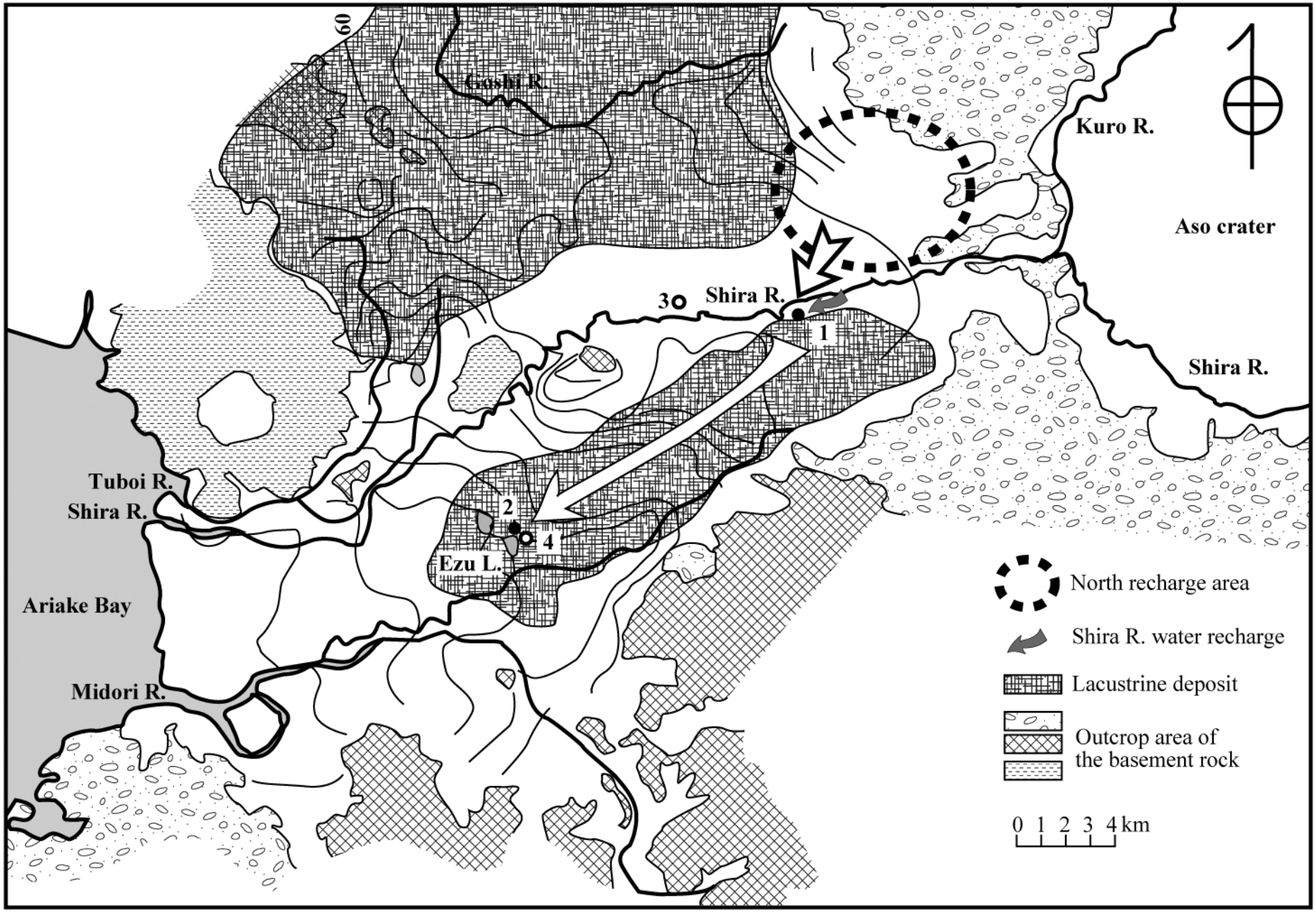
60
Goshi R.
Kuro R.
Aso crater
Shira R.
3
1
Shira R.
Tuboi R.
Shira R.
2
4
Ezu L.
Ariake Bay
Midori R.
North recharge area
Shira R. water recharge
Lacustrine deposit
Outcrop area of
the basement rock
0 1 2 3 4 km

Fig. 5

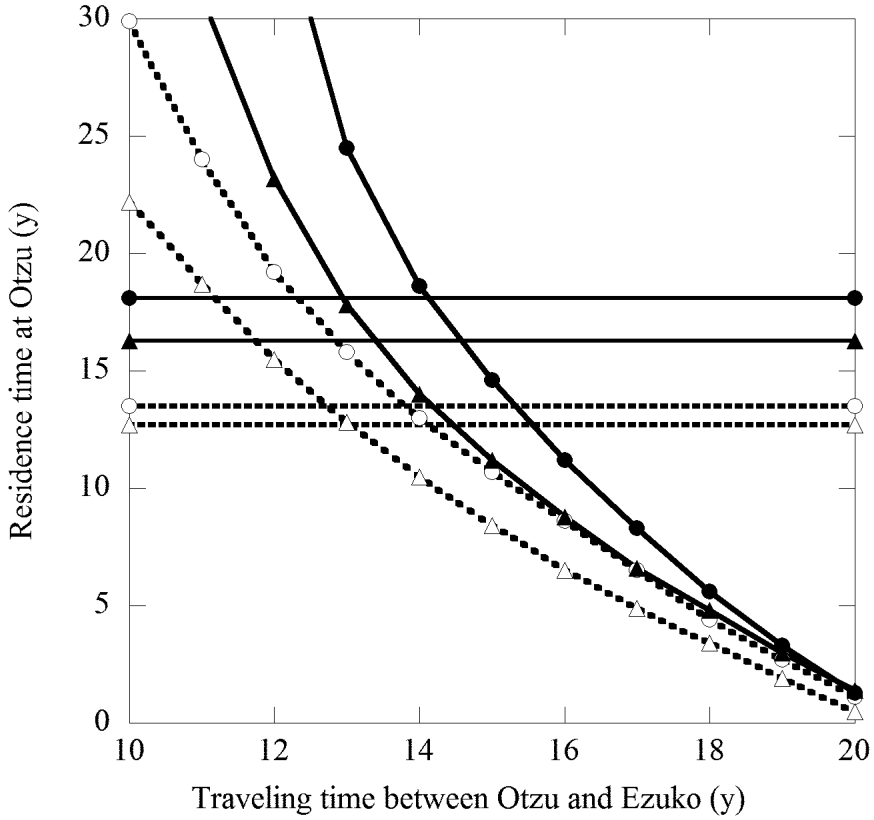
Residence time at Otzu (y)
30
25
20
15
10
5
0
10
12
14
16
18
20
Traveling time between Otzu and Ezuko (y)

Table 1. Sample description

	Otzu	Ezuko
Sampling date	Mar. 15-16, 2008	Mar. 14, 2008
Sampling location	130°52’5E, 32º51’3N	130°44’5E, 32º46’2N
Water treated (L)	6542	5178.9
Gas recovered (L)	239.6	179.4
EC (μS cm^{-1})	217	215
pH	6.86	7.05
Temperature (°C)	21.7	18.5
DO (mg L^{-1})	5.05	5.73
ORP (mV)	-	16