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Determination of Ultralow Level ^{129}I/^{127}I in Natural Samples by Separation of Microgram Carrier Free Iodine and Accelerator Mass Spectrometry Detection

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Separation of carrier free iodine from low iodine level samples and accurate measurement of ultralow level ^{129}I in micrograms of iodine target are essential but a bottleneck in geological dating of terrestrial system and tracer research using naturally produced ^{129}I. In this work, we present a carrier free method using coprecipitation of AgI with AgCl for preparing micrograms of iodine target, associated with combustion using a tube furnace for separating iodine from solid samples and anion exchange chromatography for preconcentrating iodine from a large volume of water. An accelerator mass spectrometry was used to measure ultralow level ^{129}I in micrograms of iodine target. The recovery of iodine in the entire separation procedure is higher than 80% and 65% for solid and water samples, respectively. One microgram iodine in the target (AgI−AgCl) can produce a stable ^{127}I signal for AMS measurement of ^{129}I/^{127}I, and a detection limit of this method for ^{129}I is calculated to be 10^5 atoms. This will allow us to accurately determine ^{129}I in prenuclear geological samples of low iodine concentration with ^{129}I/^{127}I of 10^{-12}, such as loess, soil, coral, rock, sediment, and groundwater. Some samples with low iodine content have been successfully analyzed, and the lowest value of the ^{129}I/^{127}I ratio of 2×10^{-11} was observed in 23.5 and 63.5 m loess samples collected in the Loess Plateau, China. The developed method sheds light on a wide application in earth science.

^{129}I, a long-lived radioisotope of iodine ($t_{1/2}$= 15.7 Ma), is a naturally occurring as well as anthropogenic radionuclide in the environment but dominated by releases from human nuclear activities, which has increased the ^{129}I/^{127}I ratio to $10^{-10}-10^{-6}$ from about 10^{-12}.[1] In nature, ^{129}I is mainly produced

through reactions of cosmic rays with xenon in the upper atmosphere, spontaneous fission of ^{238}U, and thermal neutron-induced fission of ^{235}U. Because of its constant production in nature and radioactive decay of the isolated ^{129}I in the geological layer with a certain rate, ^{129}I is an ideal isotope for geological age dating. On the basis of the analysis of marine sediment samples, an atomic ratio of ^{129}I/^{127}I at 1.5×10^{-12} was suggested as the prenuclear level of ^{129}I in the marine system,[2,3] and natural ^{129}I has been successfully used for dating marine hydrate and organic matters with high iodine concentration.[2,4,5] Because of the relative higher concentration of stable iodine (^{127}I) in the marine system compared with the terrestrial environment, the prenuclear ^{129}I/^{127}I ratio in the terrestrial environment might be different with that in the marine system. Although some investigations had been completed by measuring soil collected before 1940, the reported ^{129}I/^{127}I ratios vary considerably from 5×10^{-12} to 1×10^{-9}.[6] A reliable prenuclear ^{129}I/^{127}I ratio in the terrestrial environment has not yet been estimated, and no dating of low iodine level terrestrial samples using ^{129}I has been reported. In addition, because of the high mobility of iodine, ^{129}I, not only anthropogenic but also naturally produced, is an ideal tracer for geological and environmental research. These works require a sensitive analytical method to determine ultralow level ^{129}I in the low iodine level samples.

Many methods can be used to measure ^{129}I, while accelerator mass spectrometry (AMS) is the only method for determination of ^{129}I in prenuclear age samples with a ^{129}I/^{127}I atomic ratio $< 10^{-10}$. In AMS analysis, the iodine separated from samples is normally prepared as AgI precipitate, which is pressed in a target holder for measurement. This requires obtaining a relative large amount of iodine (1−2 mg) for the target preparation, which is conventionally completed by addition of stable iodine carrier of 1−5 mg

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before analysis of low iodine level samples.[7,8] Stable iodine carrier always contains some ^{129}I, with the commonly used low ^{129}I content stable iodine reagent prepared from old brine, such as that supplied by Woodward Iodine Corporation, the measured $^{129}I/^{127}I$ ratio normally ranges from 0.5 to 2.0×10^{-13},[7–9] although the lowest value of 0.2×10^{-13} has been reported.[10,11] This small amount of ^{129}I in the iodine carrier might be negligible for the analysis of samples with $^{129}I/^{127}I > 10^{-10}$. However, the contribution of ^{129}I in the carrier will make it impossible to determine ultralow level ^{129}I in samples with a low total iodine concentration. To avoid this problem, a carrier free method for the iodine separation and target preparation has to be applied.

In the reported ^{129}I studies, only high iodine content samples, such as seaweed, marine sediment, brine, lignite, and thyroid, have been analyzed for $^{129}I/^{127}I$ by the carrier free method.[2,3,12–15] For separation of iodine from solid samples with low iodine content, such as soil, sediment, and rock, three methods are normally used, i.e., combustion, alkali fusion, and acid digestion, for sample decomposition associated with solvent extraction using CCl_4 (or $CHCl_3$) for separation of iodine from the matrix.[3,7,16,17] In these procedures, stable iodine carrier has to be added to improve the extraction efficiency of iodine from less than 20% to more than 90%.[18,19] A carrier free method has been reported for the separation of iodine from a small volume of seawater sample (<0.1 L) by adding silver powder directly to the acidified seawater and keeping agitated for 24–48 h.[20] However, our tracer experiment showed that the recovery of iodine is lower than 30% when the water volume is 0.05–0.1 L. For separation of iodine from a large volume of water sample (0.1–50 L), solvent extraction or anion exchange followed by solvent extraction is normally used.[2,10,21,22] It is the same as for solid samples; the iodine

carrier has to be added before solvent extraction to improve the chemical recovery. To the best of our knowledge, no reliable method has been reported for separation of carrier free iodine for the measurement of ultralow level ^{129}I in geological and environmental samples with a low total iodine concentration including soil, sediment, and large volumes of water, which prevents the application of ^{129}I as a geological dating tool in the terrestrial environment, as well as an environmental tracer study for low iodine concentration samples such as fumaroles and deep groundwater.[21–23] To achieve the geological dating of terrestrial events, a sensitive and reliable analytical method has to be first established to determine ultralow $^{129}I/^{127}I$ in terrestrial samples with low iodine concentration. With the use of this method, a pernuclear initial value of $^{129}I/^{127}I$ in the terrestrial environment can be established by analyzing suitable terrestrial samples, and a calibration curve for geological dating can be established by determine the $^{129}I/^{127}I$ ratios in a series of known age geological samples (measured by other methods). By determination of the $^{129}I/^{127}I$ ratio in the substance and comparison with the calibration curve, the geological events can be dated.

This work aims at developing a carrier free method for AMS measurement of ultralow level ^{129}I in prenuclear or less anthropogenic ^{129}I contaminated geological and environmental samples with low total iodine concentration, such as soil, loess, sediment, rock, coral, and large volumes of water. With this method, the useful $^{129}I/^{127}I$ ratio is directly determined in the sample, which will not only improve the analytical reliability and precision for low level ^{129}I but also avoid an extra measurement of ^{127}I by another method.

EXPERIMENTAL SECTION

Samples and Chemicals. Two soil samples with depths of 150 and 300 cm to the surface were collected from a freshly exposed soil profile at a construction site in Xi'an, China (34° 13.37′N, 109° 0.02′E) in July 2009; a surface soil sample was collected from a site nearby the above profile in Xi'an in August 2009. A loess profile of 70 m depth was collected in Xifeng, China (35° 43.85′N, 107° 39.10′E) in September 2007, and two samples from this profile at depth of 23.5 and 63.5 m were analyzed in this work. A coral sample was collected at Xuwen, Zhanjiang, China (20°14.3′N, 110°06.8′E) in January 2002. ^{129}I standard solution NIST-SRM-4949c and soil standard reference material NIST-SRM-2711 were purchased from National Institute of Standard and Technology (Gaithersburg, MD), Chinese soil standard reference materials GSS-1 from National Research Center for Certified Reference Materials (Beijing, China), carrier free ^{125}I from China Institute of Atomic Energy, (Beijing, China), ^{127}I carrier (in iodine crystal form) from Woodward Iodine Corporation, (MICAL Specialty Chemicals, New Jersey), and Bio-Rad AG1-X4 anion exchange resin of 50–100 mesh and Cl$^-$ form from Bio-Rad Laboratories (Richmond, CA) were used. All chemical reagents used were of analytical grade, and all solutions were prepared using deionized water (18.2 MΩ).

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Separation of Iodine from Soil, Loess, and Coral Samples. The soil/loess sample was first air-dried after removal of stones and roots; a piece of coral sample was washed with deionized water and air-dried. They were then ground and sieved through a 200 mesh sieve. A total of 20.0 g of dried soil/loess or 5.0 g of coral sample was taken to a quartz boat and mixed with 0.2 mL of ^{125}I tracer (200 Bq). The boat was put into a tube furnace in a combustion system (Fig. S-1 in the Supporting Information). For release of iodine from the sample, the temperature of the tube furnace was gradually increased to 850 °C and remained for 60 min under oxygen gas flashing. The released iodine was carried by the flashing gas, passed through the furnace tube, and trapped in a bubbler, which was connected to the tube furnace in the combustion system and filled with 35 mL of trap solution of 0.4 M $NaOH-0.02$ M $NaHSO_3$. After combustion, the trap solution was collected. The detailed combustion system and method have been reported elsewhere.[24] A volume of 3.0 mL of the trap solution was taken to measure ^{125}I using a gamma counter (model FJ-2021, Xi'an Nuclear Instrument factory, Xi'an, China) for monitoring the recovery of iodine in this step. After the measurement, the solution was analyzed for stable iodine ([127]I) using inductively coupled plasma mass spectrometry (ICPMS) (see the Supporting Information). The remaining trap solution was used for the separation of iodine by coprecipitation.

Two blank samples were prepared using the same method as for soil and coral but without sample. For Blank-2, only ^{125}I tracer was added to quartz boat, while for Blank-3, 300 μg of Woodward iodine and ^{125}I tracer were added to the quartz boat.

Two standard addition samples were prepared. A total of 20 g of Soil-3 (deep soil from Xi'an, China) was first combusted to remove iodine, then 0.100 g of [129]I standard solution was added to the combusted soil in the quartz boat. The spiked soil was analyzed using the same procedure as the soil samples. In 0.100 g of [129]I standard solution, there are 5.04×10^6 atoms of [129]I and 10.0 μg of [127]I, with a [129]I/[127]I atomic ratio of 1.14×10^{10}.

Separation of Iodine from a Large Volume of Water Sample. The water sample was first filtered through a filter paper to remove the suspended matter. After addition of 200 Bq [125]I (NaI) and 0.5 g of $NaHSO_3$, the water was acidified to pH 1−2 using HCl to convert iodine to iodide. The prepared water sample was loaded into a chromatographic column (i.d. 1.5 and 30 cm length for up to 50 L of water) filled with anion exchange resin (Bio-Rad AG1-X4, NO_3^- form, 50−100 mesh). The column was washed with 50 mL of 0.5 M $NaNO_3$ solution. Iodide adsorbed on the column was finally eluted with 400 mL of 2.0 M $NaNO_3$ solution. A volume of 3.0 mL of the eluate was taken to measure ^{125}I to monitor the recovery of iodine in this step, and the remaining eluate was used for the separation of iodine by coprecipitation.

Separation of Carrier Free Iodine from Trap Solutions and Eluate. To the trap solution or eluate, 0.2−2.0 mg of Cl^- as NaCl and $NaHSO_3$ were added, and the pH of the solution was adjusted to 1−2 using HNO_3. A volume of 0.2−1.0 mL of 1.0

M of $AgNO_3$ solution was then added to the solution to coprecipitate iodide as $AgI-AgCl$. After centrifugation, the precipitate was sequentially washed with 3.0 M HNO_3 and deionized water. Finally the precipitate was transferred to a 1.5 mL cone centrifuge tube with water and centrifuged. To investigate the losses of iodine in each step during the method development, 3 mL of supernatant and washes and the final precipitate of the testing samples were counted for [125]I. Figure 1 shows a schematic procedure for the separation of carrier free iodine from solid and water samples for AMS measurement of [129]I/[127]I.

Preparation of [129]I Standards. A series of [129]I standards were prepared as $AgI-AgCl$ coprecipitation for investigation of AMS response to [129]I and [127]I in micrograms of iodine coprecipitated target. Two [129]I standard solutions, with a total iodine concentration of 1.00 mg/mL and [129]I/[127]I atomic ratios of 9.95×10^{-12} and 1.13×10^{-10}, respectively, were first prepared by dilution of [129]I standard solution (NIST-SRM-4949c) with [127]I solution prepared from Woodward iodine. Two [129]I working solutions were prepared using the [129]I standard solution with the [129]I/[127]I ratio of 9.95×10^{-12} by mixing with NaCl solution in Cl/I mass ratios of 2:1 and 4:1, respectively. Six other working solutions of [129]I were prepared using the [129]I standard solution with a [129]I/[127]I ratio of 1.13×10^{-10} by mixing with NaCl solution in Cl/I mass ratios of 10:1, 20:1, 40:1, 100:1, 200:1, and 1000:1, respectively. The concentration of Cl in the working solutions was 1.00 mg/mL. From each standard, 0.50 mL of working solution was taken to a 15 mL centrifuge tube, after addition of about 200 Bq ^{125}I tracer, 0.1 mL of 0.1 M $NaHSO_3$, 0.2 mL of 1 M HNO_3, 10 mL of deionized water, and 0.1 mL of 1.0 mol/L $AgNO_3$ were added to coprecipitate iodine as $AgI-AgCl$. After centrifugation, the precipitate was sequentially washed with 3.0 M HNO_3 and deionized water.

Preparation of Target and AMS Measurement of [129]I. The $AgI-AgCl$ coprecipitate (after drying at 60−70 °C) in the 1.5 mL centrifuge tube was weighed and ground to a fine powder; 2−3 times by mass of niobium powder (325 mesh, Alfa Aesar, Ward Hill, MA) was added to the tube and mixed with the coprecipitate. The mixture was transferred and pressed into a copper holder for AMS measurement. The amount of total iodine pressed in the holder for the standards shown in Table 3 are calculated by the amount of total coprecipitate; the chemical yield during preparation was measured by ^{125}I and the Cl−I ratio in the working solution. A 3 MV Tandetron AMS system (HVEE) at the Xi'an AMS Center was used to measure [129]I. I^{5+} sputtered from the ion source was chosen for the measurement, where $^{127}I^{5+}$ was measured as charges (current) using a Faraday cup, and [129]I was measured using a gas ionization detector. All samples were measured for 6 cycles and for 5 min per sample in each cycle. A detailed description of AMS system and measurement of [129]I has been reported elsewhere.[24]

RESULTS AND DISCUSSION

Reliability of Combustion Method for Separation of Iodine from Solid Samples. In this work, 20 g of soil/loess and 5 g of coral samples were combusted to separate iodine, and an iodine recovery of 90−100% in the trap solution monitored by ^{125}I, in most case higher than 95%, was obtained. The recovery of lower than 95% for some samples might be attributed to occasionally

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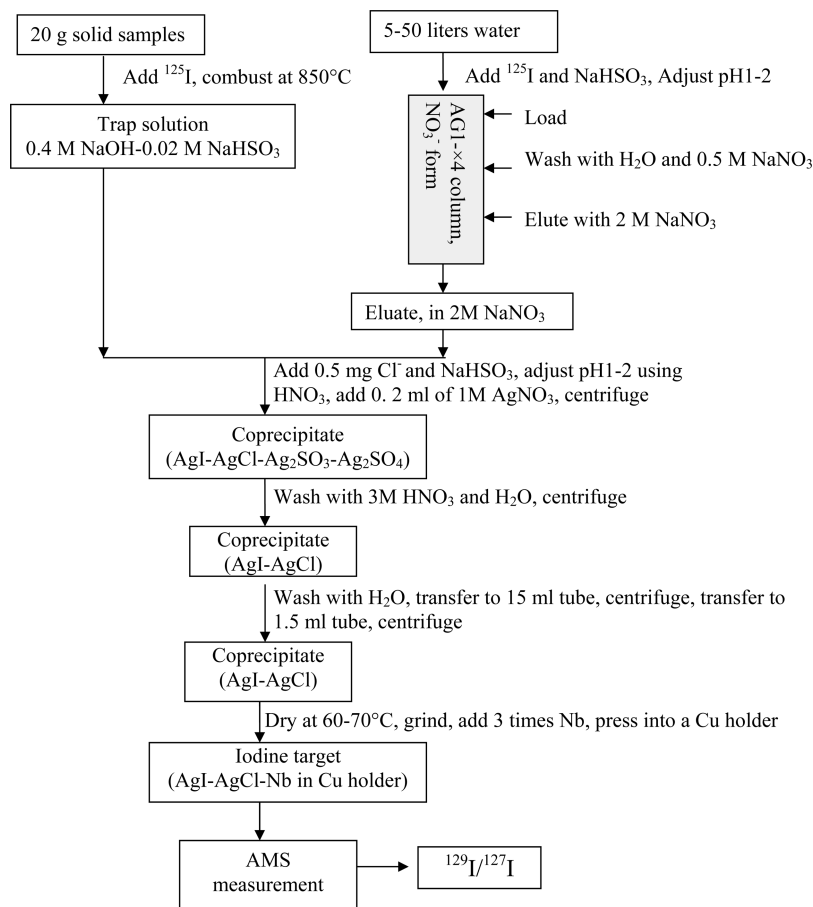
Figure 1. Schematic diagram of the analytical procedure for separating micrograms of carrier free iodine from solid and water samples.

reduced trapping efficiency of iodine in the trap solution. Two cascade trapping bubblers have been tested to collect the released iodine, and the results indicate that the ^{125}I in the second trap solution ranges 0.1%−10% and in most case less than 2%. This observation agreed with those observed by Muramatsu et al.[17] Therefore only one bubbler was used for collecting iodine in this work. Since the chemical forms of iodine in the samples are not only iodide, the ^{125}I tracer might not represent behavior of all iodine in the combustion process. To confirm that all species of iodine in the sample are released during combustion at 850 °C, iodine in two soil standard reference materials (Montana soil NIST-SRM-2711 and Chinese soil GSS-1) were separated using the established combustion system, and iodine in the trap solution was measured using ICPMS; the analytical results (3.22 ± 0.21 $\mu g/g$ for NIST-271 and 1.75 ± 0.24 $\mu g/g$ for GSS-1) agreed well with the certified or information values (3 $\mu g/g$ for NIST-2711 and 1.9 ± 0.4 $\mu g/g$ for GSS-1) reported in the certification datasheets, indicating that all forms of iodine can be completely released from the sample at the experimental conditions.

Since the ^{129}I level in the analyzed environmental and geological samples might be 3−4 orders of magnitude different, the $^{129}I/^{127}I$ atomic ratio ranges from 10^{-12} in the aged geological samples to 10^{-8} in the surface soil. The memory effect, i.e., the interference of iodine that remains in the combustion system from one sample to the immediately following sample, is a pivotal issue in the determination of ^{129}I

in low level samples. An experimental procedure blank, i.e., only ^{125}I tracer without sample in the quartz boat, was analyzed immediately after a high ^{129}I level sample (Soil-1, Table 1) using the same furnace tube in the combustion system. The results (Table 1) show no significant ^{129}I and ^{127}I signal was observed in the blank (Blank-2), indicating no significant memory effect occurred in the combustion system; this result also confirms the complete release of iodine from the soil sample during combustion.

It has been reported that iodine released from the solid sample during combustion could be adsorbed on the outlet of the furnace tube.[16] The author had also observed that 20−50% of iodine was adsorbed in the outlet when using a combustion system supplied by Carbolite (Hope Valley, England), wherein an extra exhaust manifold between combustion tube and trap bubbler was applied. In this work, the length of the outlet part of the combustion tube (out of the furnace) was kept to less than 2 cm to avoid condensation and adsorption of iodine on the outlet of the work tube. Because the catalyst zone in the furnace (see Fig. S-1 in the Supporting Information) was heated to 900 °C, the outlet part of the combustion tube was at high temperature (>350 °C), no adsorption of iodine in the outlet was detected in this combustion system.

Anion Exchange Separation of Iodine from Large Volumes of Water Samples. Iodine in up to 50 L of groundwater has been successfully separated by an anion exchange chromatography using a 53 mL column (i.d.1.5 cm, and 30 cm in length)

Table 1. Analytical Results of ^{129}I and ^{127}I in Blanks and Some Solid Samples Using Combustion and AgI–AgCl Coprecipitation for Separation of Carrier Free Iodine and AMS for Measurement

sample	sampling location in China	sampling depth, cm	intensity of signals in 5 min[a]		measured ^{129}I/^{127}I ratio by two methods[b]	
			^{127}I, (Coulomb)	^{129}I, (counts)	coprecipitate	conventional
Blank-1 (Nb powder)[c]			$(7.25 \pm 0.87) \times 10^{-8}$	0.38 ± 0.33		
Blank-2 (combustion)[d]			$(7.72 \pm 1.35) \times 10^{-8}$	0.42 ± 0.41		
Blank-3 (300 μg of WWI)[e]			$(8.38 \pm 0.59) \times 10^{-5}$	16.73 ± 2.42	$(2.10 \pm 1.31) \times 10^{-13}$	$(2.21 \pm 1.23) \times 10^{-13}$
Soil-1	Shanghai	0–10	$(4.42 \pm 0.46) \times 10^{-6}$	6314.46 ± 704.64	$(1.14 \pm 0.04) \times 10^{-9}$	$(1.15 \pm 0.09) \times 10^{-9}$
Soil-2	Xi'an	0–10	$(6.38 \pm 1.89) \times 10^{-7}$	376.51 ± 278.1	$(4.53 \pm 0.22) \times 10^{-10}$	$(4.68 \pm 0.32) \times 10^{-10}$
Soil-3	Xi'an	140–160	$(1.04 \pm 0.27) \times 10^{-6}$	48.26 ± 13.32	$(3.72 \pm 0.62) \times 10^{-11}$	$(4.82 \pm 1.13) \times 10^{-11}$
Soil-4	Xi'an	290–310	$(3.05 \pm 0.58) \times 10^{-6}$	74.35 ± 21.73	$(1.97 \pm 0.56) \times 10^{-11}$	$(3.37 \pm 1.01) \times 10^{-11}$
Loess-1	Xifeng	2350–2360	$(1.43 \pm 0.21) \times 10^{-6}$	28.95 ± 5.91	$(1.67 \pm 0.52) \times 10^{-11}$	$(3.17 \pm 0.87) \times 10^{-11}$
Loess-2	Xifeng	6350–6360	$(2.18 \pm 0.47) \times 10^{-6}$	48.03 ± 4.72	$(1.83 \pm 0.41) \times 10^{-11}$	$(3.24 \pm 0.98) \times 10^{-11}$
Coral	Zhanjiang		$(3.71 \pm 0.69) \times 10^{-7}$	22.44 ± 7.74	$(4.83 \pm 1.47) \times 10^{-11}$	$(5.53 \pm 1.06) \times 10^{-11}$
std addition sample 1[f]			$(1.73 \pm 0.42) \times 10^{-6}$	229.78 ± 61.46	$(1.06 \pm 0.03) \times 10^{-10}$	$(1.21 \pm 0.12) \times 10^{-10}$
std addition sample 2[f]			$(1.22 \pm 0.11) \times 10^{-6}$	175.91 ± 36.88	$(1.16 \pm 0.08) \times 10^{-10}$	$(1.15 \pm 0.11) \times 10^{-10}$

[a] The results are given as average and 1 standard division of 6 measurements for samples prepared by coprecipitation; the high SD of ^{129}I and ^{127}I signals are attributed to the inhomogeneity of iodine in targets and variation in the ionization efficiency. [b] The ^{129}I/^{127}I ratio was given as an average of six measurements, which was corrected by comparison with standard and blank subtraction. The uncertainty was estimated including the measurement errors for the samples, blanks, and standards. The analytical results by both the developed carrier free AgI–AgCl coprecipitation method and the conventional stable iodine addition and AgI precipitation method are given. In the conventional method, the listed ^{129}I/^{127}I ratio was calculated by the measured ^{129}I/^{127}I ratio in the target, the added amount of ^{127}I carrier (1.05 mg of Woodward iodine), and measured ^{127}I concentration in samples by ICPMS, and no correction was made for the contribution of ^{129}I from ^{127}I carrier. [c] Only niobium powder was pressed in the holder. [d] The same analytical procedure as for soil/loess using combustion and AgI–AgCl coprecipitation, but no sample was applied. [e] The same procedure as Blank-2, but 300 μg of Woodward iodine was added to the boat before combustion. [f] 20 g of Soil-2 sample was first combusted to remove iodine, then 0.100 g of ^{129}I standard solution was added to the combusted soil. The spiked soil was analyzed using the same procedure as other solid samples. In 0.100 g of ^{129}I standard solution, there are 5.04×10^6 atoms of ^{129}I and 10.0 μg of ^{127}I, with a ^{129}I/^{127}I atomic ratio of 1.14×10^{10}.

filled with AG1-X4 resin in NO_3^- form, and an iodine recovery of 80−85% was obtained. This method is based on a strong affinity of iodide compared with other common anions in the water including NO_3^-, Cl^-, Br^-, IO_3^-, and NO_3^-. In the water sample, iodine mainly exists as iodate, iodide, and organic iodine. With the the low affinity of iodate and periodate, the high oxidation states of iodine are often reduced to iodide using sulphite in acidic medium before loading to the column to separate all inorganic iodine. However, this process could not convert organic iodine to iodide and collect it on the column. In most of groundwater, organic iodine is minor,[25] and it is sufficient to separate most iodine by sulphite reduction combined with anion exchange separation. However, in river, lake, and rainwater, a large fraction of iodine might be organic iodine, and an extra step has to be applied to decompose organic matter in the water and convert all organic iodine to iodide. Since this work focuses on the ultralow level ^{129}I in groundwater, no organic iodine was involved.
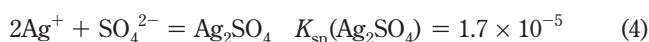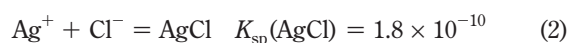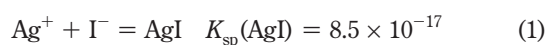
To improve separation efficiency, the strong basic anion exchange resin has to be converted to the NO_3^- form. Because the affinity of NO_3^- to the resin is higher than Cl^- and Br^- but lower than I^-, a larger volume of water, especially high chloride content water, can be treated by resin in nitrate form without breakthrough of iodide.[26]

Hypochlorite is often used to elute iodide from the column by on-column oxidizing iodide to iodate because of the low affinity of iodate with the resin.[21] However, this method introduces a huge amount of chlorine to the eluate, so a step of stable iodine carrier addition and solvent extraction using CCl_4 (or $CHCl_3$) has to be followed to separate iodine from the eluate for AgI target preparation, which makes it impossible to prepare carrier free

iodine. In this work, 2 M nitrate was selected to elute iodide from the column. With 400 mL of eluent, an iodine recovery of 80−85% was obtained. The slight lower recovery of iodine comparing with elution using hypochlorite is mainly attributed to the tailing of the elution. Although the affinity of Cl^- and Br^- is lower than NO_3^-, some amount of Cl^- and Br^- could still be absorbed on the column, which was successfully removed by washing with 50−70 mL of 0.5 M $NaNO_3$ solution before elution.

Coprecipitation of AgI with AgCl for Preparation of Microgram Carrier Free Iodine. AgI–AgCl coprecipitation was used to separate micrograms of carrier free iodine from the trap solution and $NaNO_3$ eluate, and an iodine recovery of 70−85% was obtained when adding 0.5 mg of Cl^- in the solution containing 20 mM $NaHSO_3$. Considering the loss of iodine in the separation of iodine from the solid matrix by combustion and preconcentration from a large volume of water by anion exchange chromatography, an overall recovery of iodine in the entire procedure is higher than 80% and 65% for soil and water samples, respectively.

In the AgI–AgCl coprecipitation process, many precipitation reactions might be involved; these reactions and the solubility products (K_{sp}) of the corresponding precipitation products are listed below:
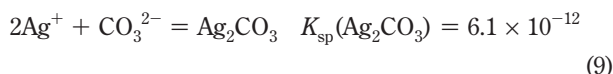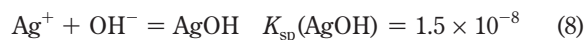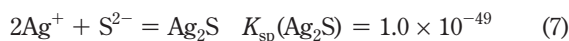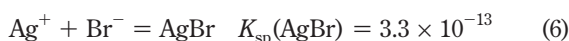
$$Ag^+ + I^- = AgI \quad K_{sp}(AgI) = 8.5 \times 10^{-17} \quad (1)$$

$$Ag^+ + Cl^- = AgCl \quad K_{sp}(AgCl) = 1.8 \times 10^{-10} \quad (2)$$

$$2Ag^+ + SO_3^{2-} = Ag_2SO_3 \quad K_{sp}(Ag_2SO_3) = 1.5 \times 10^{-14} \quad (3)$$

$$2Ag^+ + SO_4^{2-} = Ag_2SO_4 \quad K_{sp}(Ag_2SO_4) = 1.7 \times 10^{-5} \quad (4)$$
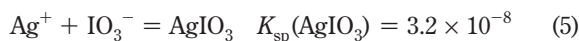
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Table 2. Effects of Cl⁻ Amount and Concentration of NaHSO₃ on Iodine Recovery in the Separation of Iodine Using AgI−AgCl Coprecipitation[a]

Cl⁻ add, mg	NaHSO₃ concn, mM	loss of iodine in the coprecipitation process, %			final recovery%
		first precipitation	HNO₃ wash	H₂O wash	
0.20	20.0	25.4 ± 3.5	45.4 ± 5.7	0.6 ± 0.4	33.2 ± 5.6
0.50	20.0	6.5 ± 3.3	16.3 ± 2.4	0.4 ± 0.4	77.9 ± 6.7
0.80	20.0	3.1 ± 2.1	9.3 ± 3.6	0.5 ± 0.5	87.4 ± 5.2
1.00	5.0	14.5 ± 1.7	0.8 ± 0.4	0.4 ± 0.5	84.3 ± 2.6
1.00	12.5	7.8 ± 1.4	4.5 ± 1.6	0.4 ± 0.4	89.8 ± 2.4
1.00	20.0	2.5 ± 3.1	7.1 ± 2.2	0.5 ± 0.3	91.5 ± 4.3
1.00	25.0	2.2 ± 1.3	11.5 ± 2.7	0.5 ± 0.3	86.5 ± 4.7
1.00	50.0	1.7 ± 1.0	40.8 ± 5.4	0.4 ± 0.4	57.8 ± 6.0
1.00	60.0	1.5 ± 0.7	60.5 ± 8.8	0.5 ± 0.4	38.8 ± 8.9
1.00	80.0	1.2 ± 0.6	65.7 ± 4.3	0.4 ± 0.4	33.9 ± 4.4
2.00	20.0	1.6 ± 1.2	2.5 ± 1.7	0.6 ± 0.4	95.1 ± 2.1
5.00	20.0	1.2 ± 0.7	1.6 ± 0.7	0.5 ± 0.4	96.9 ± 1.8

[a] Average ± SD, $n = 3$. Solution: 35 mL of 1.0 M NaNO₃ containing 500 Bq ¹²⁵I, 20 μg of iodide, and 2 mmol of Ag⁺, pH = 1−2.

$$Ag^+ + IO_3^- = AgIO_3 \quad K_{sp}(AgIO_3) = 3.2 \times 10^{-8} \quad (5)$$

$$Ag^+ + Br^- = AgBr \quad K_{sp}(AgBr) = 3.3 \times 10^{-13} \quad (6)$$

$$2Ag^+ + S^{2-} = Ag_2S \quad K_{sp}(Ag_2S) = 1.0 \times 10^{-49} \quad (7)$$

$$Ag^+ + OH^- = AgOH \quad K_{sp}(AgOH) = 1.5 \times 10^{-8} \quad (8)$$

$$2Ag^+ + CO_3^{2-} = Ag_2CO_3 \quad K_{sp}(Ag_2CO_3) = 6.1 \times 10^{-12} \quad (9)$$

During combustion at high temperature with oxygen gas flow, iodine might be released as molecular iodine, which was trapped in alkali solution through a disproportion reaction and converted to iodide and iodate. Because of the relative higher solubility of AgIO₃ compared with other compounds, especially AgCl, and a low concentration of iodine in the solution, iodate has to be converted to iodide to obtain a better recovery in the coprecipitation process, which is often completed by sulfite at pH < 2. During the acidification with HNO₃ and reduction of iodate to iodide, some sulfite was oxidized to sulfate. Some sulfite added to the trap solution for improving the trapping efficiency could be also converted to sulfate during combustion under oxygen flow. Sulfur, sulfide and organic sulfur in the sample can be released during combustion, oxidized to SO₂, and collected in the trap solution as sulfite and sulfate. The formation of Ag₂S might be less important for soil and sediment samples during the coprecipitation step. The concentration of bromine in solid samples (except the marine sample) is normally low (<10 μg/g in soil), and the bromine containing compounds are also less volatile. A small amount of Br⁻ in the trap solution will not significantly influence the formation of AgI−AgCl and the amount of final precipitate. Carbon in the samples was released as CO₂ from the sample during combustion and converted to carbonate in the NaOH trap solution, but it was decomposed to CO₂ again and removed from the solution during acidification to pH < 2 using HNO₃ and did not influence the AgI−AgCl coprecipitation. Therefore the reactions 1−4 are the most important ones for preparation of carrier free iodine from the trap solution and eluate, amount of

Cl⁻ added as a coprecipitation agent, sulphite concentration, amount of Ag⁺ added to form precipitation, and pH of the solution might be critical parameters affecting the recovery of iodine and purity of the final coprecipitate.

The results (Table 2) show that iodine recovery increases with the increased amount of Cl⁻ from 0.2 to 0.8 mg, and iodine can be quantitatively coprecipitated when more than 0.8 mg of Cl⁻ was added and the NaHSO₃ concentration was 20 mM. For a given amount of Cl⁻ (1.0 mg) in the solution, the iodine recovery increases from 85% to 98% when increasing the NaHSO₃ concentration from 5 to 20 mM and then keeping it constant when the NaHSO₃ concentration is higher than 60 mM (Table 2). However, the amount of precipitate is quite large (>200 mg) when the NaHSO₃ concentration is higher than 20 mM, this is attributed to the formation of Ag₂SO₃ precipitate and probably also Ag₂SO₄ due to their low solubility. It is known that Ag₂SO₃ and Ag₂SO₄ precipitates are easily dissolved in acidic solution, especially in a high concentration of HNO₃. Therefore, the coprecipitate was washed with 3 M HNO₃ to remove the Ag₂SO₃ and Ag₂SO₄ followed by a water wash to remove the acid. The final precipitate contains only AgI and AgCl, which was confirmed by the final precipitate weight of about 4 mg and about 90% recovery of iodine for a solution containing 1.0 mg of Cl and 20 μg of iodide.

It was observed that some iodine was lost during the acid wash, and the loss of iodine increases from 1.6% to 45% with decreasing the amount of Cl⁻ from 5.0 to 0.2 mg in 20 mM NaHSO₃ solution. With a given amount of Cl⁻ (1.0 mg), the loss of iodine increases from 0.8% to 66% when increasing the NaHSO₃ concentration from 5.0 to 80 mM. There was no significant loss of iodine in the water wash of the precipitate. As a consequence, the recovery of iodine in the final coprecipitate of AgI−AgCl increases from 33% to 78% when increasing the Cl⁻ amount from 0.2 to 0.5 mg. With a further increase of Cl⁻ from 0.5 to 5 mg, a small increase of iodine recovery from 78% to 97% was obtained. Considering only 1−2 mg of coprecipitate can be pressed in the target holder for AMS analysis, 0.5 mg of Cl⁻ was chosen in the optimized protocol. In the 2 M NaNO₃ eluate, iodine exists as iodide and it is not necessary to add reductant NaHSO₃ and to acidify the solution. However, for improvement

Table 3. Results of AMS Measurements for ^{129}I and ^{127}I in a Series of ^{129}I Standards with Different Amounts of Iodine (as AgI−AgCl Coprecipitate) in the Target Holder

Cl/I, mass ratio	iodine in holder μg	reference value of $^{129}I/^{127}I$, 10^{-11} at/at	measured ^{129}I signal in 5 min.[a]		measured ^{127}I signal in 5 min.[a]		$^{129}I/^{127}I$ atom ratio $\times 10^{-11}$ [b]
			counts	RSD, %	Coulomb, $\times 10^{-6}$	RSD, %	
	0	Nb blank	1.6	151.35	0.05	60.94	
2	75.54	0.995	141.0	15.44	11.51	11.55	0.99 ± 0.05
4	41.65	0.995	86.7	18.99	6.82	20.39	1.02 ± 0.07
10	17.75	11.38	275.6	12.64	2.19	9.79	11.75 ± 0.49
20	9.08	11.38	198.7	8.81	1.54	9.11	11.32 ± 0.63
40	4.59	11.38	80.5	11.34	0.64	10.39	10.62 ± 0.77
100	1.85	11.38	36.0	27.57	0.29	15.64	11.51 ± 1.15
200	0.93	11.38	28.4	20.25	0.23	21.46	11.33 ± 1.25
1000	0.19	11.38	4.8	49.09	0.08	44.33	11.97 ± 2.92

[a] Average and 1 SD of 6 measurements. [b] Average of 6 measurements, corrected by blank subtraction and against the standard. The bigger variations (SD) for ^{127}I and ^{129}I signals are attributed to the inhomogeneity of AgI in the holder as well as the variation of the ionization efficiency of the iodine target. However, this does not affect the uncertainty of the measured $^{129}I/^{127}I$ ratio because ^{129}I and ^{127}I are simultaneously sputtered in the ion source and injected to the AMS system. The uncertainty of the $^{129}I/^{127}I$ value was estimated by the measurement errors in the samples, standards, and blanks.

of iodine recovery, $NaHSO_3$ was also added to a concentration of 20 mM before coprecipitation.

Because of similar chemical properties and crystal structures of AgI and AgCl, AgI can be carried as a coprecipitate with AgCl during the coprecipitation. When the amount of Cl^- plus iodide is low, the loss of precipitate is significant due to adsorption on the wall of the centrifuge tube as well as other tools contacting the solution. With an increased amount of Cl^- in the solution, the loss of iodine is reduced. Chemical properties and the crystal structure of Ag_2SO_3 are different from those of AgI, but the precipitates of Ag_2SO_4 and Ag_2SO_4 can wrap AgI during the formation of the precipitate and the centrifugation processes. This causes an increased recovery of iodine with the increased $NaHSO_3$ concentration in the coprecipitation step, especially when the amount of added Cl^- is small. When Ag_2SO_3 and Ag_2SO_4 precipitates were dissolved by HNO_3 during the acid wash, the wrapped AgI was released to the solution. Since the amount of AgI was too small, it was suspended in the solution and could not be precipitated in the following centrifugation process. The amount of AgI wrapped in the Ag_2SO_3 and Ag_2SO_4 precipitates is directly related to the relative amount of AgCl compared with the amount of Ag_2SO_3 and Ag_2SO_4. As a consequence, the losses of iodine increase with the increased $NaHSO_3$ concentration and with a decreased amount of Cl^- (Table 2).

In principle, for a certain iodide concentration, the larger the Ag^+ amount that is added to the solution, the better is the recovery of iodine. However, it was observed that the recovery of iodine in AgI and AgI−AgCl precipitation decreased when the concentration of Ag^+ was higher than 0.4 M (Table S-1 in the Supporting Information). When the Ag^+ concentration was higher than 0.8 M, no AgI precipitate was formed and the formed AgI precipitate can even be dissolved in 1 M $AgNO_3$ solution. The reason for this process is unknown; a soluble complex of AgI with $AgNO_3$ probably formed at a high concentration of $AgNO_3$. In this work, Ag^+ added to the trap solution and the eluate was adjusted to a molecular ratio of $Ag^+/(I^- + Cl^-)$ higher than 2 but the concentration of Ag is less than 30 mM. In summary, the optimum coprecipitation conditions are 0.5 mg of Cl^-, 20 mM $NaHSO_3$, and a $Ag^+/(I^- + Cl^-)$ molecular ratio of 2−5.

AMS Measurement of ^{129}I and ^{127}I in Micrograms of Iodine. An I^{5+} current of 1−15 nA was observed in the AMS measurement of carrier free iodine targets prepared as AgI−AgCl coprecipitate from soil/loess samples (Table 1), while I^{5+} current was normally less than 0.3 nA in blank samples (no iodine). The analytical results of a series of ^{129}I standards prepared as AgI−AgCl coprecipitates with Cl/I ratios of 2−1000 (Table 3) show that the ^{127}I signal in a AgI−AgCl target containing 0.9 μg of iodine is about 4 times higher than that in the blank. When the iodine amount was reduced to 0.19 μg, the ^{127}I signal was close to the blank, while the ^{129}I signal was still 3 times higher than that in the blank when the $^{129}I/^{127}I$ ratio in the sample is 1.1×10^{-10}. After a correction by subtraction of the blank (for ^{129}I and ^{127}I signals in Nb powder), a good positive correlation ($R^2 = 0.996$) was observed between the ^{127}I signal and the amount of iodine in the target holder in the range of 0.19−75 μg (Fig. S-2 in the Supporting Information). In addition, the measured $^{129}I/^{127}I$ values in the standards are also in good agreement with the expected values (Table 3, Fig. S-3 in the Supporting Information).

These results indicate that 1 μg of iodine in the target can produce a reliable ^{127}I signal for AMS measurement and used for analysis of samples with a $^{129}I/^{127}I$ ratio higher than 3×10^{-11}. While for sample with a $^{129}I/^{129}I$ ratio at 1×10^{-12}, 30 μg of iodine need to be separated and pressed in the holder, and more than 200 μg iodine is necessary for sample with a $^{129}I/^{127}I$ ratio lower than 1×10^{-13}. On the basis of this result, a detection limit of this method for ^{129}I can be calculated as 3 times the blank to be 10^5 atoms (or 2×10^{-17} g).

The iodine concentration in soil sample is normally 1−5 $\mu g/g$. In this work, 20 g of sample was used; iodine in the prepared AgI−AgCl target might be higher than 15 μg considering a 80% recovery of iodine, which enables one to determine a $^{129}I/^{127}I$ ratio down to 2×10^{-12}. For fresh water including groundwater, the iodine concentration is normally higher than 0.5 $\mu g/L$, a ratio of $^{129}I/^{127}I$ higher than 2×10^{-12} can be determined in 50 L of sample using the developed method. Therefore, the developed method can be used to determine a $^{129}I/^{127}I$ ratio higher than 2×10^{-12} in both water and solid samples with low level iodine (>1 $\mu g/g$ or >0.5 $\mu g/L$). For samples with a $^{129}I/^{127}I$ ratio lower than 10^{-12}, a large size sample has to be analyzed, which can

be completed by repeating the combustion or anion exchange procedure.

In conventional AMS measurement of [129]I, approximate 1−2 mg of AgI is normally used to obtain a reliable [129]I and [127]I signal. Lu et al.[27] recently reported that 0.3 mg of AgI is sufficient to provide a stable beam current, and 0.1 mg is the lowest mass of AgI that can be manipulated and used in AMS to produce a sustainable current for a [129]I/[127]I ratio measurement. Yiou et al.[20] reported that as low as 2 μg of iodine in the target can produce a high energy I^{5+} current of 5 nA, and they had successfully used less than 2 μg of iodine to measure [129]I/[127]I in seawater. Our results show that 1 μg of iodine is needed to produce a stable and reliable current of iodine ion in our AMS measurement.

Analytical Quality Control. There is no suitable standard reference material (SRM) with a certified [129]I value available. Although a few SRMs including IAEA-375 (soil), NIST-SRM-4359 (seaweed), and IAEA-414 (fish flesh) give [129]I information, none of them is a certified value. In addition, the [129]I or/and total iodine concentrations in these materials are very high, and it is not suitable to use them as an analytical quality control SRM when analyzing low iodine concentration samples for ultralow level [129]I. A standard addition method was therefore used in this work by spiking [129]I standard solution into a combusted soil sample (20 g) for analytical quality control. The measured [129]I/[127]I atomic ratios ((1.08−1.16) $\times 10^{-10}$) in the spiked samples agree very well with the expected value (1.14 $\times 10^{-10}$), indicating the developed method is accurate and reliable (Table 1). In addition, the analytical results of two standard addition samples agree very well with each other, indicating a very good repeatability of the analytical method.

In additional, the samples listed in the Table 1 were also analyzed using the conventional separation method, i.e., after combustion, stable iodine carrier was added to the trap solution and the iodine in the trap solution was then separated by solvent extraction and finally precipitated as AgI. The separated AgI was dried, mixed with Nb powder, and measured by AMS (see the Supporting Information). The results (Table 1) show that the [129]I/[127]I values measured by the developed carrier free method are in a very good agreement with those by the conventional method for samples with a [129]I/[127]I ratio higher than 10^{-10}, confirming the reliability of the developed method. However for the samples with a [129]I/[127]I ratio lower than 10^{-10}, the [129]I/[127]I values measured by the conventional carrier addition method are significantly higher than those by the developed carrier free method depending on the [129]I/[127]I level and total iodine content in the samples (Table 1). This result indicates that for the low iodine sample, e.g., soil, the conventional carrier addition method is not suitable due to the relative significant contribution of [129]I from the stable iodine carrier.

Application of the Developed Method for Analyzing Low Iodine Samples for Ultralow Level [129]I. Table 1 shows the analytical results of some environmental and geological samples using the developed method. The lowest [129]I/[127]I ratio in the analyzed soil/loess samples is about 2 $\times 10^{-11}$, which was observed in the soil collected from a 3.0 m depth in Xi'an,

China, and in the loess from 23.5 and 63.5 m depth in Xifeng, China. The measured [129]I/[127]I ratio in the surface soil ranges from 4 $\times 10^{-10}$ to 1 $\times 10^{-9}$ (Table 1), and this is 1−2 orders of magnitudes lower than that observed in Europe and falls within the weapons testing fallout level.[28] The lowest [129]I/[127]I ratio ((1.7−2.0) $\times 10^{-11}$) measured in deep soil/loess is more than 1 order of magnitude lower than that in the surface soil sample in China but approximately 1 order of magnitude higher than the proposed prenuclear [129]I/[127]I ratio of 1.5 $\times 10^{-12}$ in marine systems.[2,3] Szidat et al.[6] reported varied [129]I/[127]I ratios of (0.57−16.8) $\times 10^{-11}$ in three soil samples collected in Russia before human nuclear activity (1909−1930), where 1 mg of iodine carrier was added to the sample before analysis, the lower [129]I/[127]I ratio in one sample might not reflect the real value. Wallner et al.[12] reported a [129]I/[127]I ratio of (0.6−2.1) $\times 10^{-11}$ in lignite formed in the tertiary period and collected from an underground mine in Austria in 1960−1965. The measured [129]I/[127]I ratio in the deep soil in this work is similar to their values in lignite. Because iodine concentration in the lignite sample is relatively high (30−70 $\mu g/g$), no carrier was added before analysis and the measured values might reflect the actual level of the [129]I/[127]I ratio in the sample. However, since the lignite was formed in the tertiary period (>65 Ma ago), most of the cosmogenic [129]I originating from atmospheric deposition should decay away and the calculated [129]I/[127]I ratio by fission of uranium is lower than 10^{-14}, the observed higher [129]I/[127]I level was attributed to possible migration or contamination of [129]I from uranium ore or modern [129]I. Because only four deep soil samples were analyzed in this work and the migration of [129]I from the top layer to the deep layer of the soil profile has not yet been investigated, it might not be sufficient to propose a value of 2 $\times 10^{-11}$ as the prenuclear [129]I/[127]I ratio in the terrestrial environment. Some more samples collected from different locations and depths are being analyzed in our lab for this purpose. In addition, iodine is a highly mobile element; the anthropogenic [129]I on the surface soil might migrate to the deep soil. A sequential analysis of soil samples is also being carried out in our lab to investigate and evaluate this effect.

A [129]I/[127]I ratio of 4.8 $\times 10^{-11}$ was observed in one coral sample collected in Zhanjiang, China. There is no report of [129]I in coral samples collected from China. A [129]I/[127]I ratio of 2.7 $\times 10^{-10}$ has been reported in seaweed collected from Zhanjiang, China, in 1996,[29] about 5 times higher [129]I/[127]I ratio than that in the analyzed coral, this might be attributed to that this coral sample was collected in an offshore area, as a consequence, less effect from the runoff from the inland. In addition, the analyzed coral is a bulk of sample and reflects an average [129]I level in some years recorded in the bulk of coral. Very few works have been completed on the determination of [129]I in a coral sample. Biddulph et al.[30] investigated the [129]I distribution in two 60 year coral profiles collected from the South Pacific Ocean and reported [129]I/[127]I ratios varying from 1 $\times 10^{-12}$ to 7 $\times 10^{-12}$ in one coral profile and from 1 $\times 10^{-12}$ to 22 $\times 10^{-12}$ in

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another coral profile (1935−1995). The higher ^{129}I/^{127}I value in this work compared with the reported values in coral from the South Pacific Ocean is attributed to the lower level of weapons testing fallout in the southern hemisphere compared with those in the northern hemisphere, especially the middle latitude region.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.