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# Analysis of $^{129}\text{I}$ and its Application as Environmental Tracer

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## Abstract

Iodine-129, the long-lived radioisotope of iodine, occurs naturally, but anthropogenic generated  $^{129}\text{I}$  has dominated the environment in the past 60 years. Due to active chemical and environmental properties of iodine and the enhanced analytical capacity for  $^{129}\text{I}$  measurement, the application of  $^{129}\text{I}$  as an environmental tracer has highly increased in the past 10 years. Neutron activation analysis and accelerator mass spectrometry are the only techniques for measurement of  $^{129}\text{I}$  at environmental level. This article mainly compares these two analytical techniques for the determination of  $^{129}\text{I}$  at environmental level, and highlights the progress of these analytical methods for chemical separation and sensitive measurement of  $^{129}\text{I}$ . The naturally occurred  $^{129}\text{I}$  has been used for age dating of samples/events in a range of 2-80 Ma. For the purpose of this study, an initial value of  $^{129}\text{I}$  has to be measured. Some progress on the establishment of an initial  $^{129}\text{I}$  level in the terrestrial system are presented in this paper. A large amount of anthropogenic  $^{129}\text{I}$  has been released to the environment, mainly by reprocessing nuclear fuel. Anthropogenic  $^{129}\text{I}$  provides a good oceanographic tracer for studying the circulation and exchange of water mass. The speciation analysis of  $^{129}\text{I}$  can also be used to investigate the geochemical cycle of stable iodine. Some representative works on the environmental tracer application of  $^{129}\text{I}$  are summarized.

**Key words:** Grx1, *Clostridium oremlandii*, backbone assignment, NMR

## Introduction

$^{129}\text{I}$  is a long-lived radioisotope of iodine with a half life of  $1.57 \times 10^7$  years. It is naturally produced

mainly through the reactions of cosmic rays with xenon in the upper atmosphere, the spontaneous fission of  $^{238}\text{U}$  and the thermal neutron-induced fission of  $^{235}\text{U}$  in the earth's crust. A relative constant production rate of  $^{129}\text{I}$  from these processes is expected. In an equilibrium situation with a loss of the  $^{129}\text{I}$  due to its radioactive decay, a steady state

concentration of  $^{129}\text{I}$  can be reached in the environment. The estimated atom ratios of  $^{129}\text{I}/^{127}\text{I}$  in the marine environment are  $3 \times 10^{-13} \sim 3 \times 10^{-12}$  with an even lower ratio of  $10^{-15} \sim 10^{-14}$  in the lithosphere[1]. These ranges correspond to a steady state inventory of about 180 kg of  $^{129}\text{I}$  in the hydrosphere and about 60 kg in the lithosphere (total at about 250 kg) [1]. A representative ratio of  $^{129}\text{I}/^{127}\text{I}$  at  $1.5 \times 10^{-12}$  has been considered in marine systems based on the measurement of marine sediment samples[2,3]. Due to the low concentration of iodine in the terrestrial environment compared to the marine system, the initial ratio of  $^{129}\text{I}/^{127}\text{I}$  in the terrestrial sample might not be the same as that in the marine system. However, up to now, no reliable ratio of this data has been reported.

Since 1945, a large amount of  $^{129}\text{I}$  has been produced and released to the environment by human nuclear activities. Nuclear weapons testing have released about 57 kg of  $^{129}\text{I}$  to the environment[4,5]. The  $^{129}\text{I}$  injected to the atmosphere, particularly to the stratosphere, has a relatively long residence time, which implies mixing and fallout over a large area. A globally elevated  $^{129}\text{I}$  level has been observed in the environment. In general, the  $^{129}\text{I}/^{127}\text{I}$  ratio has increased to  $10^{-11} \sim 10^{-10}$  in the marine environment and  $10^{-11} \sim 10^{-9}$  in the terrestrial environment due to the nuclear weapons testing[4-6].

Routine operation of nuclear reactors for power production and research has produced large amounts of  $^{129}\text{I}$  by fission of uranium. It has been estimated that about 68000 kg  $^{129}\text{I}$  has been produced in nuclear power reactors in the years up to year 2005[6]. However, most of the  $^{129}\text{I}$  generated in nuclear power production has remained in the spent fuel. The fuel elements were encased in cladding that prevents the release of gaseous radioiodine to the atmosphere. However, some amount of  $^{129}\text{I}$  has been released to the environment because of nuclear accidents and the reprocessing of spent nuclear fuel. It is estimated that 1.3-6 kg of  $^{129}\text{I}$  was released from the Chernobyl accident[4], causing a significantly increased  $^{129}\text{I}$  level ( $^{129}\text{I}/^{127}\text{I}$  ratio of  $10^{-6}$ ) measured in environmental samples collected from the Chernobyl accident contaminated area[7,8]. The accident

happened in Fukushima, Japan in March 2011 has also released  $^{129}\text{I}$  to the environment. The short lived radioisotopes of iodine ( $^{131}\text{I}$ ,  $^{132}\text{I}$  and  $^{133}\text{I}$ ) have been measured in wide areas far away from Japan, like America and Europe[9], but the estimated amount of  $^{129}\text{I}$  released from the Fukushima accident has not yet been reported. The two largest spent fuel reprocessing plants (SFRP) at La Hague (France) and Sellafield (UK) have discharged 4200 kg and 1400 kg of  $^{129}\text{I}$  to the English Channel and Irish Sea, respectively, until 2008[6]. Meanwhile these two SFRPs have also released 75 kg and 180 kg of  $^{129}\text{I}$  to the atmosphere, respectively[6,10]. As a consequence, the  $^{129}\text{I}$  concentration in the Irish Sea, English Channel, North Sea, and Nordic Seas has increased significantly and the  $^{129}\text{I}/^{127}\text{I}$  ratio in the seawater has elevated to values of  $10^{-8} \sim 10^{-5}$ [11-18]. Even high levels of  $^{129}\text{I}$  with  $^{129}\text{I}/^{127}\text{I}$  ratios to  $10^{-6} \sim 10^{-4}$  has been measured in the terrestrial samples collected near the reprocessing plants at La Hague and Sellafield [19, 20]. Other spent fuel reprocessing plants have also released  $^{129}\text{I}$  to the environment, mainly to the atmosphere, which include about 200 kg of  $^{129}\text{I}$  from the SFRP at Marcoule (France) and 274 kg  $^{129}\text{I}$  from the SFRP at Hanford (USA)[6,10, 21]. An elevated  $^{129}\text{I}$  level with  $^{129}\text{I}/^{127}\text{I}$  ratios of  $10^{-6} \sim 10^{-4}$  has also been reported in samples collected in regions near the reprocessing plants at WAK, Germany, Hanford, USA, Tokai, Japan, and India[22-24].

The sources, inventory and environmental levels of  $^{129}\text{I}$  are summarized in Table 1. It can be seen that most of the  $^{129}\text{I}$  in the environment originated from the discharges of reprocessing plants, such as those at La Hague and Sellafield. However, the majority of  $^{129}\text{I}$  produced in reactors around the world, mainly power reactors (>90%), is still stored or pending for future reprocessing. At present, the different levels of  $^{129}\text{I}/^{127}\text{I}$  in the environment are envisaged as  $10^{-12}$  for the pre-nuclear era,  $10^{-11} \sim 10^{-9}$  for the baseline level from global fallout and  $10^{-9} \sim 10^{-6}$  in regions affected by the releases from the nuclear facilities. The highest ratio of  $^{129}\text{I}/^{127}\text{I}$  at  $10^{-6} \sim 10^{-3}$  was observed in the vicinity of the reprocessing plants and nuclear accident sites.

**Table 1. Sources, inventory/releases and environmental level of <sup>129</sup>I**

Source	Inventory / release *	<sup>129</sup> I/ <sup>127</sup> I ratio in the environment
Nature	250 kg	~1×10 <sup>-12</sup>
Nuclear weapons testing	57 kg	0 <sup>-11</sup> -10 <sup>-9</sup>
Chernobyl accident	1.3-6 kg	10 <sup>-8</sup> -10 <sup>-6</sup> (in contaminated area)
Marine discharge from European NFRP by 2008	5600 kg	10 <sup>-8</sup> -10 <sup>-6</sup> (North Sea and Nordic Sea water)
Atmospheric release from European SFRP by 2007	440 kg	10 <sup>-8</sup> -10 <sup>-6</sup> (in rain, lake and river water in west Europe) 10 <sup>-6</sup> -10 <sup>-3</sup> (in soil, grass near NFRP)
Atmospheric release from Hanford NFRP	275 kg	10 <sup>-6</sup> -10 <sup>-3</sup> (in air near NFRP)

**Analytical methods for determination of <sup>129</sup>I in the environment**

<sup>129</sup>I, as a radioisotope of iodine, decays by beta emission to <sup>129</sup>Xe with a maximum energy of 154 keV, accompanied with emission of 39.6 keV gamma ray (7.5% intensity) and X-rays of mainly 29.5 keV (20.4%) and 29.8 keV (37.7%). Therefore, <sup>129</sup>I can be measured by gamma and X-ray spectrometry, as well as by beta counting mainly using liquid scintillation counting due to its low energy of beta particles[6]. As a result of the low energies and intensities of the gamma and X-rays of <sup>129</sup>I, the  $\gamma$ - and X-ray spectrometry is insensitive compared to LSC. The very long half-life of <sup>129</sup>I, and therefore extremely low specific activity (6.5 × 10<sup>6</sup> Bq/g), make radiometric methods insensitive and only suitable for samples in which the radioactivity of the radionuclides is fairly high (Table 2). Such samples are normally found in nuclear waste or samples heavily contaminated by human nuclear activities. <sup>129</sup>I has also been measured

by inductively coupled plasma mass spectrometry (ICP-MS), but its detection limit for <sup>129</sup>I is more or less the same as radiometric methods due to less ionization efficiency to iodine and the serious interference of <sup>129</sup>Xe isobar. By applying dynamic reaction cells and introducing gas iodine directly to the plasma, the detection limit of ICP-MS can be improved[25], but it is still difficult to use ICP-MS to determine <sup>129</sup>I in environmental samples in which the <sup>129</sup>I/<sup>127</sup>I ratio is below 10<sup>-7</sup>. More sensitive methods are neutron activation analysis (NAA) and accelerator mass spectrometry (AMS). Table 2 summarizes all methods used for measuring <sup>129</sup>I. Of them, NAA and AMS are the only suitable methods for determining <sup>129</sup>I in environmental samples[26]. Because this article aims to present the analytical methods of <sup>129</sup>I in the environment, and the application of <sup>129</sup>I as an environmental tracer, only NAA and AMS are presented in detail.

**Table 2. Comparison of Analytical methods for measurement of <sup>129</sup>I**

Detection method	Target preparation	Detection limit	
		Bq	<sup>129</sup> I/ <sup>127</sup> I ratio
X- $\gamma$ spectrometry	Direct measurement	100-200 mBq	10 <sup>-4</sup> -10 <sup>-5</sup>
X- $\gamma$ spectrometry	Separated iodine (AgI)	20 mBq	10 <sup>-5</sup> -10 <sup>-6</sup>
LSC	Separated iodine	10 mBq	10 <sup>-5</sup> -10 <sup>-6</sup>
RNAA	Separated MgI <sub>2</sub> /I <sub>2</sub> absorbed on charcoal	1 $\mu$ Bq	10 <sup>-10</sup>
AMS	AgI	10 <sup>-9</sup> Bq	10 <sup>-13</sup>
ICP-MS	Direct water measurement	40-100 $\mu$ Bq/ml	10 <sup>-5</sup> -10 <sup>-6</sup>
ICP-MS	Gaseous iodine	2.5 $\mu$ Bq/g	10 <sup>-7</sup>

In NAA, the <sup>129</sup>I separated from sample is irradiated in a nuclear reactor to convert the long-lived <sup>129</sup>I to short-lived <sup>130</sup>I (12.3 h) via neutron activation reaction <sup>129</sup>I(n,  $\gamma$ )<sup>130</sup>I. By measuring the activity of <sup>130</sup>I through its high energy gamma rays of

536 keV (99%) and 668.5 keV (96%) by gamma spectrometry, the <sup>129</sup>I in the sample can be quantitatively measured by comparing with a <sup>129</sup>I standard that is irradiated and measured together with the samples. A detection limit of 10<sup>-13</sup> g or

1  $\mu$ Bq has been achieved by NAA[27]. Because of the interference of stable  $^{127}\text{I}$  to the determination of  $^{129}\text{I}$  via reaction  $^{127}\text{I}(2n, \gamma)^{129}\text{I}(n, \gamma)^{130}\text{I}$ , the lowest  $^{129}\text{I}/^{127}\text{I}$  ratio measured by NAA is  $10^{-10}$ . Due to low concentration of  $^{129}\text{I}$  and high content of matrix component in environmental samples, which will induce an extremely high radioactivity after neutron irradiation, the iodine in the samples has to be separated from the sample matrix by chemical methods before neutron irradiation. In addition, the interferences from uranium and tellurium via neutron activation can be removed by chemical separation. The separated iodine needs to be prepared to solid form, such as  $\text{PbI}_2$  and  $\text{MgI}_2$ , or adsorbed in active charcoal and sealed in a quartz ampoule for the neutron irradiation in a reactor due to high volatility and possible loss of iodine during neutron irradiation[23, 27]. A further purification of iodine in the irradiated iodine sample is often carried out to remove interferences, such as  $^{82}\text{Br}$ , which could not be completely eliminated during chemical separation before irradiation due to similar chemical properties of bromine to iodine, in order to reduce the Compton background in the  $\gamma$  spectrum, and therefore to improve the detection limit[27]. The finally separated iodine is normally prepared as  $\text{PdI}_2$  precipitate for measurement of  $^{130}\text{I}$  by  $\gamma$ -spectrometry. Due to the exact same chemical properties as  $^{129}\text{I}$ , stable  $^{127}\text{I}$  is also separated and irradiated with  $^{129}\text{I}$ , which therefore can be determined by measuring its fast neutron activation product  $^{126}\text{I}$  ( $t_{1/2}=13.0$  day) formed through  $^{127}\text{I}(n, 2n)^{126}\text{I}$  reaction. By this way, both  $^{129}\text{I}$  and  $^{127}\text{I}$  can be determined at the same time. However, this requires that no stable iodine carrier is added during the chemical separation before neutron irradiation.

In AMS,  $^{129}\text{I}$  separated from samples and prepared as  $\text{AgI}$  is normally mixed with conductive material, such as silver or niobium powder, and pressed in a target holder that is put in the ion source of AMS. Negative iodine ions are sputtered from the target in the ion source using  $\text{Cs}^+$  ions, guided to the injector, pre-accelerated and selected by an electrostatic analyzer, and a bouncer magnet for negative  $^{129}\text{I}$  and  $^{127}\text{I}$  ions. The preliminarily selected negative ion

beams of  $^{129}\text{I}$  and  $^{127}\text{I}$  are directed to the tandemron accelerator for accelerating. At the terminal of the accelerator, several electrons are stripped off from the accelerated iodine anions. Iodine negative ions are converted to multiple charged positive ions, for example,  $\text{I}^+$ ,  $\text{I}^{2+}$ ,  $\text{I}^{3+}$ ,  $\text{I}^{4+}$ ,  $\text{I}^{5+}$ , and  $\text{I}^{7+}$ , which are then accelerated again. After passing through a magnetic analyzer, a specifically charged iodine ion, normally  $\text{I}^{3+}$  or  $\text{I}^{5+}$ , is isolated. The stable isotope  $^{127}\text{I}$  is measured by a Faraday cup immediately after the magnetic analyzer.  $^{129}\text{I}$  ions from the magnetic analyzer is further separated by an electrostatic analyzer and a magnetic analyzer, and is finally measured by a gas ionization detector or a time of the flight detector[28]. A  $^{129}\text{I}/^{127}\text{I}$  ratio is normally reported instead of the  $^{129}\text{I}$  signal in order to overcome the variation of ionization efficiency and intensity of the iodine ion beam. If the amount of  $^{127}\text{I}$  in the sample and/or  $^{127}\text{I}$  carrier added to the sample is known, the amount of  $^{129}\text{I}$  in the sample can be calculated by multiplying the measured  $^{129}\text{I}/^{127}\text{I}$  value with the total amount of  $^{127}\text{I}$  in the sample. The calibration of the AMS instrument by analyzing the standard with a known  $^{129}\text{I}/^{127}\text{I}$  ratio has to be carried out with samples for each batch of samples. The reported detection limit of AMS is  $10^5$  atoms for  $^{129}\text{I}$  (nBq), and  $10^{-14}$  for the  $^{129}\text{I}/^{127}\text{I}$  ratio[28-30]. This makes AMS the only method allowing the analysis of pre-nuclear era samples with a  $^{129}\text{I}/^{127}\text{I}$  ratio lower than  $10^{-10}$ , even for values as low as  $10^{-14}$ . Normally, a few milligrams of iodine as  $\text{AgI}$  needs to be prepared for AMS measurement, which is carried out by adding stable iodine ( $^{127}\text{I}$ ) carrier to the samples of low iodine concentration, or directly separating the iodine from high iodine concentration samples, such as seaweed, brine and thyroid[2, 3, 29]. A carrier free method has been recently reported for AMS determination of  $^{129}\text{I}$  in low iodine concentration samples, which was implemented by preparing the separated iodine as a co-precipitate of  $\text{AgI-AgCl}$ . In this case, micrograms of iodine can be analysed for  $^{129}\text{I}$  using AMS[28].

For all measurement techniques,  $^{129}\text{I}$  has to be separated from the sample matrix before measurement, especially for low level environmental

samples. The iodine separation methods for all measurement techniques are more or less the same, the differences arise only from the final form of the separated sample. For  $\gamma$ - and X-ray spectrometry, the separated iodine is normally prepared as small size solid, such as AgI precipitate, although liquid form in small volume can also be used. For LSC measurement, an aqueous sample needs to be prepared so it can be mixed with a liquid scintillation cocktail for measurement. NAA requests to prepare the separated iodine as solid  $MgI_2$  source or be adsorbed in active charcoal, while the AgI precipitate mixed with silver or niobium powder is normally used for AMS measurement.

Typically, iodine in water sample is separated by solvent extraction using  $CCl_4$  or  $CHCl_3$ . In this case, all iodine in the sample is first converted to  $I^-$  or  $IO_3^-$ , then converted to  $I_2$  to be extracted to organic phase.  $I_2$  in the organic phase is then back extracted to aqueous phase by reducing  $I_2$  to  $I^-$ . 2-3 extraction and back extraction cycles are normally carried out to purify iodine from interferences. An  $^{125}I$  tracer or stable iodine ( $^{127}I$ ) is often used to monitor the chemical yield of iodine during separation. For a large volume of water samples, including seawater, urine and milk (2-50 litres), iodine needs to be preconcentrated first. This is often carried out by ion exchange after converting all iodine species to iodide, which has a strong affinity to anion exchange resin. The adsorbed iodide is then eluted from the column using a small volume of high concentration of nitrate or  $NaClO$  solution for further separation using solvent extraction[31-35]. It should be mentioned that organic iodine in the liquid samples has to be decomposed before extraction because only inorganic iodine can be separated using solvent extraction[33, 36]. For solid samples, such as soil, sediment, vegetations, tissues, and filters, iodine is often separated by combustion. Iodine, as  $I_2$ , released from the sample at a high temperature ( $>800$  °C) is trapped in a NaOH solution or onto an activated carbon column cooled with liquid nitrogen. The  $^{129}I$  on active charcoal can then be measured using

gamma and X-ray spectrometry or used for NAA. Iodine trapped in a NaOH solution is further separated by solvent extraction[23, 27, 37, 38]. Furthermore, alkali fusion has also been used to separate iodine from solid samples. In this case, NaOH or  $Na_2CO_3$  is added and the mixture is fused at 500-650°C for 3-4 hours. The fused sample is leached with hot water, and iodine in the leachate is separated by solvent extraction[27, 35, 39]. Acid digestion technique has also been used to decompose solid samples for separating iodine[3]. Based on the volatility of molecular iodine, iodine can be removed from the digested solution by oxidizing and bubbling. Then, the released  $I_2$  is trapped in an alkaline solution. However, this procedure normally takes a long time to ensure all organic matters are decomposed. To improve the analytical efficiency of the acid digestion method, microwave assisted acid digestion has been applied to separate iodine from vegetation samples[40]. However, this method is only suitable for treating small samples ( $>1$  g), and the loss of iodine and cross contamination might be a potential problem due to the high volatility and adsorption of molecular iodine on the walls of Teflon containers used for digestion.

Iodine Iodine exists in different species in environmental samples. In water samples it mainly occurs as  $I^-$ ,  $IO_3^-$  and organic bound iodine. Chemical speciation analysis of  $^{129}I$  can significantly extend fields of its tracer application. Based on the different affinity of iodine species to anion exchange resin, ion exchange chromatography has been applied for separation of different species of iodine in water samples[13,14]. Fig. 1 shows a schematic procedure for chemical speciation analysis of  $^{129}I$  and  $^{127}I$  in water samples. The speciation analysis of  $^{129}I$  in soil and sediment is often implemented by sequential extraction method, iodine associated to different components of the sample is leached with different reagents, the leached iodine is then separated using the method as for liquid samples[7, 41, 42]. The study of  $^{129}I$  in air mainly focus on aerosol associated iodine, while some speciation

analysis of  $^{129}\text{I}$  has also been carried out by collecting inorganic and organic gas iodine as well as particle iodine using different filters. In this case, a sequential filtration is normally used. The air first pass through a filter to collect particles associated with iodine.

Then a filter paper impregnated with NaOH to trap inorganic gaseous iodine such as  $\text{I}_2$ , HI and HIO. Finally organic gaseous iodine is trapped using an active charcoal cartridge impregnated with amine

reagent. The different fractions of iodine collected on the solid materials are further separated using combustion or alkali fusion followed by solvent extraction or precipitation for  $^{129}\text{I}$  measurement [18, 43-45]. A comprehensive review on speciation analysis of  $^{129}\text{I}$  in the environment has been reported by Hou et al [6].

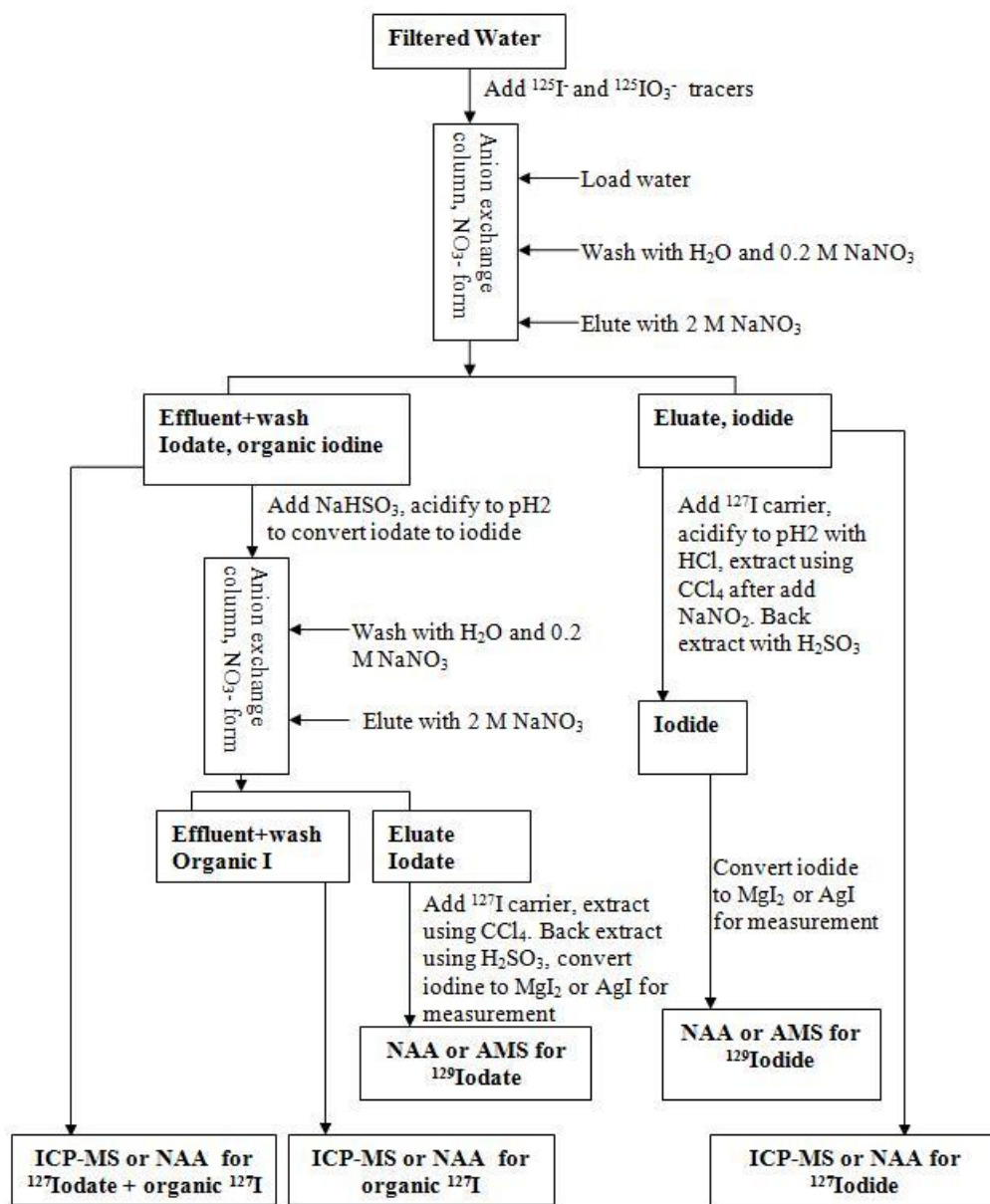


Fig. 1. Schematic procedure for chemical speciation analysis of  $^{129}\text{I}$  and  $^{127}\text{I}$  in water samples (adopted from Hou et al [6].)

### Environmental and geological tracer application

Due to the low sensitivity of radiometric method for  $^{129}\text{I}$ , the researches on  $^{129}\text{I}$  in the early years mainly focused on the investigation of  $^{129}\text{I}$  in the nuclear waste and highly contaminated environmental samples. With the application of NAA since 1960's, determination of  $^{129}\text{I}$  in the present environmental level became possible, the researches on the radioecology of  $^{129}\text{I}$  including the migration and transfer of  $^{129}\text{I}$  in the ecosystem have been carried out in past 40 years. With the increased number of AMS facilities installed in the past 20 years, the determination of low level  $^{129}\text{I}$  in environmental samples has become relatively easy, and the determination of cosmogenic  $^{129}\text{I}$  becomes possible. Since 1990's, researches on tracer application of  $^{129}\text{I}$  in environmental and geological sciences have being significantly increased, some representative application fields are presented below, mainly focusing on the works completed in the author's group.

### Geological dating using naturally generated $^{129}\text{I}$

Due to the long half life and the unique characteristics of cosmogenic and fissionogenic  $^{129}\text{I}$ , the naturally generated  $^{129}\text{I}$  has been used for geological dating and source identification of carbon hydrate by analysis of pore water, brine, ground water and sedimentation[2, 46-52]. The geological dating using natural  $^{129}\text{I}$  is based on the principle that cosmogenic  $^{129}\text{I}$  produced by spallation of Xe isotopes in the atmosphere in a constant rate and fissionogenic  $^{129}\text{I}$  from  $^{238}\text{U}$  in the surface environment quickly reaches to isotopic equilibrium with stable  $^{127}\text{I}$  at the surface reservoir to a steady state of  $^{129}\text{I}/^{127}\text{I}$  ratio (initial value). When sample containing iodine is buried in a certain geological media and isolated from the surface environment,  $^{129}\text{I}$  in this sample will be removed with its radioactive decay in a constant rate following its half-life. Comparing the  $^{129}\text{I}/^{127}\text{I}$  ratio in the investigated samples with the initial value of  $^{129}\text{I}/^{127}\text{I}$ , the formation age of the sample containing iodine can be deduced as shown in Fig. 2.

Based on the analysis of marine sediment samples, an atomic ratio of  $^{129}\text{I}/^{127}\text{I}$  of  $1.5 \times 10^{-12}$  was suggested

as pre-nuclear level of  $^{129}\text{I}$  (initial value) in the marine system[2,3]. Using this method, natural  $^{129}\text{I}$  has been successfully used for dating carbon hydrate, oil and organic matters using pore water, brine, ground water and sediment of marine origination[2, 46-52]. In these samples, iodine concentration is normally high (a few tens to hundreds  $\mu\text{g}/\text{ml}$  or even a few  $\text{mg}/\text{g}$ ), the separation of milligram of iodine for AMS measurement can easily be implemented using some milliliter or grams of sample.

Due to the relatively low concentration of stable iodine ( $^{127}\text{I}$ ) in the terrestrial environment and insufficient exchange of iodine with marine system, the initial value of  $^{129}\text{I}/^{127}\text{I}$  ratio in the terrestrial environment might be different to that in the marine system. No reliable pre-nuclear  $^{129}\text{I}/^{127}\text{I}$  ratio in terrestrial environment has yet been estimated, and no dating of low iodine level terrestrial samples using  $^{129}\text{I}$  has been reported. This is partly attributed to the difficulties in the separation of sufficient amounts of iodine from terrestrial samples for  $^{129}\text{I}$  measurement using AMS. Recently, our laboratory has developed a method for separation of carrier free iodine from terrestrial samples of low iodine concentration for AMS measurement of  $^{129}\text{I}$  in microgram of iodine target, and successfully analyzed some soil profiles down to 70 meters from the surface[28]. With this method, it is expected to establish an initial value of  $^{129}\text{I}/^{127}\text{I}$  ratio in terrestrial samples and to date terrestrial samples using  $^{129}\text{I}$ . Considering the half life of 15.7 Ma and uncertainty of AMS in measurement of ultra low level  $^{129}\text{I}$ , the reasonable age scale using  $^{129}\text{I}$  dating will be 2-80 Ma.

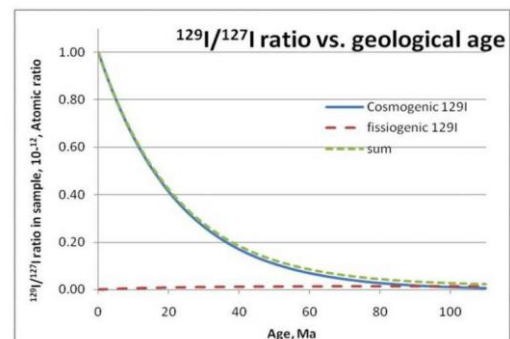


Fig. 2. Schematic illustration of  $^{129}\text{I}$  geological dating principle using natural  $^{129}\text{I}$ .



### Recorders of $^{129}\text{I}$ in loess, sediment and ice cores, coral, and tree rings

Since the formation age of loess is normally younger than 2.5 Ma,  $^{129}\text{I}$  could not be used for age dating of loess. However, the analysis of loess in deep layer, especially in areas with low precipitation can provide a possibility of establishing the initial value of  $^{129}\text{I}/^{127}\text{I}$  in terrestrial environments, which will be valuable for the  $^{129}\text{I}$  dating of terrestrial samples. Depth profiles of loess collected in Luochuan in Shaanxi and Xifeng in Gansu, China, as well as some deep loess sample from Xi'an, China have been analyzed for  $^{129}\text{I}$ . A relative constant  $^{129}\text{I}/^{127}\text{I}$  value of  $1.8 \times 10^{-11}$  has been observed in deep loess,[28] which is about one order of magnitude higher than the suggested initial  $^{129}\text{I}/^{127}\text{I}$  value in marine system[2, 3]. A relatively high  $^{129}\text{I}/^{127}\text{I}$  ratio

up to  $600 \times 10^{-11}$  was observed in the top layer of loess from China. This is attributed to the contribution of anthropogenic  $^{129}\text{I}$  fallout from the weapons testing and reprocessing releases which have been spread all over the world. With the increase of depth, the  $^{129}\text{I}/^{127}\text{I}$  ratio decreases exponentially in the first 50 cm, and then gradually decreases to less than  $3 \times 10^{-11}$  in layers deeper than 300 cm, and keep relatively constant in the deep layer. While the concentration of stable  $^{127}\text{I}$  in the loess profile is relatively constant at 1.5-2.5  $\mu\text{g}/\text{g}$ . Fig.3 shows a  $^{129}\text{I}$  depth profile in a loess core from Luochun, China[53]. The rapid decrease of  $^{129}\text{I}/^{127}\text{I}$  ratios in the top 50 cm soil can be explained by the strong retention of iodine in the loess, and the very slow migration of iodine in the loess core.

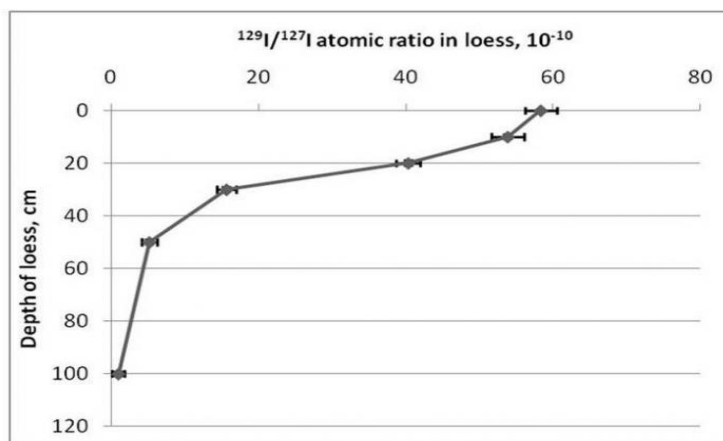
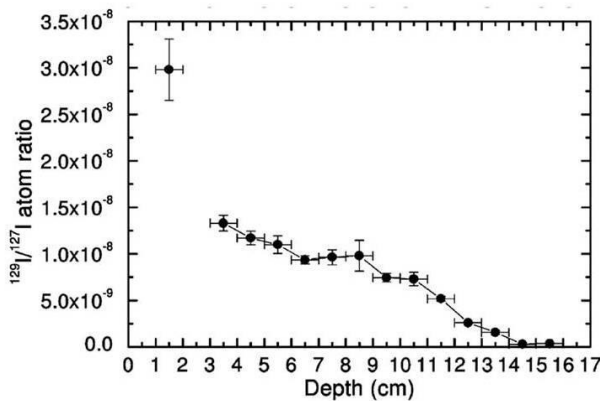


Fig. 3. Distribution of  $^{129}\text{I}$  in the depth profile of loess from Xifeng, China. (adopted from Luo [53])

The sea and lake sediments are formed by deposition of suspended particles in the water body. Analysis of the sediment core can be used to retrieve deposits/events in the past. The distributions of  $^{129}\text{I}$  in marine sediment cores collected in Kattegat [54] and in lake sediment collected from Sweden[41, 55] and UK[56] have been reported. Fig. 4 shows a  $^{129}\text{I}$  profile in the sediment core collected in Kattegat, North Europe[54]. A relative higher  $^{129}\text{I}/^{127}\text{I}$  ratio, especially in the top layer, with a value of  $10^{-8}$  was observed, compared to the value in the surface environmental samples such as soil and vegetation in the baseline area ( $10^{-10}$ - $10^{-9}$ ). This is attributed to the

contribution of marine discharges of two European spent nuclear fuel reprocessing plants. The  $^{129}\text{I}$  discharged from La Hague reprocessing plant to the English Channel is transported to the North Sea, and  $^{129}\text{I}$  discharged from Sellafield reprocessing plant to the Irish Sea is also transported to the North Sea along the Scottish coast. The  $^{129}\text{I}$  is further transported northwards along European continental coast, part of them enters to Skagerrak and Kattegat. With the increased depth,  $^{129}\text{I}/^{127}\text{I}$  ratios decrease to less than  $10^{-9}$  in the layer of more than 14 cm depth. The lower  $^{129}\text{I}$  level in the deep layer corresponds to the gradually increased marine discharges of  $^{129}\text{I}$

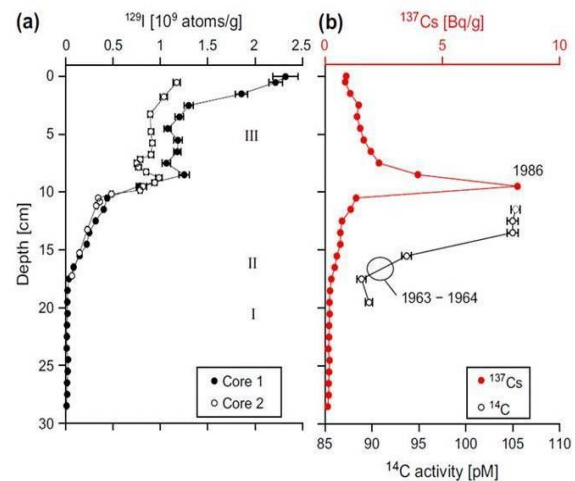
from the two reprocessing plant from about 3 kg in 1952-1966 to about 55 kg in 1983. The reprocessing plants in La Hague and Sellafield started in operation from 1966 and 1952, respectively[6]. Meanwhile, this distribution also indicates that  $^{129}\text{I}$  is strongly fixed in the sediment, and the migration of  $^{129}\text{I}$  from the top layer to the deep layer is very limited. However, because significantly increased discharges of  $^{129}\text{I}$  from the two European reprocessing plants started from 1990's, the  $^{129}\text{I}/^{127}\text{I}$  value in this sediment core collected in 1984, is still much lower than the present level of  $^{129}\text{I}/^{127}\text{I}$  in seawater in this area ( $10^{-6}\sim 10^{-7}$  in 2005)[14, 18, 57].



**Fig. 4.** Depth profile of  $^{129}\text{I}/^{127}\text{I}$  in sediment core collected from Kattegat, North Europe ( $57^{\circ}40'35''\text{N}$ ,  $11^{\circ}24'04''\text{E}$ ) in 1984. (Adopted from Lopez-Gutierrez et al. [54])

Fig. 5 shows the depth profile of  $^{129}\text{I}$  in two sediment cores of 30 cm collected from a lake (Loppesjön) in middle Sweden in 2004[55]. Below 18 cm depth,  $^{129}\text{I}$  levels are very low, while above that, an increased  $^{129}\text{I}$  level towards top layer up to a  $^{129}\text{I}$  concentration of  $(1\sim 2)\times 10^9$  atoms/g was observed,. The depth profile of  $^{137}\text{Cs}$  and  $^{14}\text{C}$  in these sediment cores are also shown in Fig.5. With these dates[55], the sediment cores can be dated to about 80 years from 2004. It is therefore estimated that the  $^{129}\text{I}$  level in the sediment cores has increased from 1960's, in the top 5 cm, corresponding to the date of 1990's and 2000's. This agrees well with the increased marine discharge of  $^{129}\text{I}$  from the two reprocessing plants at La Hague and Sellafield. However, the atmospheric emission of  $^{129}\text{I}$  from these two reprocessing plants did not

change significantly in 1970-2004. The origination of  $^{129}\text{I}$  in this lake sediment is therefore mainly attributed to re-emission of  $^{129}\text{I}$  discharged from the two reprocessing plants to the seas.  $^{129}\text{I}$  discharged to the sea can be re-emitted to the atmosphere as gaseous forms, which is transported over a large area, mainly in Europe and deposited onto the surface by both dry and wet precipitation[58-60], finally binding to particles in the lake water which is deposited to the bottom of the lake sediment.

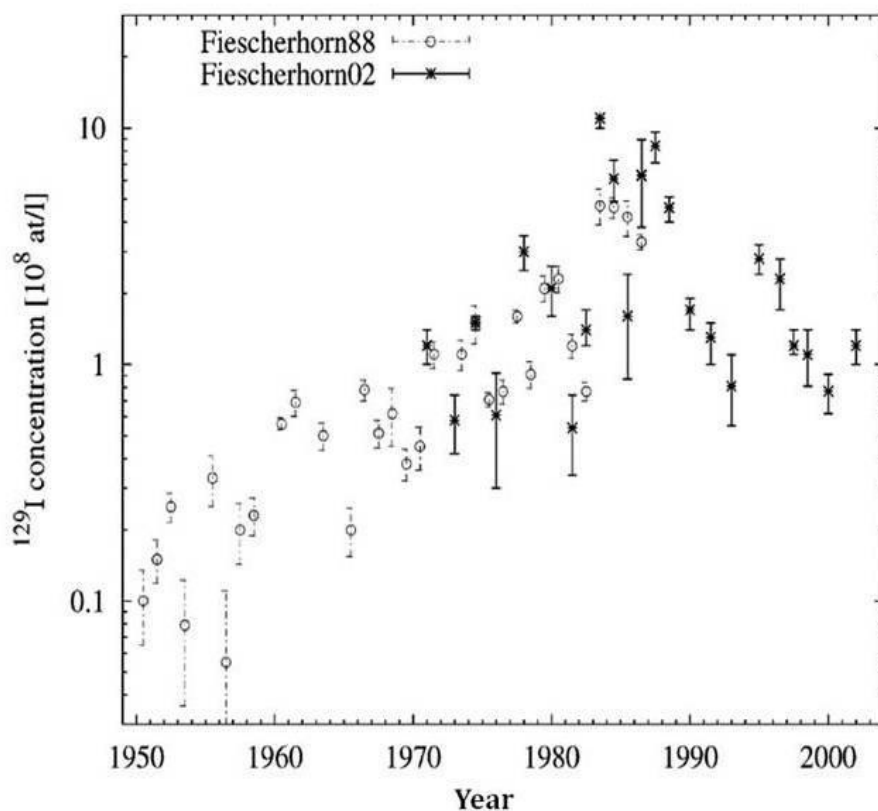


**Fig. 5.** Depth profile of  $^{129}\text{I}$ ,  $^{137}\text{Cs}$  and  $^{14}\text{C}$  in two lake sediment cores collected in middle Sweden ( $61.7^{\circ}\text{N}$ ,  $16.8^{\circ}\text{E}$ ) in 2004. (Adopted from Englund et al. [55])

Compared to the lake sediment core which reflects the variation of  $^{129}\text{I}$  deposition in the catchment area of the lake,  $^{129}\text{I}$  distribution in the ice core can directly be used for retrieving the atmospheric deposition of  $^{129}\text{I}$  in a specific location. Thus it is used to reconstruct the  $^{129}\text{I}$  releases from the nuclear facilities in the surrounding areas[10, 61]. Fig. 6 shows  $^{129}\text{I}$  profiles of two ice cores collected at Fiescherhorn glacier, Swiss Alpines in Europe in 1988 and 2002, which cover an age range from 1950 until 2002[10,61]. Gradually increased  $^{129}\text{I}$  concentration in the ice core was observed from 1950 to 1988 with slightly lower values observed in middle 1960's. From 1988,  $^{129}\text{I}$  concentration in the ice core slowly decreases. The gradually increased  $^{129}\text{I}$  concentration in the ice core from 1950 to middle

of 1960's reflects the atmospheric nuclear weapons testing which peaked in 1962, and the continuously increased  $^{129}\text{I}$  concentrations from 1960's to 1988 are attributed to the gradually increased air emission of  $^{129}\text{I}$  from European reprocessing plants from 1955 to a relatively constant value in 1988. The decreased  $^{129}\text{I}$  concentrations in ice from 1990 are attributed to the decreased air emission of  $^{129}\text{I}$  from reprocessing plant at Marcoule (France) from 1990 until its close and decommissioning in 1997. This reprocessing plant has a larger air emission of about 60 GBq/y in

1976-1990 compared to about 20 GBq/g from both reprocessing plants in Sellafield and La Hague at their highest air emission rates. Since the significantly increased marine discharge of  $^{129}\text{I}$  from reprocessing plants in La Hague and Sellafield from 1990, the re-emission of  $^{129}\text{I}$  from the seawater in the North Sea, Irish Sea and Norwegian Sea is another source of  $^{129}\text{I}$  in the ice core, but this might be not the major source due to a relatively long distance (>600 km) from Swiss Alpines to the marine sources and high altitude of the sampling site.

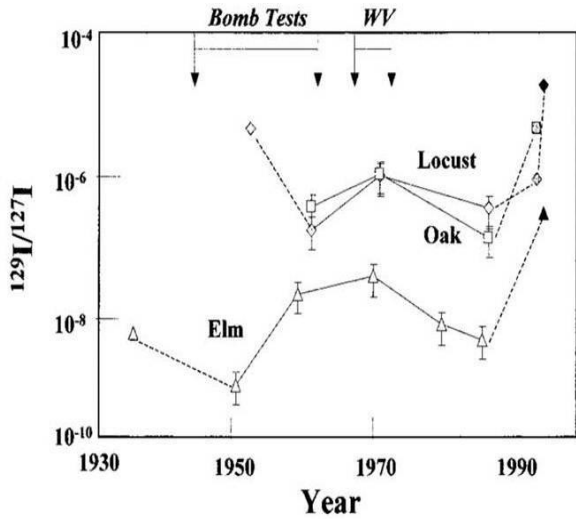


**Fig. 6.** Depth profile of  $^{129}\text{I}$  concentration in two ice cores drilled in 1986 and 2002 from the Fiescherhorn glacier. (Swiss Alps,  $46^{\circ}33\text{ N}$ ,  $8^{\circ}4\text{ E}$ ), (Adopted from Reithmeier et al. [10])

Tree rings are also specimen used to retrieve the  $^{129}\text{I}$  level in the environment if the cross section migration is small [62, 63]. However, because the tree can absorb iodine from both atmosphere directly through leaves and the soil through root, a special correction might be needed to retrieve the  $^{129}\text{I}$  level in the atmosphere using the  $^{129}\text{I}$  concentration in the tree ring. In addition, the selection of the tree species

is also critical, since the fixation of iodine in the specific year layer and cross section migration of absorbed iodine will seriously interfere with the application of  $^{129}\text{I}$  for reconstruction of atmospheric  $^{129}\text{I}$  level. It has been suggested that elm, oak, and locust are three optimal species for this application [62]. Fig. 7 shows  $^{129}\text{I}$  records in tree rings of three species, of them locust and oak

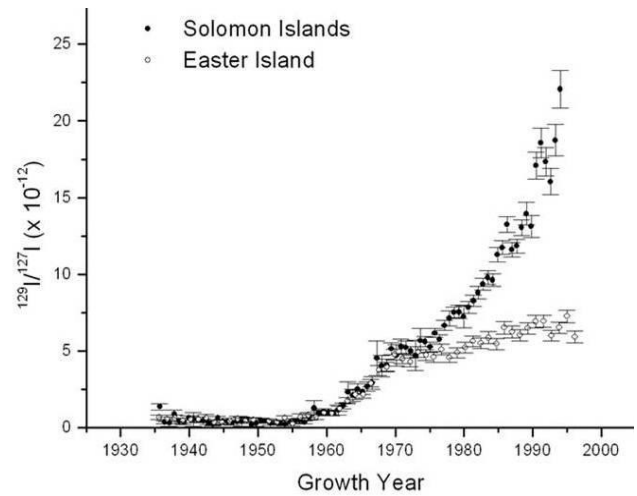
samples were collected from West Valley, and another tree rings of elm from Rochester, the background area in USA. A high  $^{129}\text{I}/^{127}\text{I}$  level was observed in tree rings of oak and locust, this corresponds to the air emission of  $^{129}\text{I}$  from a reprocessing plant located in West Valley (USA) [62].



**Fig. 7.** Variation of  $^{129}\text{I}$  level in tree rings of oak, locust from West Vally and elm from Rochester (UAS). (Adopted from Rao et al[62].)

Corals live in shallow waters, generally within 100 meters depth. Coral skeleton is a good specimen to provide an archive of the chemical and physical conditions present in the surface waters of the ocean that coral has grown in. Iodine as a trace element integrates in the coral skeletons with a concentration of a few  $\mu\text{g/g}$ , and therefore coral samples can also be used for the retrieval of  $^{129}\text{I}$  variation in the surface seawater. Compared to other specimen, the high time resolution due to relatively rapid growth (10 to 20 mm/year) and the absence of mixing processes commonly occurring in sediments (such as bioturbation), make the coral an ideal specimen to reconstruct the temporal variation of  $^{129}\text{I}$  level in the surface and subsurface water[64, 65]. Fig. 8 shows  $^{129}\text{I}$  distribution in two coral columns collected from the Solomon Islands ( $9.5^\circ\text{ S}$ ,  $162^\circ\text{ E}$ ) in 1994 and Easter Island ( $27^\circ\text{ S}$ ,  $109^\circ\text{ W}$ ) in 1996 in South Pacific Ocean[64]. Very low  $^{129}\text{I}/^{127}\text{I}$  ratios of  $(1-$

$3)\times 10^{-12}$  were observed in the coral layers before 1955. This corresponds to the initial level of  $^{129}\text{I}$  of pre-nuclear era, and agrees with the reported initial value of  $^{129}\text{I}/^{127}\text{I}$  in marine sediment[2, 3], indicating that the migration of iodine across different layers in coral skeleton is negligible. After 1955, the  $^{129}\text{I}/^{127}\text{I}$  ratios in the coral columns gradually increased to  $7\times 10^{-12}$  and  $2\times 10^{-11}$  in the two locations (Solomon Islands and Easter Island), respectively. This might be contributed to the  $^{129}\text{I}$  fallout as well as the marine transport. The continuously increased  $^{129}\text{I}$  level might indicate that sources of  $^{129}\text{I}$  arise from both weapons testing and reprocessing releases [64].



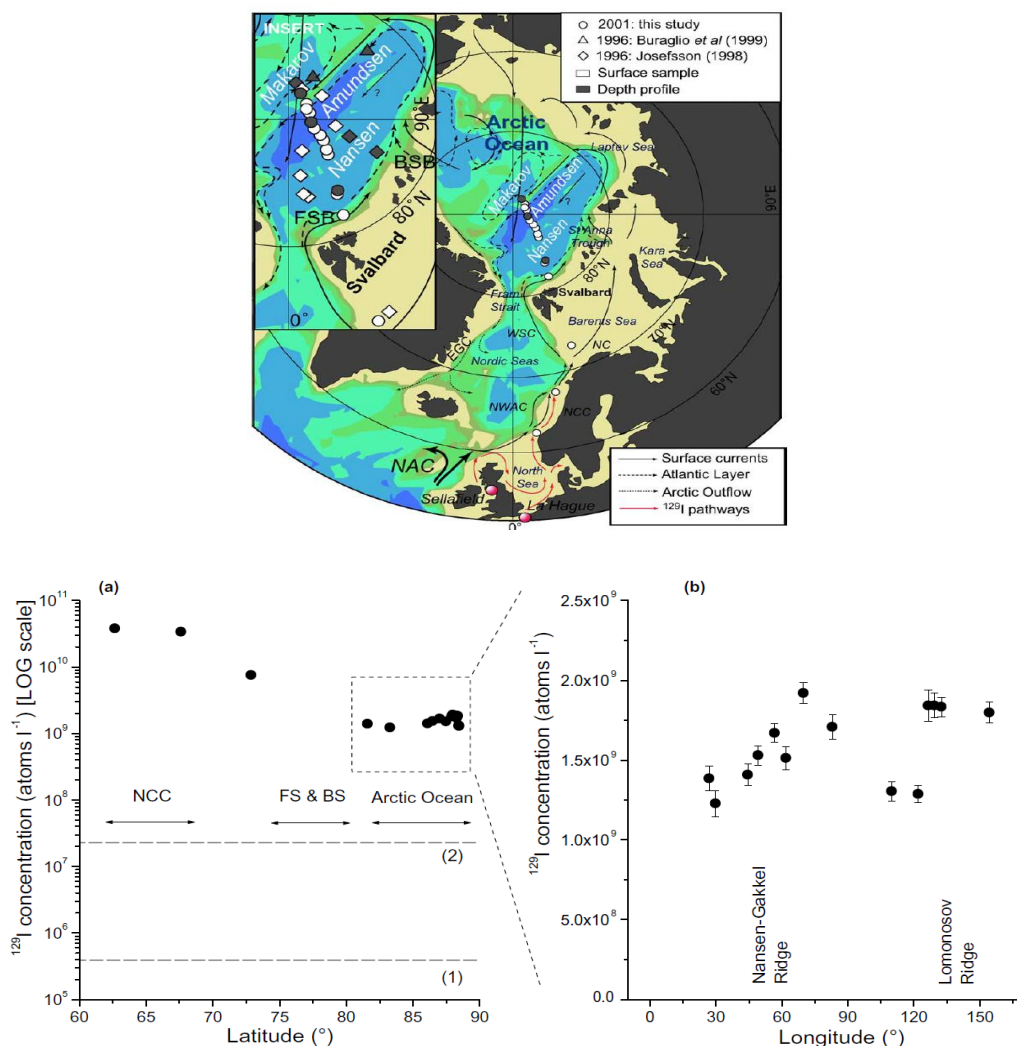
**Fig. 8.** Distribution of  $^{129}\text{I}/^{127}\text{I}$  ratio in coral skeleton from the South Pacific Ocean. (Adopted from Biddulph et al[17].)

**Application of anthropogenic  $^{129}\text{I}$  as oceanographic tracer**

The large amounts of marine discharges of  $^{129}\text{I}$  from reprocessing plants at La Hague and Sellafield (5600 kg until 2008) provide a unique point source of  $^{129}\text{I}$ . With the sensitive detection technique of AMS for  $^{129}\text{I}$  in seawater (down to  $10^5$  atoms/L or  $10^{-16}$  g/L) and the high solubility and long residence time of iodine in ocean, the anthropogenic  $^{129}\text{I}$  can be used as an ideal tracer for water mass transport and exchange in the long term[11-18, 66-68]. Fig. 9 shows variation of  $^{129}\text{I}$  concentrations in the surface water from the Norwegian coast to the Arctic and in 3 depth profiles in the Arctic[15]. The profiles clearly show decreased  $^{129}\text{I}$  concentrations from the

south Norwegian coast, north Norwegian coast, to the Barents Sea and then the Arctic, indicating the transport of Norwegian coastal current from South to North, and entrance to the Arctic through the Barents Sea. While the  $^{129}\text{I}$  concentrations in the surface water in different locations in the Arctic do not vary

significantly, all depth profiles of  $^{129}\text{I}$  in Nansen, Amundsen and Makarov basin show a similar distribution of  $^{129}\text{I}$ , the highest values occur in the surface water, and a sharp decline of  $^{129}\text{I}$  concentrations to the depth of 300-500m followed by a weaker gradient which extends to a depth of 2000m.



**Fig. 9.** Distribution of  $^{129}\text{I}$  in surface seawater from the Norwegian coast to the Arctic and in the depth profile of water column in the Arctic. (Adopted from Alfimov et al [64].)

Fig.10 shows  $^{129}\text{I}$  profiles in the south Greenland Sea, the highest  $^{129}\text{I}$  concentrations were measured below a depth of 3000m and an increased trend of  $^{129}\text{I}$  concentrations was observed from top to the bottom, this indicates that the Denmark Strait overflow water (DSOW) carrying high reprocessing  $^{129}\text{I}$  signal moves down to the bottom when it is

transported southwards[67]. By measuring the time series of seawater samples, the transit time and transfer factor of  $^{129}\text{I}$  can be deduced.

Seaweed, especially brown seaweed, concentrates iodine from seawater by a factor of  $10^3\sim 10^5$ [69]. Compared to seawater, it is easy to collect and store

and therefore suitable for investigation of temporal variation of  $^{129}\text{I}$  in seawater[11, 17, 39, 70]. Fig. 11 shows  $^{129}\text{I}/^{127}\text{I}$  ratios in a time series of seaweed (Fucus) samples collected from different locations in North Europe. A sharply increased  $^{129}\text{I}/^{127}\text{I}$  ratio in seaweed from Utsira and Klint was observed from 1992, which corresponds to the increased marine

discharges of  $^{129}\text{I}$  from reprocessing plants at La Hague and Sellafield from 1990. By comparing with the discharge data, transit time from La Hague can be estimated to be about 1.5 and 1.8 years to Utsira and Klint respectively, and the transfer factor was estimated to be 60 and 54  $\text{ng m}^{-3}/\text{ton yr}^{-1}$ , respectively[11].

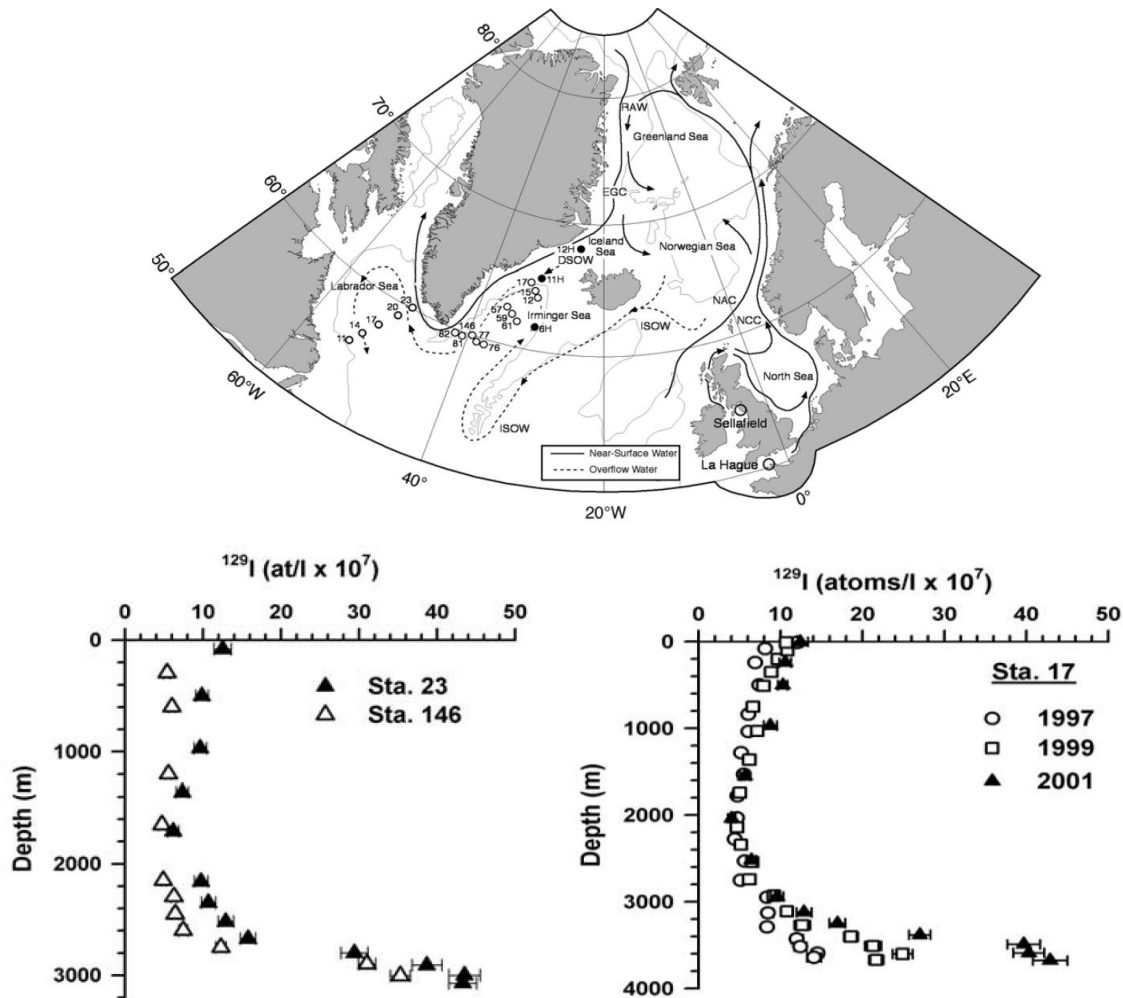


Fig. 10. Depth profiles of  $^{129}\text{I}$  in the irmingier Sea (station 146) and Labrador Sea. (Station 17 and 23), (Adopted from Smith et al[67].)

**Geochemical cycle of stable iodine**

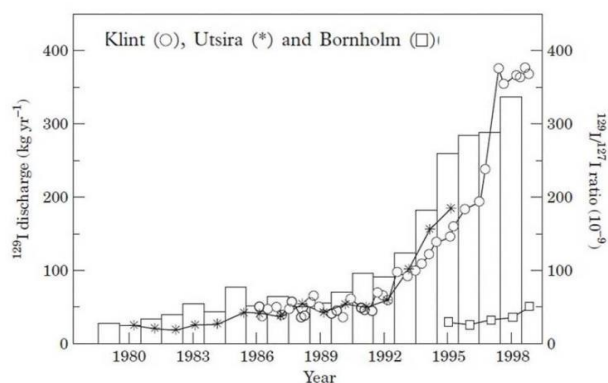
Iodine is an essential element to humans and other mammals, insufficient intake of iodine from foodstuff and drink water causes iodine deficiency disorder (IDD), which is attributed to the low concentration of iodine in soil and agricultural

products. Oceans are the main pool of iodine on the Earth’s surface, it has been generally accepted that iodine in terrestrial environment, especially in soil, originates mainly from the oceans through gaseous iodine emission from the oceans, transported by clouds and aerosols and subsequent deposition. Low concentrations of iodine in soil are attributed to long

distances of the locations from marine areas, as a consequence low deposition of marine derived iodine to the soil. However, there is conflicting evidence about this issue showing less correlation between iodine deposition flux on the soil and its distance to the ocean and the relatively high emission of iodine from terrestrial plants and soil[71, 72]. For some years it has been accepted that iodine is mainly emitted to the atmosphere from the surface of the oceans as methyl iodide and other alkyl iodides of biological origin[73]. Recent experiment showed that molecular iodine ( $I_2$ ) is released from macroalgae and a high concentration of  $I_2$  was observed in coastal areas of the ocean[74]. It has also been shown that atmospheric iodine chemistry plays an important role in ozone destruction, formation of particulates, and cloud condensation nuclei formation[75]. The complicated atmospheric chemistry of iodine ultimately feeds into the general geochemical cycle of iodine through precipitation. Therefore, speciation analysis of iodine in precipitation will provide important information about the geochemical cycle of iodine and related atmospheric chemical process.

Iodine exists in the ocean waters predominantly as dissolved iodate, iodide, and a minute amount of organic iodine. Iodide is a thermodynamically unfavorable species in oxygenated water, so its formation through the reduction of iodate cannot occur spontaneously by chemical means alone. Although iodate is a thermodynamically favourable species of iodine in seawater, kinetic barrier prevents the direct oxidation of iodide to iodate. Numerous studies have been carried out to investigate the origin of iodide, the conversion of iodine between different species, and the marine geochemical cycle of iodine by determining the concentrations of various species of iodine in seawater in certain areas. However, the conversion mechanism of chemical species of iodine is still not clear, the data on the mass transfer of iodine among geochemical reservoirs are still too fragmentary to construct a reliable geochemical cycle of iodine. This is specially associated with the difficulties in distinguishing the origin and conversion of various chemical species of iodine, practically distinguishing between newly produced, and converted iodine species.

The huge amount of  $^{129}I$  in the European seas discharged from the two European reprocessing plants in a certain chemical forms provides a unique isotopic tracer for the investigation of geochemical cycle of stable iodine in the marine and atmosphere environment. By analyzing seawater collected from different locations in the North Sea and Baltic Sea for chemical species of both  $^{129}I$  and stable  $^{127}I$ , the author's group has investigated the conversion of different species of inorganic iodine (Figure 11)[13, 14, 57, 76, 77].

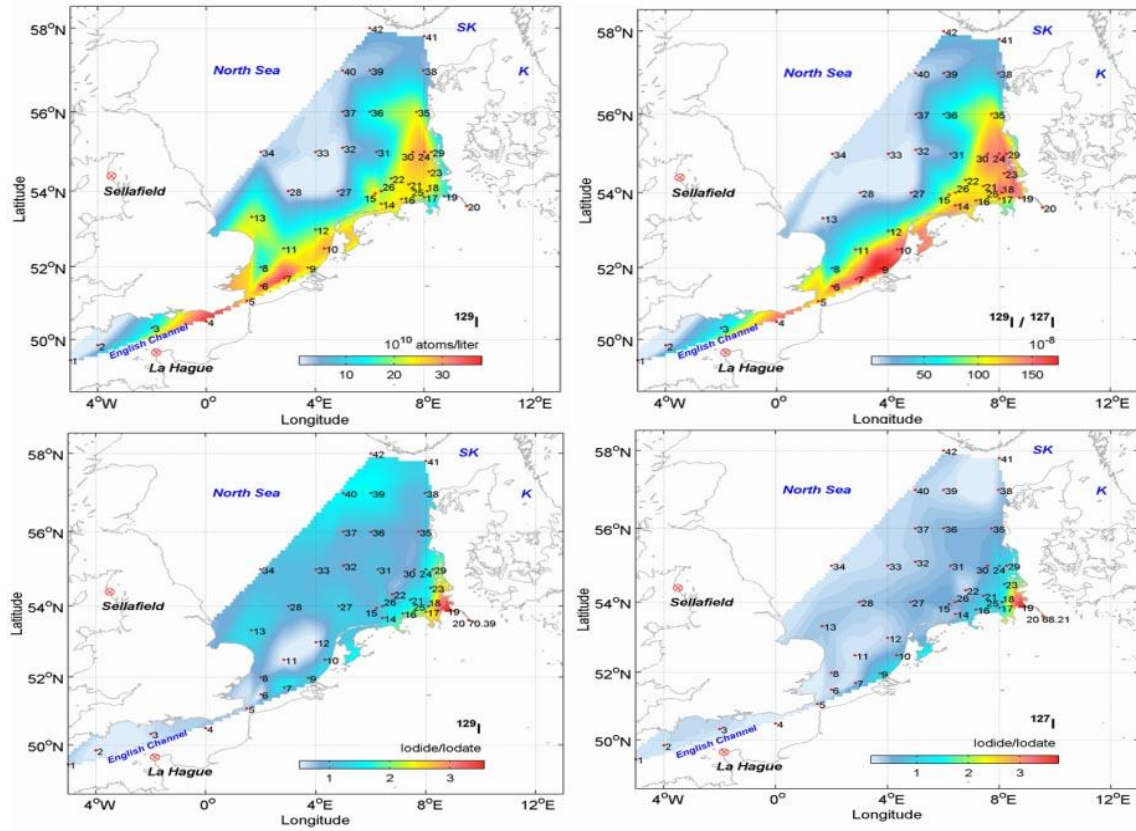


**Fig. 11.** The  $^{129}I/^{127}I$  ratios in times series of seaweed from Noewegian Sea (Utsira), Kattegat (Klint) and Bornholm (Baltic Sea). (Adopted from Hou et al[11].)

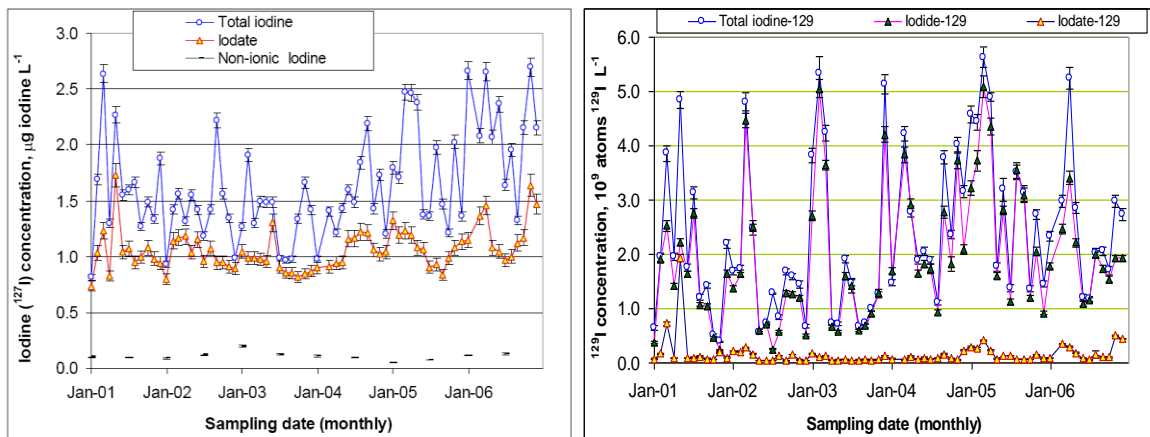
It was found that reduction of iodate to iodide occurs during the transport of water along the European continental coast, and the reduction of iodate to iodide in the Dutch coast and Øresund between Kattegat and Baltic Sea is a fast process; No oxidation of newly produced  $^{129}I$  to  $^{129}IO_3^-$  occurs during the water exchange between the coastal area and open sea and reduction of iodate or oxidation of iodide in the open sea seems to be a slow process. By chemical speciation analysis of  $^{129}I$  and  $^{127}I$  in time series of precipitation samples collected in Denmark, the author's group[58] has investigated the sources of  $^{129}I$  in the precipitation and its transformation during the transport. It was found that iodide is the major species of  $^{129}I$ , while iodate dominates the species of  $^{127}I$  in the precipitation (Fig.12); Re-emission of  $^{129}I$  from the surface water of the English Channel, Irish Sea, North Sea, and Norwegian Sea, especially from the European continental coast areas,

are evidently the major source of  $^{129}\text{I}$  in the precipitation. While stable  $^{127}\text{I}$  in the precipitation has multiple sources, i.e. marine, as well as terrestrial emission. The dominating  $^{129}\text{I}$  species in the precipitation and the marine source of  $^{129}\text{I}$  might

indicate that the re-emitted  $^{129}\text{I}$  is mainly in form of molecular iodine, which is mainly converted to iodide in the precipitate through a series of atmospheric process.



**Fig. 12** Distribution of total  $^{129}\text{I}$  (a),  $^{129}\text{I}/^{127}\text{I}$  atomic ratios iodide (b),  $^{129}\text{I}/^{129}\text{IO}_3^-$  (c), and  $^{127}\text{I}/^{127}\text{IO}_3^-$  molecular ratio (d) in the English Channel and the North Sea. (Adapted from Hou et al[9].)



**Fig. 13** Variations of (a)  $^{127}\text{IO}_3^-$ , and non-ionic and total  $^{127}\text{I}$  concentration ( $\mu\text{g iodine L}^{-1}$ ), (b)  $^{129}\text{I}$ ,  $^{129}\text{IO}_3^-$ , and total inorganic  $^{129}\text{I}$  concentrations in precipitation from Roskilde, Denmark in 2001-2006 (Adopted from Hou et al[14].)



## Summary and perspectives

The features of natural production by cosmic ray reaction with xenon in the atmosphere and fission of  $^{238}\text{U}$  on the earth as well as long half-life facilitate the application of  $^{129}\text{I}$  for dating geological events of 2-80 Ma. The present dating applications is mainly focused on the marine samples with high iodine concentration. With the establishment of effective technique to separate iodine from low level geological samples and high sensitive AMS measurement technique to detect  $^{129}\text{I}$  in microgram of carrier free iodine target in the recent years, the application of  $^{129}\text{I}$  dating in terrestrial environment will become more realistic. Human nuclear activities, especially reprocessing of spent nuclear fuel have released a huge amount of  $^{129}\text{I}$  to the environment. The anthropogenic  $^{129}\text{I}$  dominates in the surface environment, which provides an ideal tracer for environmental tracer researches. The  $^{129}\text{I}$  discharged from the European reprocessing plants to the marine system has been successfully used for investigation of water mass transport and exchange. By chemical speciation analysis of  $^{129}\text{I}$  in seawater and precipitation, reprocessing  $^{129}\text{I}$  has also been used to investigate the geochemical cycle of stable iodine. With the development of analytical techniques for speciation analysis of  $^{129}\text{I}$  in atmosphere, aerosol, seaweed, and sediment, the investigation of geochemical cycles and atmospheric chemistry of stable iodine, enrichment mechanism of iodine in seaweed will become possible. A few researches have been launched in the recent years to investigate the source and atmospheric chemistry of stable iodine using reprocessing  $^{129}\text{I}$  and chemical speciation analysis of both  $^{129}\text{I}$  and  $^{127}\text{I}$  in atmosphere, aerosol, marine water and organism. In addition, the anthropogenic  $^{129}\text{I}$  has also been used as a mark to retrospect the former nuclear activities and accidents. With the development of analytical techniques including the more sensitive AMS detection technique and chemical speciation analytical method, the application fields of  $^{129}\text{I}$  are rapidly increasing. Of them, the migration of  $^{129}\text{I}$  in the geological repository sites and fields of nuclear facilities is attracting more attention due to high mobility of iodine and high radiation risk of  $^{129}\text{I}$ ; anthropogenic as well as naturally produced  $^{129}\text{I}$  has also shown a

potentially useful application in hydrological research.

## Acknowledgements

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