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大气¹²⁹I水平对超低¹²⁹I含量地质样品分析中流程空白的影响

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摘要:为了采用¹²⁹I进行地质定年研究,该类样品中的¹²⁹I/¹²⁷I原子比值通常低于10⁻¹²,因此低的¹²⁹I流程空白是分析地质定年样品的前提条件之一。在全球范围内,大气中¹²⁹I的水平呈现显著变化趋势,¹²⁹I/¹²⁷I原子比值范围在10⁻¹⁰到10⁻⁶。然而,在样品制备过程中,是否大气中的¹²⁹I会影响流程空白尚未可知。本研究调查了三种常用的¹²⁹I分析方法,包括直接沉淀法、溶剂萃取法和管式燃烧法(分别以压缩空气和氧气作为载气)来比较流程空白中的¹²⁹I/¹²⁷I比值。研究结果表明:在最佳实验室条件下,流程空白均被控制在较低的水平,可用于分析各种环境和地质样品。另外,通过研究溶液的长时间储存,发现当0.4 mol·L⁻¹NaOH溶液储存一年以上时,¹²⁹I/¹²⁷I比值比新配制的NaOH溶液有所提高,但基本在实验室正常本底2×10⁻¹³以内。采用压缩空气作为载气的管式燃烧法比氧气为载气时具有明显提高的¹²⁹I/¹²⁷I比值。研究表明样品和试剂的储存,以及制样过程中与大气的交换程度均会影响流程空白中¹²⁹I的水平。因此在分析超低¹²⁹I含量的地质样品时,固体样品中碘的分离应采用低本底的分析方法(如以纯气体作为载体的管式燃烧法),如有必要还可在低大气¹²⁹I水平的实验室进行实验。

关键词:碘-129; 流程空白; ¹²⁹I的地质定年

Influence of atmospheric ¹²⁹I level on procedural blanks in analysis of ultra-low ¹²⁹I geological samples

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Abstract: Background, aim, and scope For the purpose of geological dating using ¹²⁹I, low procedural background is a prerequisite for analysis of ultra-low ¹²⁹I geological samples generally below the level of 10⁻¹² of ¹²⁹I/¹²⁷I atomic ratio. Significant variation of atmospheric ¹²⁹I level is found in a wide range of 10⁻¹⁰ to 10⁻⁶ of ¹²⁹I/¹²⁷I atomic ratio on a global scale depending on the sources of ¹²⁹I, however, whether

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^{129}I level in air could affect procedural background during sample preparation is crucial, but unclear.

Materials and methods This study performed three conventional ^{129}I analytical methods including direct precipitation of iodine, solvent extraction with CCl_4 , as well as combustion in a Pyrolyser furnace to compare $^{129}\text{I}/^{127}\text{I}$ ratio in the procedural blanks. In the combustion method, four experimental conditions were conducted under air or oxygen as carrier gas with or without system heating. Finally, ^{129}I along with carrier iodine was precipitated as AgI , which is then dried, mixed with niobium powder and pressed in copper holder as target. 3 MV Tandem Accelerator Mass Spectrometer (AMS) was used to measure ^{129}I in the target. **Results** $^{129}\text{I}/^{127}\text{I}$ atomic ratios in the procedure blanks are ranging from 1.48×10^{-13} to 28.5×10^{-13} . Slightly increase of ^{129}I background level was observed when NaOH solid reagent and solution stored over one year in contrast to the newly opened and prepared alkaline solution. In the three methods, the results also showed that the lowest $^{129}\text{I}/^{127}\text{I}$ ratio was generated by direct precipitate method, while the highest ^{129}I background level was from the combustion method with condensed air as carrier gas. In particular, the $^{129}\text{I}/^{127}\text{I}$ ratio of combustion method with oxygen as carrier gas was 2—4 times higher than the direct precipitation. Most notably, $^{129}\text{I}/^{127}\text{I}$ ratio of combustion method with condensed air as carrier gas has significantly raised one order of magnitude compared to the direct precipitation, especially the first preparation for both experimental conditions of room temperature and heating. **Discussion** The results suggest procedural blanks are well controlled in our laboratory. The increase in $^{129}\text{I}/^{127}\text{I}$ ratio of procedural blanks prepared with long time stored NaOH solution is attributed to the exposure of alkaline solution into the air during frequent usage, because it could easily adsorb and react with molecular iodine in the air. $^{129}\text{I}/^{127}\text{I}$ ratio in solvent extraction method (1.75×10^{-13} in average) was slightly higher than the lowest ^{129}I level, which indicates solvent extraction could only introduce negligible iodine during sample preparation. Obviously elevated $^{129}\text{I}/^{127}\text{I}$ ratio up to 10^{-12} was observed for sample combustion with condensed air as carrier gas in comparison with oxygen, which is likely caused by iodine adsorption onto the plastic transfer pipe of condensed air and higher atmospheric ^{129}I level in Denmark where the experiment was conducted, rather than ^{129}I residue in the combustion furnace system. **Conclusions** These results suggest ^{129}I level of procedural blank could be influenced by storage of samples and reagents, as well as by the degree of exchange with ambient air during sample preparation. This work shows that the procedural blank can be well controlled using the methods, direct precipitate, solvent extraction and combustion with oxygen as carrier gas, except combustion method with condensed air as carrier gas. The results suggest interfusion of air during sample preparation could increase the blank $^{129}\text{I}/^{127}\text{I}$ ratio depending on the blending extent. Ultralow ^{129}I level geological samples, especially aqueous samples should be carefully stored and analyzed as soon as possible in case of atmospheric iodine adsorption. Selection of sample preparation methods needs to minimize the mixing of sample with air, especially in high atmospheric ^{129}I regions.

Recommendations and perspectives In the aspect of sample preparation, geological samples for dating can be categorized to two types, high ^{127}I concentration samples and low ^{127}I concentration samples. Since the target source and AMS measurement need sufficient stable ^{127}I amount, the former samples can be prepared by direct precipitation after simple samples pretreatment (e.g. oilfield brine by filtration through filter paper), while the latter samples have to be treated by relatively complex and long procedures for either extraction of sufficient stable ^{127}I or addition of stable iodine carrier. On the basis of the observation in this study, therefore, it is recommended that analysis of ultra-low ^{129}I geological samples should adopt low background analytical method (combustion with pure gas as carrier gas) and performed in low ambient ^{129}I level laboratory if necessary. The iodine carrier-free or small iodine carrier addition method developed in recent years provide a great potential for geological dating of low ^{129}I and low ^{127}I samples.

Key words: Iodine-129; procedural blank; geological dating of ^{129}I

1 Introduction

Because of covering an age range of wide applicability to geologic processes, ^{129}I geochronometer has received considerable attention since it was firstly used for dating of meteorites and lunar rocks in 1983 (Nishiizumi et al, 1983). ^{129}I dating has been successfully applied in meteorite, geothermal fluid, brine, marine sediment etc. (Moran et al, 1998; Tomaru et al, 2009; Fehn, 2012). As widely shown in literatures (Fehn, 2012 and references therein), $^{129}\text{I}/^{127}\text{I}$ ratios in geological samples for ^{129}I dating are generally below 1.5×10^{-12} , the initial ratio achieved by analysis of marine sediments off the coast of the Carolinas in the Atlantic Ocean and other marine locations (Fehn et al, 2007). Resulted from the human nuclear activity (NCRP, 1983; Raisbeck et al, 1995; Jabbar et al, 2013), $^{129}\text{I}/^{127}\text{I}$ ratios in modern environment are in the range of 10^{-10} to 10^{-6} , remarkably higher than the old geological samples (Hou et al, 2009; Snyder et al, 2010). For the purpose of dating using ^{129}I , analysis of geological samples generally containing ultra-low level of ^{129}I should be paid much attention, especially on procedural background of ^{129}I during sample preparation, because it may be subjected to introduction of external ^{129}I (e.g. ^{129}I in the air) and further increase $^{129}\text{I}/^{127}\text{I}$ ratios in procedural blanks. Previous studies have investigated $^{129}\text{I}/^{127}\text{I}$ ratios in procedural blanks samples for oil field brine samples (Chen et al, 2014) using solvent extraction. While the fact of high ^{129}I background in laboratory ambient likely gives rise to large uncertainty and even failure of ^{129}I dating, and whether atmospheric ^{129}I could influence background $^{129}\text{I}/^{127}\text{I}$ ratio, in particular at the locations with high atmospheric ^{129}I level is not clear. The purpose of this work is to investigate the influence of reagent storage and sample preparation methods on the $^{129}\text{I}/^{127}\text{I}$ ratios in procedural blanks.

2 Experiment

2.1 Samples and materials

All chemical reagents used were of analytical grade reagents, including NaHSO_3 , HNO_3 , NaNO_2 , and AgNO_3 , and prepared using deionized water

($18.2 \text{ M}\Omega\cdot\text{cm}$) produced by a water purification system (Sartorius, Göttingen, Germany). The ^{127}I carrier (solid I_2 crystal with low ^{129}I level) was obtained from Woodward Company (Colorado, USA), which was dissolved in a $0.4 \text{ mol}\cdot\text{L}^{-1} \text{NaOH}-0.05 \text{ mol}\cdot\text{L}^{-1} \text{Na}_2\text{S}_2\text{O}_5$ solution. The ^{129}I standard solution (NIST-SRM-4949c) was purchased from the National Institute of Standard Technology (Gaithersburg, MD, USA). ^{125}I in the form of iodide was purchased from PerkinElmer Corporate (Waltham, USA). Niobium powders (325 mesh) was purchased from Alfa Aesar Company (Ward Hill, MA, USA).

2.2 Sample preparation

Sample preparation was conducted at the Division of Radioecology, Technical University of Denmark at Roskilde, Denmark. Three conventional analytical methods including direction precipitation, solvent extraction, and combustion were used to separate iodine from procedural blanks and samples (Table 1).

2.2.1 Direct precipitation

In order to investigate if storage of reagent and solution, NaOH in particular, can absorb ^{129}I from ambient air, three $0.4 \text{ mol}\cdot\text{L}^{-1} \text{NaOH}$ solutions were prepared in Danish laboratory. The first NaOH solution was prepared in January 2014 and stored in a glass bottle until analysis in May 2015. The second NaOH solution was newly prepared with a NaOH reagent stored in bottle opened in September 2014. The third NaOH solution was newly prepared with a newly opened NaOH reagent. 35 mL NaOH aliquot was taken out from each solution, added with 1.00 mg iodine carrier, acidified to pH of 1—2 with HNO_3 and precipitated directly with AgNO_3 to AgI . The precipitate was centrifuged, washed with 10 mL $3 \text{ mol}\cdot\text{L}^{-1} \text{HNO}_3$ once, centrifuged again and washed with 10 mL deionized water twice.

2.2.2 Solvent extraction

Using the classic solvent extraction method as described in elsewhere (Hou et al, 2000), 20 mL of deionized water was used for solvent extraction for testing the procedural blanks. With addition of 200 Bq of ^{125}I tracer solution, 1.0 mg iodine carrier and 2—

3 mL of $1 \text{ mol} \cdot \text{L}^{-1}$ NaHSO_3 , water was transferred to a separation funnel and adjusted pH to 1—2 using HNO_3 . Iodine forms in the sample was reduced to iodide. Iodide in the sample was oxidized to molecular iodine by 2—4 mL of $1 \text{ mol} \cdot \text{L}^{-1}$ NaNO_2 solution and extracted with 30 mL of CCl_4 by shaking. The extraction step was repeated 2—3 times until the CCl_4 phase became colorless. All these CCl_4 phases were combined and transferred to a clean separation funnel for back-extraction of iodine. 10 mL of H_2O and 0.5—

1.0 mL of $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaHSO_3 solution were added to the funnel to reduce molecular iodine to iodide and transferred back to water phase. This extraction/back-extraction procedure was repeated once again. After removal of CCl_4 phase, the water phase was transferred to a 15 mL centrifuge tube, and the funnel was washed two times using deionized water, and the washes were combined with back extraction solution in the centrifuge tube. Iodine was precipitate following the procedure of direction precipitate in subsection 2.2.1.

Tab.1 $^{129}\text{I}/^{127}\text{I}$ atomic ratios in procedural blanks prepared by different methods

Method	No	Solution*	Condition	$^{129}\text{I}/^{127}\text{I}$ atomic ratio, $\times 10^{-13}$	Uncertainty, 1σ $\times 10^{-14}$
Direct precipitate	B01	35 mL NaOH Old-1	Prepared in 2014	1.87	1.06
	B02	35 mL NaOH Old-1		1.56	1.58
	B03	35 mL NaOH Old-2	Bottle opened in 2014 and prepared in 2015	2.02	2.65
	B04	35 mL NaOH Old-2		1.70	1.93
	B05	35 mL NaOH New	Bottle opened in 2015 and prepared in 2015	1.57	1.02
	B06	35 mL NaOH New		1.48	0.81
Solvent extraction	B07	20 mL deionized water		1.83	1.69
	B08	20 mL deionized water		1.67	1.49
Combustion, condensed air as carrier gas	B09	35 mL NaOH New	Air, no heating for 3 h	28.5	8.06
	B10	35 mL NaOH New		7.08	3.20
	B11	35 mL NaOH New	Air, heating at 800 °C for 3 h	23.9	6.91
	B12	35 mL NaOH New		4.78	3.04
Combustion, oxygen as carrier gas	B13	35 mL NaOH New	O_2 , no heating for 3 h	4.17	2.13
	B14	35 mL NaOH New		2.64	2.18
	B15	35 mL NaOH New	O_2 , heating at 800°C for 3 h	4.32	2.63
	B16	35 mL NaOH New		6.19	3.81

* NaOH solution Old-1 was prepared in January 2014 and stored in a glass bottle until analysis in May 2015. NaOH solution Old-2 was newly prepared with a NaOH reagent stored in bottle opened in September 2014. NaOH solution New was newly prepared with a newly opened NaOH reagent.

2.2.3 Combustion

The sample was combusted in a Pyrolyser furnace to release iodine from the matrix, and the released iodine was trapped by 35 mL of $0.4 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution (Hou et al, 2009). In order to study the influence of pyrolysis method on procedural blank level, we investigated four experimental conditions, including combustion with condensed air as carrier gas, combustion with condensed air as carrier gas under heating, combustion with oxygen as carrier gas, as well as combustion with oxygen as carrier gas under heating. A 3-hour temperature program was

used as described elsewhere: (1) heating up from room temperature to 250°C in 20 min and keeping for 10 min; (2) heating up to 400°C in 30 min and keeping for 20 min; (3) heating up to 800°C in 40 min and keeping for 60 min (Zhou et al, 2010; Luo et al, 2011). Gas flow rate was about $200 \text{ mL} \cdot \text{min}^{-1}$. After combustion, 1.0 mg iodine carrier was added to the trap solution and precipitated directly with AgNO_3 following the procedure in subsection 2.2.1.

2.3 Target preparation and measurement of ^{129}I

The AgI precipitate (after drying at 60—70°C)

was weighed and ground to a fine powder. Three times by mass of niobium powder was added to the tube and mixed well with the precipitate. The mixture was transferred and pressed into a copper holder for AMS measurement (Hou et al, 2010).

$^{129}\text{I}/^{127}\text{I}$ ratios in the prepared targets were measured by AMS using 3 MV Tandem AMS system (HVEE) in Xi'an AMS center (Chen et al, 2010; Zhou et al, 2010; Liu et al, 2015). I^{5+} ions sputtered from the ion source was chosen for the measurement, where $^{127}\text{I}^{5+}$ 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 5 min per sample in each cycle (Zhang et al, 2011).

3 Results and discussion

3.1 Storage of alkaline solution

The measured $^{129}\text{I}/^{127}\text{I}$ ratios of NaOH solutions prepared by direct precipitation (Samples no. B01—B06) were in the range of $(1.48\text{--}2.02)\times 10^{-13}$, which are consistent with the generally observed $^{129}\text{I}/^{127}\text{I}$ background level of 2×10^{-13} in our laboratory (Table 1 and Fig.1). However, statistical analysis shows that $^{129}\text{I}/^{127}\text{I}$ ratios of third NaOH solution (B05—B06) is significantly different the other two groups ($P>>0.05$), and also shows that the former two group has no significant difference ($P<0.05$). The results thus indicate that to some extent, storage of NaOH solution and solid NaOH reagent may increase in $^{129}\text{I}/^{127}\text{I}$ ratio. Even though only a slight increase of ^{129}I level in NaOH solution was observed, it is important for accurate determination of ^{129}I concentration in geological samples, especially for the application of geochronometry.

The increase of $^{129}\text{I}/^{127}\text{I}$ ratio in stored NaOH solution and solid reagent for long time might be attributed to the alkaline properties that could easily adsorb and react with molecular iodine in the air. Because of multiple usage of reagent bottle, the overlying air will remained in the bottle and iodine in the air might be unavoidably assimilated by alkaline reagent.

We hence suggest that geological samples, such as oilfield brine should be better fully filled in a container and stored as short as possible before analysis. For sample preparation, the solutions are needed to newly prepare in order to avoid increased ^{129}I background.

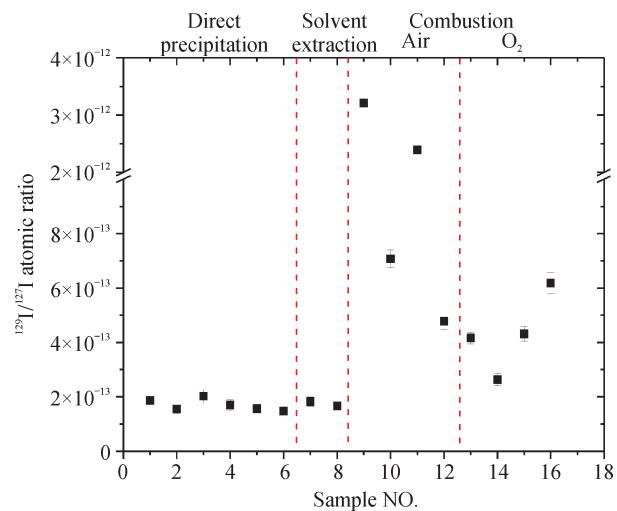


Fig.1 Influence of different sample preparation methods on $^{129}\text{I}/^{127}\text{I}$ ratios in procedural blanks

3.2 Influence of different separation methods on $^{129}\text{I}/^{127}\text{I}$ ratio of procedural blanks

$^{129}\text{I}/^{127}\text{I}$ ratios in procedural blanks prepared by three methods were compared. The results showed that the lowest $^{129}\text{I}/^{127}\text{I}$ ratio was generated by direct precipitation method (1.53×10^{-13} in average of samples B05—B06), while the highest $^{129}\text{I}/^{127}\text{I}$ ratio (16.1×10^{-13} in average of samples B09—B12) was from the combustion method with condensed air as carrier gas (Table 1 and Fig.1). In contrast to direct precipitation with newly prepared NaOH solution, a slight increase in $^{129}\text{I}/^{127}\text{I}$ ratio (1.75×10^{-13} in average) was observed in solvent extraction of iodine, which indicates solvent extraction could only introduce negligible iodine during sample preparation. The average $^{129}\text{I}/^{127}\text{I}$ ratio of combustion method with oxygen as carrier gas (4.33×10^{-13} in average of samples B13—B16) has significantly increased by 2—4 times compared to the direct precipitation. Most notably, $^{129}\text{I}/^{127}\text{I}$ ratio of combustion method with condensed air as carrier gas ($(4.78\text{--}28.5)\times 10^{-13}$) has significantly raised one order

of magnitude compared to the direct precipitation, in particular the first preparation for both experimental conditions of room temperature and heating.

The reasons probably caused such an increase of $^{129}\text{I}/^{127}\text{I}$ ratio in combustion method may include, (1) higher $^{129}\text{I}/^{127}\text{I}$ ratio residue in combustion work tube from previous sample preparation; (2) interfusion of air with $^{129}\text{I}/^{127}\text{I}$ ratio in the level of 10^{-7} in Denmark into the NaOH trap solution (Zhang et al, 2015, 2016); (3) Adsorption of atmospheric iodine in transfer pipes. Two experimental conditions, combustion with and without heating programs were conducted to investigate the procedural blanks of this method. There was no notable different between the two conditions, which suggests that residue in the work tube is impossible since a complete combustion was performed prior to this experiment. Despite no condensed air used in samples B13—B16, increased $^{129}\text{I}/^{127}\text{I}$ ratios were still observed. During sample combustion with oxygen as carrier gas, the air in the work tube (i.d. 3 cm by length 1.2 m) was trapped into NaOH trap solution, which may result in the increase of $^{129}\text{I}/^{127}\text{I}$ ratio of procedural blanks. However, this case is not as same as in our Chinese laboratory (^{129}I laboratory in Xi'an AMS center), where $^{129}\text{I}/^{127}\text{I}$ ratio in combustion procedural blanks are normally below 2×10^{-13} (Hou et al, 2010). The difference between the blank ^{129}I level can be attributed to the enormous difference of atmospheric ^{129}I level, for which the atmospheric $^{129}\text{I}/^{127}\text{I}$ ratios in Denmark is about three orders of magnitude higher than in China (Zhang et al, 2011, 2015, 2016). When condensed air was used as carrier gas during combustion, it seems hard to explain the abnormally high $^{129}\text{I}/^{127}\text{I}$ ratio as much as 28.5×10^{-13} in the first experiment. This is likely related to iodine adsorption onto the plastic transfer pipe of condensed air. Since the two replicated experiments for each group were conducted in one day, the condensed air used in the first experiment for 3 h likely flushed the transfer tube and decreased the adsorption of iodine. This hence resulted in a comparable $^{129}\text{I}/^{127}\text{I}$ ratio with the result from the combustion with oxygen. Therefore, the increase of $^{129}\text{I}/^{127}\text{I}$ ratio in combustion

procedural blanks mainly results from the relatively high atmospheric ^{129}I , as well as iodine adsorption in transfer pipe. Of the two reasons, the influence of the latter one can be completely avoided by using ^{129}I -free pure gas as carrier gas, and the influence of the former issue can be decreased by aeration of pure gas for a certain time and then trapping iodine with alkaline solution.

3.3 Recommendation for analysis of ultra-low ^{129}I geological samples

In the application of geochronometry, the initial $^{129}\text{I}/^{127}\text{I}$ ratio measured in marine sediments sampled off the coast of the Carolinas in the Atlantic Ocean is reported to be $(1.5 \pm 0.15) \times 10^{-12}$ (Fehn et al, 1986, 2007; Moran et al, 1998). This initial ratio of $^{129}\text{I}/^{127}\text{I}$ implies the old geological samples for dating is much lower even down to the level of 10^{-14} (Fehn et al, 1990). High procedural blanks during sample preparation might cause inaccurate dating of geological processes. In this study, all the procedural blanks prepared are based on the addition of an iodine carrier produced by Woodward Company (USA). In the aspect of sample preparation, geological samples for dating can be categorized to two types, high ^{127}I concentration samples and low ^{127}I concentration samples. Since the target source and AMS measurement need sufficient stable ^{127}I amount, the former samples can be prepared by direct precipitation after simple samples pretreatment (e.g. oilfield brine by filtration through filter paper) (Chen et al, 2014), while the latter samples have to be treated by relatively complex and long procedures for either extraction of sufficient stable ^{127}I or addition of stable iodine carrier. No matter which way selected, additional ^{129}I will be introduced to final sample target source for AMS measurement. For the methods investigated in this work, we therefore recommended the combustion method with pure gas as carrier gas and make sure as little contact as possible with air during sample preparation. It is worthy to note that iodine carrier-free method has great potential for geological dating of low ^{127}I concentration samples (Hou et al, 2010; Fehn, 2012; Zhang et al, 2013). Controlling of ^{129}I

background level is not only by decreasing chemical procedural blanks in sample preparation steps, but also by removal of instrumental interferences, for example, $^{127}\text{IH}_2$, ^{129}Xe and other molecular fragments during AMS measurement. All the reagents in each condition and instrumental parameters of AMS measurement are identical. In principle, the instrumental interferences are basically consistent. As the aim of this work is to investigate the influence of chemical preparation on ^{129}I background level, the ^{129}I spectrum and instrumental interferences are not shown in the context, whereas it has been and will further be focused and minimized in our work.

4 Conclusion

This work investigated the influences of NaOH solution storage and sample preparation methods on $^{129}\text{I}/^{127}\text{I}$ ratios on procedural blanks. This work shows that the procedural blank can be well controlled using the methods, direct precipitate, solvent extraction and combustion with oxygen as carrier gas, except combustion method with condensed air as carrier gas. The results suggest interfusion of air during sample preparation could increase the blank $^{129}\text{I}/^{127}\text{I}$ ratio depending on the blending extent.

On the basis of the result in this work, for geochronometry of geological samples, we recommended that,

(1) Ultralow ^{129}I level geological samples, especially aqueous samples should be carefully stored and analyzed as soon as possible.

(2) Selection of sample preparation methods needs to decrease the mixing of sample with air, especially in the area with relatively high atmospheric ^{129}I concentration.

(3) Low ^{129}I background methods are recommended for Iodine separation from ultra-low ^{129}I geological sample.

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