Talanta 140 (2015) 20–28

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

# Determination of lead isotopes in a new Greenland deep ice core at the sub-picogram per gram level by thermal ionization mass spectrometry using an improved decontamination method

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ARTICLE INFO

*Article history:*
Received 26 December 2014
Received in revised form
2 March 2015
Accepted 3 March 2015
Available online 10 March 2015

*Keywords:*
Lead isotopes
Greenland deep ice core
Improved decontamination procedure
Silica-gel activator
TIMS

ABSTRACT

An improved decontamination method and ultraclean analytical procedures have been developed to minimize Pb contamination of processed glacial ice cores and to achieve reliable determination of Pb isotopes in North Greenland Eemian Ice Drilling (NEEM) deep ice core sections with concentrations at the sub-picogram per gram level. A PL-7 (Fuso Chemical) silica-gel activator has replaced the previously used colloidal silica activator produced by Merck and has been shown to provide sufficiently enhanced ion beam intensity for Pb isotope analysis for a few tens of picograms of Pb. Considering the quantities of Pb contained in the NEEM Greenland ice core and a sample weight of 10 g used for the analysis, the blank contribution from the sample treatment was observed to be negligible. The decontamination and analysis of the artificial ice cores and selected NEEM Greenland ice core sections confirmed the cleanliness and effectiveness of the overall analytical process.



## 1. Introduction

Analytical methods for stable Pb isotopes ($^{204}$Pb, $^{206}$Pb, $^{207}$Pb and $^{208}$Pb) have proven to be very powerful tools for tracing the provenance of atmospheric Pb, which have also been applied for the analysis of glacial ice [1–4]. However, there are very few reliable measurements of Pb isotopes in the deep polar ice cores, due to extremely low Pb concentrations at or below the picogram per gram level and contaminants being brought to the outside of the core during the drilling operations. Until now, reliable data regarding Pb isotopes from such deep ice cores has been obtained successfully only in a handful of laboratories using thermal ionization mass spectrometry (TIMS) [5–8].

Although ultraclean protocols and techniques for TIMS have previously been established [9,10], the accurate measurement of Pb isotopes at ultralow Pb levels remains an analytical challenge for individual laboratories. This is because it is tremendously difficult to achieve the application of identical laboratory procedures and to ensure minimal analyte contamination. Another problem is the necessity of a stable and enhanced Pb ion beam intensity that is very important to improve both the reproducibility and the reliability of an isotope ratio measurement on a small polar sample size (tens of pg Pb). Since Akishin et al. [11] used a silica–zirconia gel as an ionization activator for thermal ionization of Pb isotopes in TIMS analysis, the silica-gel activator method using different silica-gels has been widely used in various research areas [12]. Until now, two different silica-gel products were used to determine Pb isotopes in polar snow and ice. The first product is a silica-gel prepared by distilling AR grade silicon tetrachloride ($SiCl_4$; BDH Chemicals) into high-purity water [9], however, the primary drawback of the $SiCl_4$ is its high reactivity during the reaction, making it difficult to handle. Therefore, it is not easy to produce silica-gel activator with constantly high ion yield efficiency [13]. The second product is a silica-gel produced from the colloidal silicic acid solution (Merck Art. no. 12475) [10,14], however, this product is no longer available commercially. To replace the Merck colloidal silica, Miyazaki et al. [13] evaluated silica-gel activators synthesized using different silica-gels and found that the silica-gel activator synthesized by a silicic acid colloidal solution (PL-7) with a particle size of 0.122 μm and concentration of 23.2% from the Fuso Chemical Co., Ltd., is the optimal silica-gel activator for Pb isotope analysis using TIMS. However, they examined the efficiency of the silica-gel activator by loading samples with 100 ng of NIST (National Institute of Science and Technology, Washington,

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http://dx.doi.org/10.1016/j.talanta.2015.03.007
0039-9140/

DC, USA) SRM 981, which requires verification for samples containing much smaller quantities of Pb comparable to polar samples. Moreover, no data on the blank level for PL-7 was provided from their study.

Herein, we report a reliable Pb isotope measurement using an improved decontamination method for deep ice core samples and an optimal silica-gel activator for the thermal ionization of Pb isotopes in TIMS analysis. Our ultraclean analytical procedures proved to ensure contamination control and extremely low blank signals, enabling the reliable simultaneous determination of Pb and Ba concentrations and Pb isotopic ratios at or below the picogram per gram level encountered in polar deep ice cores.

## 2. Experimental

### 2.1. Clean laboratories

Analysis of the polar ice core samples with extremely low amounts of Pb requires all the analytical procedures to be performed in a clean environment to minimize contamination. Our experiments were carried out in new non-laminar flow class 1000 (US Federal Standard 209D) clean laboratories that were specially designed for ultra-trace analysis at the Korea Polar Research Institute (KOPRI). Critical care for the clean laboratory design was taken to ensure that construction substances neither contained the analytes to be analyzed, nor posed any contamination problems. All custom made items such as tables, shelves, and hoods used in the clean laboratories were made of PVC or high-density polyethylene (HDPE).

Sample preparations and all analytical procedures were performed inside class 10 vertical laminar flow clean booths or on clean benches installed inside the class 1000 laboratories. These were all made of plastic (PVC) and equipped with ultra-low penetration air (ULPA) filters and plastic pumps. The operators always wore full clean-room clothing and low-density polyethylene (LDPE) gloves during experiments.

### 2.2. Ultrapure reagents

The first priority for the reliable investigation of ultralow Pb concentration and its isotopes in polar samples is the availability of high-purity water used during every step of the analytical process, from the cleaning of lab ware and decontamination apparatus to the final analysis. In our laboratory, two grades of ultrapure water are used: Millipore Milli-Q water (MQW) obtained by coupling a Millipore RO water purification (Model Elix-3) with a Milli-Q system (Millipore Corp., Model Milli-Q Academic) and sub-boiling distilled ultrapure water (SUW) by a sub-boiling distillation system with two high-purity quartz distillation units (Milestone, DuoPUR) using the MQW. The MQW and SUW are produced inside a class 10 clean booth and the final output rate of the SUW is limited to about 500 mL/day. The SUW produced is stored in a 1 L (or 500 mL) LDPE acid-cleaned bottle (see Section 2.4) and used within 2 days of production.

The Pb content of the water was determined by inductively coupled sector field mass spectrometry (ICP-SFMS), after preconcentration by non-boiling evaporation and acidification to 1% using Merck “Optima” grade ultrapure $HNO_3$ [15,16]. The MQW and SUW contained $\leq 0.4$ and $< 0.05$ pg Pb $g^{-1}$, respectively.

We used different purity grades of $HNO_3$ for cleaning lab ware and decontamination apparatus. For a series of four acid cleaning baths, guaranteed reagent (GR) grade $HNO_3$ and Merck “Suprapur” $HNO_3$ were mainly used for the first and second baths, and Fisher “Optima” grade ultrapure $HNO_3$ was used for the third and fourth baths. Other reagents used for the preparation of the silica-gel activator and analysis are described in next sections.

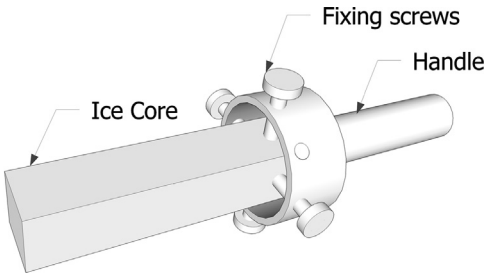


**Fig. 1.** Schematic drawing of ice core holder for decontamination.

### 2.3. Selection of laboratory materials

The material and quality of all the lab ware, which contain or come in direct contact with ultrapure samples or reagents, are of primary importance because they may introduce contaminants into the samples or provide an active surface onto which the analytes may be absorbed [17]. As previously proved to be the optimal choice [18,19], LDPE sample bottles and containers (volumes ranging from 15 mL to 20 L) fitted with a polypropylene (PP) cap from Nalgene Company, USA, are always preferred to be used at temperatures less than about 60 °C or for diluted acid concentrations, while fluorinated ethylene propylene (FEP) or PFA Teflon material is employed for storage of concentrated acids and high-temperature evaporation of samples because of the lower chemical inertness and thermal stability of LDPE. Polypropylene is used only for the tips (epT.I.P.S.) of Eppendorf micropipettes and custom-made tongs that are used to handle laboratory items during the cleaning procedures (see next section).

Newly designed decontamination apparatus including ice sample holder and screws (Fig. 1) is all made of Teflon. The exceptional items are the stainless steel chisels and ceramic knives used for the decontamination process. The stainless steel chisels were made using a single plate of 2 mm thick stainless steel type 316 L, which are similar to those used by Ng and Patterson [20] and Boutron and Patterson [21] for Pb analysis in polar samples. To test the purity of ceramic material, of which the cleaning procedures are relatively simpler, commercially available ceramic knives (Kyocera Advanced Ceramics, Models: FK075WH) were also used.

### 2.4. Cleaning lab ware

Rigorous cleaning of lab ware is critical for controlling contamination levels. The cleaning procedures were originally adopted and slightly modified from the methods as given in detail elsewhere [16,19,22].

In brief, new LDPE lab ware is first degreased with chloroform, rinsed with MQW whilst being held with custom-made PP tongs, and then immersed for a week in the first acid bath (25% GR grade $HNO_3$ diluted in ultrapure MQW) at room temperature. After rinsing with MQW, we sequentially transfer them into three successive acid baths heated on hotplates at about 40 °C: the second acid bath (25% Merck “Suprapur” grade $HNO_3$ diluted in MQW) and the subsequent two acid baths (0.2% Fisher “Optima” grade ultrapure $HNO_3$ diluted in MQW). The items remain immersed in each acid bath for a week. The LDPE bottles and containers taken out from the fourth acid bath are finally rinsed with MQW, filled with 0.1% Fisher “Optima” grade MQW, capped, and stored in sealed, acid-washed polyethylene bags until use. For FEP and PFA Teflon lab ware, they are first immersed in concentrated Merck “Suprapur” $HNO_3$ at room temperature for at least a week. The subsequent cleaning procedure is the same as LDPE items. PFA beakers used for the preconcentration of the samples by non-boiling evaporation are kept immersed in the fourth acid bath until use.